A Survey of the Van Hove Scenario for High-$T_c$ Superconductivity
With Special Emphasis on Pseudogaps and Striped Phases

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In Memoriam:
Carson Jeffries
Leo Falicov

The Van Hove singularity (VHS) provides a paradigm for the study of the role of peaks in the density of states (dos) on electronic properties. More importantly, it appears to play a major role in the physics of the high-T\textsubscript{c} superconductors, particularly since recent photoemission studies have found that the VHS is close to the Fermi level in most of the high-T\textsubscript{c} cuprates near the composition of optimum T\textsubscript{c}. This paper offers a comprehensive survey of the VHS model, describing both theoretical properties and experimental evidence for the picture. Special topics discussed include a survey of the Fermi surfaces of the cuprates and related compounds, and an analysis of the reliability of the slave boson approach to correlation effects. While many properties of the cuprates can be qualitatively understood by a simple rigid-band-filling model, this is inadequate for more quantitative results, since correlation effects tend to pin the Fermi level near the VHS over an extended doping range, and can lead to a nanoscale phase separation. Furthermore, the peaks in the dos lead to competition from other instabilities, both magnetic and structural (related to charge density waves). A novel form of dynamic structural instability, involving dynamic VHS-Jahn-Teller effects has been predicted. Scattered through the literature, there is considerable experimental evidence for both nanoscale phase separation of holes, and for local, possibly dynamic, structural disorder. This review attempts to gather these results into a comprehensive database, to sort the results, and to see how they fit into the Van Hove scenario. Recent experiments on underdoped cuprates are found to provide a strong confirmation that the pseudogap is driven by a splitting of the VHS degeneracy.
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I. INTRODUCTION

A. What is a Van Hove Singularity?

In 1953, Leon Van Hove demonstrated the crucial role played by topology in the band structure of either electrons or phonons. He showed that any nonanalytic behavior is caused by a change in the topology of the bands – changes now known as Van Hove singularities (VHS) [2]. The simplest such changes are associated with the opening or closing of new sheets of the energy bands \( (M_3 \text{ and } M_4 \text{ points in a three-dimensional (3D) band structure}) \). But there are additional VHS’s interior to the band, associated with changes of the signs of one of the principal curvatures of the band \( (M_1 \text{ and } M_2 \text{ points in 3D}) \). These interior VHS’s produce peaks in the density of states (dos) of the bands. As such, these VHS’s are expected to play an important role in the electronic properties of these materials.

In materials of lower spatial dimension, the role of some VHS’s is enhanced, because the dos \( N(E) \) can actually diverge at a VHS. In one-dimensional (1D) materials, the divergence is power law, \( N(E) \propto (\Delta E)^{-1/2} \), where \( \Delta E = E - E_{\text{VHS}} \) is the distance in energy from the VHS. However, the importance of this VHS is somewhat limited, because the VHS falls at a threshold at which a new band opens or closes, so the number of free carriers is very small. On the other hand, in a two-dimensional (2D) material, the relevant VHS falls near the center of the band, where the number of free carriers is maximal. At this VHS, the dos diverges logarithmically \( N(E) \propto \ln(B/2\Delta E) \), where \( B \) is the bandwidth.

The topology of this VHS is that of a saddle point, associated with a crossover from electron-like to hole-like condensation, Figure 1a. This figure will be discussed in more detail in Section IV.A, but the logarithmic divergence of the dos is clear from Fig. 1c. The electron-to-hole crossover can be seen by looking at the Fermi surfaces themselves, Fig. 1b. [The dashed lines are the generic behavior expected for the cuprates; the solid lines represent an anomalously strong singularity – perfect nesting – which corresponds to special choices of the band parameters.] For an underdoped sample (surface tagged with a filled square) the Fermi surface is an electron-like surface closed around the \( \Gamma \)-point of the Brillouin zone; for overdoping (circle-tagged curves) the Fermi surface is hole-like, closed about the \( S \)-point.

At a saddle point, the two principal curvatures have opposite signs; in electronic terms, the effective mass is electron-like in one direction, and hole-like in the other (see the \( X \)-point in Fig. 1a). In general, if an energy band has one saddle point, there will be other, symmetry related saddle points at the same energy. In addition to the divergence of the dos, there can also be divergences of the susceptibilities at wave vectors \( Q \) coupling two of these saddle points.

Hence, the anomalies of this VHS are of three sorts: associated with divergences in the dos \( N(E) \), divergent susceptibilities \( \chi(Q, \omega) \), and with the electron-hole crossover which implies that both electron-like and hole-like carriers are simultaneously present at the VHS. This paper is intended to serve as an introduction to the ‘natural history’ of this 2D saddle point VHS, pointing out some of the consequences of these three, competing anomalies. One of these consequences may be high-temperature superconductivity.

B. The Van Hove Scenario

In broadest terms, the ‘Van Hove scenario’ seeks to answer the question, how is the physics of an interacting electron liquid modified by the presence of a (saddle point) Van Hove singularity near the Fermi level? In
more detail, this may be stated as follows. (1) The saddle point Van Hove singularity (VHS) of a two dimensional (2D) metal is the simplest model with a peak in the density of states (dos), and as such can act as a paradigm for analyzing the role of dos structure in the physics of Fermi liquids. (2) In the 2D limit, the dos actually diverges, suggesting that the Fermi liquid is unstable as $T \rightarrow 0$, and hence that the underlying physics is as rich as that of 1D metals. (3) A 2D VHS is present in the immediate vicinity of the Fermi level in the high-$T_c$ cuprates, and it is necessary to understand the role of this VHS in order to develop a correct picture of the physics of these new materials. (4) The VHS can explain a number of normal-state anomalies in the cuprates, including the linear-in-$T$ and $\omega$ electron-electron scattering rate and a pronounced crossover in properties from the undoped to the overdoped regime. (5) The most exciting possibility (but only a possibility at this point) is that the VHS itself can provide a new pairing mechanism which drives the transition to high-$T_c$ superconductivity. The following paragraphs are intended to clarify these points.

The reasoning behind point (1) is straightforward. For years prior to the discovery of the cuprates, an empirical rule stated that the best way to find high-$T_c$ superconductivity is to look for a material with a peak in the dos, which could drive both structural (CDW) and superconducting instabilities. The highest $T_c$’s occur just on the edge of a structural instability, and $T_c$ can be appreciably raised by inhibiting the structural transition. In light of this, the 2D saddle point VHS should be looked on as the generic dos peak. Indeed, all 3D dos peaks are associated with 3D VHS’s, and the largest dos peaks are generally produced by closely-spaced $M_1-M_2$ VHS’s, which can be generated from the 2D saddle point by adding a small 3D coupling!

Point (2): A peak in the electronic dos signals that the electrons can behave collectively, leading to a tendency for magnetic, or structural, or superconducting instability. The 2D saddle point VHS has a (logarithmically) diverging dos, signalling an absolute instability, which must be very carefully dealt with. This was clearly brought out in the early work of Dzyaloshinskii and Schulz: the 2D VHS is a natural generalization of the one-dimensional electron gas, with competing spin and charge density wave (S/CDW), and s- and d-wave superconducting instabilities, and a correspondingly complicated renormalization group (RG) derived phase diagram.

While the 1D VHS shows a stronger divergence, it falls near the top or bottom of the electronic band, where there are too few carriers for collective effects to be important. The most interesting physics in a 1D metal is generally found near the middle of the electronic band. In 2D, the saddle point VHS provides the natural generalization of this regime of competing instabilities. Since a one-band model of the VHS can be constructed, with the same generic features, it should be possible to find essentially exact solutions describing this complex interplay of instabilities, and to much better understand under which conditions superconductivity can become the dominant instability.

Point (3) is most clearly demonstrated by angle-resolved photoemission experiments, which reveal the presence of a VHS close to the Fermi level in optimally doped Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{x}$ (Bi-22[n-1]n) (n=2) \( \square \), YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) \( \square \), and YBa$_2$Cu$_3$O$_8$ \( \square \). However, Bi-2201 \( \square \) offers evidence that the relation between the VHS and superconductivity is not simple: despite having a VHS close to the Fermi level, $T_c$ is low, $\approx 10K$. A similar result has also been found in Sr$_2$RuO$_4$, with $T_c = 0.93K$ \( \square \). Could this have something to do with competing interactions? Curiously, Bi-2201 has a squarer Fermi surface than Bi-2212, yet lower $T_c$. This is the same relation as found in comparing La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) to YBCO, and explained in terms of pseudogaps. But more of that later.

Given that a VHS is present quite close to the Fermi level, then it will have a very profound effect on any theory of high temperature superconductivity. This point must be stressed. It is often naively assumed that there is a straightforward competition between, e.g., nearly antiferromagnetic models and VHS models of superconductivity, with one excluding the other. This is by no means the case. The nearly antiferromagnetic models involve a peak in the susceptibility near $Q = (\pi/a, \pi/a)$, the VHS nesting vector, and hence are sensitive to the proximity of a VHS to the Fermi level.

But if this is granted, a whole new set of questions arises. How does one model the VHS? Isn’t it smeared out by correlation effects, disorder, and interlayer coupling (not to mention the competing structural and magnetic instabilities)? Just how smeared out? Is there still a peak (albeit finite) in the dos? The systematic analysis of these, and related issues constitutes the scientific program of the Van Hove scenario. A partial answer to these questions, based on our present state of understanding, is one goal of the current review.

Point (4): Many researchers have noted that, whereas the superconductivity of the cuprates is relatively conventional, except for the high $T_c$ values and the (probably) d-wave symmetry of the gap, the normal state properties are highly anomalous, and a key to understanding the cuprates is to understand these anomalous normal state properties. In this respect, the fact that the normal state anomalies follow rather naturally from the proximity of the VHS is very significant.

Point (5): It is entirely conceivable that the role of the VHS in superconductivity is indirect, with the density of states peak simply enhancing some underlying conventional (electron-phonon) or unconventional (spin) pairing mechanism. Nevertheless, there is a possibility that the VHS leads to a fundamentally new kind of pairing mechanism. At least two possibilities have been suggested. First, the VHS can lead to an electronic pairing mechanism, in that it is associated with the simultaneous appearance of electron-like and hole-like Fermi
C. The Purpose of this Review

There is no universally accepted model of the physics associated with a VHS. The purpose of the present review is therefore twofold: first, to survey the experimental situation, summarizing various strands of evidence which point to a role of the VHS in the physics of the high-Tc cuprates; and secondly, to summarize the various theoretical approaches which have been applied to the VHS model. In trying to make this review useful tutorially, I have found it necessary to incorporate new calculations of some properties of the VHS’s.

There are a number of earlier reviews in this field [3, 13], but most were written before the angle-resolved photoemission data became available. While the VHS model seems capable of providing a unified picture of some properties of the VHS’s.

It goes without saying that no model of high-Tc superconductivity has yet attained a high level of acceptance. For almost every experimental observation explained by the VHS scenario, there are a number of alternative interpretations. While it is difficult to do justice to all these alternative viewpoints in this review, I will at least try to briefly note some competing theories of particular phenomena, such as the pseudogap and nanoscale phase separation. For discussions of various scenarios and the related spectroscopic evidence, see the recent series of conference proceedings, Refs. [17, 20].

A number of features of this review will have an interest beyond the immediate Van Hove scenario. Thus, there is a detailed collection of the Fermi surfaces of the cuprates (Section IV), including parameters for tight binding models (Tables I-IV); a discussion of the accuracy of slave boson calculations (Section VII); a catalog of experiments observing anomalous short-range order (Section IX) and pseudogaps (Section IX.A); and a discussion of the evidence for (a possibly nanoscale) phase separation in the cuprates, both in underdoped and overdoped materials (Section XI).

It is particularly important to provide a database of experimental evidence for the most anomalous non-superconducting features of the cuprates: (a) nanoscale phase separation and (b) strong electron-phonon coupling effects and local structural disorder. These data are widely scattered throughout the literature. Taken in isolation, the evidence of any one article could easily be overlooked, but taken collectively, the data present a coherent picture of highly anomalous behavior.

At this early stage, I feel that it is important to provide a general overview, summarizing all of the data even if its relation to the VHS scenario is not clear – particularly in the case of nanoscale phase separation. Nevertheless, the picture that emerges seems to be largely explicable in terms of the VHS, complicated by commensurability effects.

D. Abbreviations

It is convenient to summarize the various abbreviations used in this review. Materials: YBa$_2$Cu$_3$O$_{7-\delta}$ = YBCO, YBa$_2$Cu$_4$O$_y$ = Y-124, YBa$_2$Cu$_3$O$_{7.5-\delta}$ = Y-123.5, Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$ = Bi-22[n-1]n, Ti$_m$Ba$_2$Ca$_{n-1}$Cu$_n$O$_x$ = Ti-m2[n-1]n (m=1,2), La$_2$CuO$_{4+\delta}$ = LCO, La$_{2-x}$Sr$_x$CuO$_4$ = LACO (where A can stand for either Sr or Ba, or Ca), and Nd$_{2-x}$Ce$_x$CuO$_4$ = NCCO. In addition, the nickelates, which have the same formula as LCO, LSCO, with Ni replacing Cu, are abbreviated LNO or LSNO. Finally, to refer to a specific oxygen stoichiometry, I will either quote $\delta$ or write the stoichiometry explicitly in the abbreviation, as, e.g., La$_{2-x}$Sr$_x$O$_{4.12}$ = LSNO$_{4.12}$. The bismuthates will be abbreviated as BPBO = BaPb$_{1-x}$Bi$_x$O$_3$, BKBO = Ba$_{1-x}$K$_x$BiO$_3$.

Structures: The various phase transitions in LBCO, LSCO, etc., will be abbreviated as high-temperature tetragonal = HTT (space group I4/mmm); low-temperature orthorhombic = LTO (Bmab, in the conventional, but non-standard notation); low-temperature tetragonal = LTT (P4$_2$/nmc); and the Pccn phase, which will just be called that, rather than LTO or some equivalent. Generic structures such as charge-density wave (CDW), spin-density wave (SDW), antiferromagnet (AFM), and antiferromagnetic insulator (AFI) are also used. In drawing the Brillouin zones and energy dispersions, I will generally simplify the structure to a 2D tetragonal (or orthorhombic) cell, defining the special points $S = (\pi/a,\pi/a)$ and $\bar{S} = S/2$. (In some figures taken from earlier publications, these points are called $M$ and $\bar{M}$, respectively.)

Doping: For the hole doping, I will use the symbol $P$, where, e.g., $P = x$ in LSCO and $P \approx 2\delta$ in LNO. The relation between $P$ and $\delta$ in YBCO and LCO is more involved, and is discussed in Subsection VI.B. For convenience, and where no confusion is likely to arise, I will often quote $x$ or $\delta$ instead of $P$. 
E. Partial Synonyms

In the recent literature, a number of papers have discussed calculations which can in principle apply to a larger class of phenomena than VHS theories - and hence have been given a new name. Nevertheless, in practice the phenomena are often found to be associated with a VHS. Thus, flat bands can in principle arise in any band structure, but in practice the interesting bands are those which are flat in the immediate vicinity of a VHS, thereby enhancing the effects of the dos divergence.

Again, a hot spot is a point on a Fermi surface associated with anomalously strong scattering, which may therefore be relevant to transport anomalies in the cuprates. When Hlubina and Rice introduced this term, they had two examples in mind - the VHS itself and the anomalous scattering associated with the peak in spin susceptibility postulated in a number of nearly antiferromagnetic theories. These latter need not in principle be associated with the VHS, although, as discussed below, the VHS is the most likely candidate for self-consistently generating the susceptibility peak. In a recent calculation of these spin-related hot spots, Stojkovic and Pines showed that the hot spots arose at those points heavily shaded in Fig. 2. Clearly, the hot spots are just those points on the Fermi surface closest to the VHS. Two points of interest: there are strong effects even though the Fermi level is not exactly at the VHS, and these VHS hot spots can explain the anomalous T-dependence of the Hall effect in these materials.

II. INSTABILITY AND FERMI SURFACE TOPOLOGY

The connection between structural instability and the topology of the Fermi surface was first made when Hum-Rothery noted that, in a series of metallic alloys based on Cu, structural phase transitions are found to occur at fixed values of the conduction electron concentration. Jones suggested an interpretation of these Hum-Rothery alloys, assuming a nearly free electron gas with spherical Fermi surface. At the critical concentrations, the size of the Fermi surface approximately matches that of the Brillouin zone (actually, of the Jones zone), so that, by introducing small gaps associated with the superstructure, large sections of Fermi surface can be gapped, lowering the electronic energy. Despite the great progress in band structure theory in the intervening years, this fundamental insight still seems to be correct, even though detailed calculations have proven difficult.

In a one-dimensional (1D) metal, the analogous situation leads to a charge density wave (CDW) accompanied by a Peierls distortion. Since all real materials have some interchain or interlayer coupling, no metal is truly 1D. Quasi-1D character is described in terms of Fermi surface nesting. This conventional nesting must be carefully distinguished from VHS nesting. In conventional nesting, the single particle dos $N(E)$ of a material is featureless, so to get a peak in the joint density of states (jdos),

$$J(\bar{Q}) = \int d^3k N(E_k)N(E_{k+\bar{Q}}),$$

it is necessary that two parts of the Fermi surface run parallel over a considerable distance, separated by a common vector $\bar{Q}$ - i.e., that the two parts of the Fermi surface 'nest'. In contrast, near a VHS the dos $N(E)$ already has a strong peak, so if $\bar{Q}$ joins two VHS's, a large peak in $J$ is assured. Under ordinary circumstances, this peak generally overwhelms the peak due to conventional nesting. For example, in Fig. 3, the jdos calculated by Pickett, et al. for LSCO, peaks associated with both conventional nesting ($Q_1, Q_2$) and VHS nesting ($Q_0$) are clearly evident (see inset a). However, the dominant feature is clearly that associated with VHS nesting.

The VHS nesting can be seen in the (spin or charge) susceptibility

$$\chi(q, \omega) = -\sum_{k} \frac{f(E_k) - f(E_{k+q})}{E_k - E_{k+q} - \hbar \omega - i\delta}.$$ (2)

At the VHS, both the intra-VHS ($q = 0$) and the inter-VHS ($q = \bar{Q}_0 = (\pi/a, \pi/a)$) susceptibilities have a logarithmic (or $ln^2$) divergence. In the absence of electron-phonon coupling, the RPA dielectric constant becomes $\epsilon_v(q, \omega) = 1 + V_v(q)\chi(q, \omega)$, with $V_v(q) = 4\pi e^2/q^2$. Near the VHS, $\epsilon_v >> 1$, so the screened Coulomb interaction becomes

$$\tilde{V}_v(q, \omega) = \frac{V_v(q)}{\epsilon_v(q, \omega)} \approx \frac{1}{\chi(q, \omega)}.$$ (3)

Thus, at a VHS, the screening is perfect, $\tilde{V}_v = 0$, both at $\bar{q} = 0$ and at $\bar{q} = \bar{Q}_0$. This is the standard form for $\tilde{V}_v$, and will be adequate for qualitative calculations. However, it must be kept in mind that very near the VHS, the polarizability has significant corrections due to electron-hole attraction (ladder diagram summation).

If the electrons are coupled to a phonon of bare frequency $\omega_l$, the phonon frequency is renormalized to $\tilde{\omega} = \omega_l R^{1/2}$, with

$$R = 1 - \tilde{V}_v \chi(\bar{Q}, \omega),$$ (4)

with $\tilde{V}_v = V_v/P_{\alpha\alpha}(Q)$ and $P_{\alpha\alpha}(Q) \approx 0.15$, a local field correction, is a complicated function of the dielectric parameters. Assuming

$$\chi(\bar{Q}, \omega \approx 0) = \frac{1}{2B} ln(\frac{1.13B}{T}),$$ (5)

there will be a structural instability, $R = 0$, at

$$T_{CDW} = 1.13B e^{-1/\lambda_1},$$ (6)
\[ \lambda_1 = \frac{\bar{V}_c}{2B}. \]  

This result must be corrected for strong fluctuations in two dimensions \[ \bar{\lambda}_1 \] , but it qualitatively shows the role of the VHS in promoting structural phase transitions.

III. VAN HOVE SCENARIO BEFORE HIGH Tc

A. Generic VHS’s – Mostly 3D

Van Hove [1] showed that the dos for both electrons and phonons is dominated by singularities associated with changes in the topology of the constant energy surfaces in momentum space (in particular, the electronic Fermi surface). For present purposes, the most important VHS is the saddle-point VHS found in the interior of a 2D energy band. This is associated with a crossover between electron-like and hole-like Fermi surface sections. In a strictly 2D limit, the dos has a logarithmic divergence at such a point [1]: Van Hove actually was calculating the dos for phonons, but since the results are purely topological, the same dos is found for electronic bands. In the presence of a weak interlayer dispersion, this VHS splits into a closely spaced pair of M1 and M2 VHS’s – i.e., the logarithmic spike is replaced by a peak with a flat top – but the integrated dos under the peak is unchanged [31–33]. Figure 4 illustrates this development, showing the dos of an individual layer (Fig. 4a), of four coupled layers (Fig. 4b), and of an infinite number of coupled layers (Fig. 4c). Even in 3D, the resulting dos peak can be quite sharp. Thus, the insert to Fig. 4 shows the calculated dos for Ni [3].

As part of a general analysis of Fermi surfaces in metals, Lifshitz [34] initiated a study of how the properties of a material are altered by varying the topology of the Fermi surface. He showed that in general, if the material properties could be varied in a quasi-continuous fashion (via pressure or doping), the change of the Fermi surface topology would produce a weak (order 2.5) phase transition, with consequences for the thermodynamic properties of the materials. In addition to the order 2.5 phase transition exactly at the VHS, Lifshitz showed that there could also be a first order phase transition, with volume discontinuity (compressibility \( \kappa < 0 \)) in the immediate vicinity of the VHS. Lifshitz’ analysis was restricted to the VHS’s of three-dimensional (3D) metals, and the extension to the 2D saddle point is given in Appendix A. Considerable research on this order 2.5 phase transition was carried out, particularly in Russia, and this has been the subject of extensive reviews [35–37]. However, the transition was typically studied in 3D materials, where the VHS leads only to a slope discontinuity in the dos, and the stronger discontinuity associated with the 2D VHS was not studied. There was some theoretical work analyzing how a VHS would affect superconductivity [38], but again, in 3D materials.

From the BCS formula for the superconducting \( T_c \), it is clear that enhancing the dos should enhance superconductivity. This simple idea was applied to the ‘old’ high-\( T_c \) superconductors, in particular the A15 compounds. The A15 structure is very suggestive of three interpenetrating chains, so the dos peaks were initially interpreted in terms of one-dimensional (1D) VHS’s, with even stronger (square-root) singularities [39]. Full 3D band structure calculations find that the Fermi level is at a peak in the dos [40], but this peak cannot be interpreted in terms of 1D features. Gorkov suggested that the physics is dominated by a 3D VHS, near the [111]-directions of the Brillouin zone [41]. Bilbro and McMillan [42] developed Gorkov’s model and showed that it leads to increased \( T_c \)’s and could explain the strong competition between superconductivity and structural instability observed in the A15’s. Weger [43] has stated that “the normal state properties [of the A15’s] ... are dominated by the Van Hove scenario [44], [but] are entirely different from those of the cuprates.” The result of this review will be a qualified agreement with this statement: to the extent that the VHS can be treated perturbatively, the striking differences in physical properties suggest that the VHS model applied to the A15’s does not work in the cuprates. Instead, the review will attempt to demonstrate that the differences between the A15’s and the cuprates are due to the reduced dimensionality of the latter, which greatly enhances the role of the VHS’s. For present purposes, the important feature is that the VHS’s play an important role in the A15’s.

In searching for higher temperature superconductivity in the A15’s, the dual role played by a competing structural instability was first recognized. The instability is often associated with phonon mode softening, and these soft, anharmonic phonons can contribute to a further enhancement of the electron-phonon coupling; after the structural phase transition, the remaining phonons are much stiffer, with weaker residual electron-phonon coupling, and hence poorer superconducting properties. Hence, the lore in high-\( T_c \) research is that the best place to search for superconductivity is in the immediate vicinity of a structural instability. For instance, \( T_c \) can be enhanced in A15 compounds by preparing quench-condensed sputtered films, in which the structural transition is arrested by disorder [44].

Many papers published in the period prior to the discovery of the cuprate superconductors concentrated on the structural instabilities. Thus, Dagens [46] calculated the phonon softening associated with a 3D VHS – the examples he gave were from superconductors Nb and (doped) Pb. These ideas were used [47] to explain the structural instability found in La under pressure.

8
B. 2D Saddle-Point VHS

Starting in \( \approx 1970 \), theoretical interest was drawn to the unusual properties of 2D saddle point VHS’s. Thus, Roth, et al. \([48]\) showed that the VHS would lead to a generalized Kohn anomaly, with a cusp in the magnetic susceptibility. Rice \([49]\) noted that near a VHS, there is a breakdown of analyticity in expansions of the free energy. He showed that this could lead to a transition to an antiferromagnetic phase. Rice and Scott \([50]\) introduced the concept of VHS nesting, in which the jdos has a peak at a \( Q \)-vector joining two VHS’s, Fig. Balseiro and Falicov \([51]\) explored the competition between superconductivity and charge density waves (CDW’s) near a 2D VHS, using a model which is now a standard one-band model for the cuprates. While their calculations were numerical, they clearly displayed the enhanced instability associated with the 2D VHS: a superconducting or structural instability always occured for any arbitrarily small electron-phonon coupling. Scalapino and coworkers \([52,53]\) showed the result analytically, both for the superconducting and for the density wave transitions.

Within a year, high-\( T_c \) superconductivity had been discovered in the cuprates, and band structure calculations had shown that a VHS is close to the Fermi level at optimum doping. A number of papers applied the VHS model to these materials, starting with Labbé and Bok \([54]\) and Hasegawa and Fukuyama \([55]\). Dzyaloshinskii \([4]\) and Schulz \([5]\) showed that VHS theory was formally very similar to the s-dogy theory of 1D metals, and applied a renormalization group (RG) theory to study the competition between CDW’s and s-wave superconductivity, and between spin-density waves (SDW’s) and d-wave superconductivity! This RG method will be discussed in Section XIV, below.

However, when early band structure calculations failed to find a VHS near the Fermi level in YBCO, most interest shifted to other models. (In fact, these early calculations failed to properly account for chain-plane charge transfer, and more recent calculations find the VHS close to the doping of optimum \( T_c \), in excellent agreement with photoemission measurements.)

C. Extended Saddle-Points

Photoemission experiments have found evidence for a potentially new kind of VHS, initially in YBCO and Y-124 \([8,10]\), but now in most cuprates. For an ordinary saddle point, the curvature of the energy bands has the opposite sign in two orthogonal directions. The magnitudes of these curvatures (inverse effective masses) can take any two independent values. In an ‘extended saddle point’, one of these masses is infinite – that is, the corresponding curvature lacks a term in \( k^2 \), and so generically starts out as \( k^4 \). Thus, in one direction, the saddle point is extremely flat. This makes the energy dispersion quasi-1D, so the dos diverges more strongly, with a square-root rather than a logarithmic divergence. Such behavior can greatly amplify the effects of a VHS, leading to enhanced \( T_c \)’s \([60]\).

However, it is important to recognize that the extended VHS does not follow automatically from Van Hove’s theorem – it is not necessary that an extended VHS appear in an energy band. Indeed, LDA calculations have been unable to produce any structure in the cuprates which leads to a power-law dos divergence, and one of the puzzles of VHS theory is to understand where the extended VHS comes from. Extended VHS’s are discussed further in Section V.D.4.

IV. FERMI SURFACES OF THE CUPRATES

A. Generic Features of a VHS

Before presenting the detailed Fermi surfaces of the individual cuprates, it is convenient to begin with a generic Fermi surface for (the antibonding band of) the CuO\(_2\) planes. These planes are generally believed to provide the dominant contribution to superconductivity. Figure 1 illustrates two different possibilities for the VHS. If the Fermi surface is square at half filling, the VHS nesting is supplemented by a conventional nesting, the Fermi surface is perfectly nested, and the susceptibility divergence is stronger. This is illustrated by the set of Fermi surfaces drawn in solid lines in Fig. 1. The dashed lines illustrate the more usual situation: the Fermi surface is curved at the VHS, so conventional nesting is weak. This greatly reduces the possibility of a CDW or SDW instability, while retaining a strong superconducting instability.

By definition, a VHS occurs at a point where the Fermi surface topology changes. The saddle-point VHS is characterized by an electron-hole crossover. Thus, just below the VHS in Fig. 1a, the Fermi surface is a closed, electron-like Fermi surface centered at the Brillouin zone center (\( \Gamma \) point); above it, the Fermi surface is again closed, but now it is a hole-like Fermi surface centered at the zone corner (\( S \) point). Exactly at the VHS, the two orbits merge, at the \( X \) and \( Y \) points of the zone. The Fermi surface is simultaneously electron-like and hole-like.

This ambiguity and degeneracy are characteristic features of the VHS. The fact that there are two degenerate VHS’s at \( X \) and \( Y \) will give rise to a novel form of band Jahn-Teller effect. The electron-hole crossover leads to complications in the magnetotransport properties – Hall
effect and magnetoooscillatory phenomena – as will be discussed below.

B. LDA and Experimental Fermi surfaces

A striking result which has come out of the studies of high-\(T_c\) superconductivity is to learn just how good the LDA (local density approximation) bandstructures can be, for such complicated materials, as long as correlation effects are not too strong. Of course, there is Luttinger’s theorem, which exercises a powerful constraint on the result: the area of the Fermi surface must enclose the correct number of holes, independently of any correlation effects. Nevertheless, there is still considerable flexibility: the Fermi surface of YBCO consists of four (interacting) sections, associated with carriers on several different layers, and there have been experimental reports that all four sections are close to the calculated shapes and sizes. For present purposes, the most important result is that band structure calculations generally find that the Fermi level is close to the VHS at optimum doping, not only for LSCO \(^5\), YBCO, and Bi-2212, but also for the new Hg compounds \(^8\) and the borocarboes \(^5\).

In principle, the Fermi surfaces can be found by a number of probes, such as de Haas - van Alphen (dHvA) measurements and positron annihilation studies. However, these probes have had restricted utility in the cuprates. The dHvA oscillations are most sensitive to the smallest Fermi surface pockets, and so far have only found some minority pockets and chain related structure in YBCO \(^6\) and TI-2201 \(^3\). Positron annihilation tends to be sensitive to specific electronic states, and so far the technique has only been successful in identifying unambiguously the chain Fermi surface in YBCO \(^6\) and \(^7\) and in Bi\(_2\)Sr\(_2\)CaCu\(_2\)O\(_8\) (Bi-2212) \(^7\). In contrast, the Fermi surface in the electron-doped cuprates, with much lower \(T_c\)’s, is much further from the VHS. So far, no photoemission results are available for the lanthanates or the Tl or Hg compounds, due to the difficulty in obtaining high enough quality samples. Shen and Dessau recently reviewed photoemission studies on the cuprates, with related results on a variety of Mott insulators \(^6\).

Figures 3 through 11 illustrate the variety of Fermi surfaces found in the cuprates. Figure 11 shows the experimentally derived dispersion of the CuO\(_2\) antibonding band(s) for a series of cuprates \(^6\), showing a remarkable similarity to one another, and to the generic form of Fig. 1. Figures 12-16 illustrate the Fermi surfaces of individual cuprates in more detail. These are taken from both LDA calculations and photoemission experiments, and are representative of the optimally doped compounds. In all cases studied, the VHS is very close to the Fermi level – always within a phonon energy. In the following subsections, the various materials will be discussed individually.

1. Bi-2212

Bi-2212 is perhaps the best studied material. Photoemission measurements have been carried out by a number of groups \(^6\), \(^7\), \(^8\), \(^9\), and there is broad agreement on a number of features of the energy dispersion and Fermi surfaces. Figure 1a is included for historical purposes, but Figs. 1b and c are believed to be more representative. In particular, there is a large Fermi surface associated with the CuO\(_2\) planes, with a VHS very close to the Fermi level. By studying the transverse dispersion, Ma, et al. \(^7\) have confirmed that this is an extended saddle-point VHS. Several groups have measured the superconducting gap directly from the shift of the photoemission edge below the Fermi level \(^7\) \(^8\). It is generally agreed to be highly anisotropic, with a maximum gap in the \(M\) direction, along the Cu-O-Cu direction (i.e., close to the VHS), and nearly zero gap at 45° from this direction \(^7\) \(^8\). The gap and its symmetry will be discussed in Section VI.D.10. There are also strong indications of a shift of spectral weight below the Fermi level, for \(T < T_c\) \(^7\) \(^8\). A very similar gap is found in Bi-2223 \(^8\).

In addition to the CuO\(_2\) plane bands, a number of particular features in the band structure have been predicted or identified. First, the LDA calculations predict that a BiO pocket should intersect the Fermi level near \(M\), thereby coupling strongly to the VHS. This is not seen experimentally, except possibly in O-overdoped materials \(^6\) \(^7\). Note that this is one place where inverse photoemission data would be quite welcome. This discrepancy probably arises because the real atomic structure of Bi-2212 is more complex than that assumed in the LDA calculations, due to superlattice structure associated with the BiO planes. There is both a commensurate \(\sqrt{2} \times \sqrt{2}\) orthorhombic supercell, and an incommensurate modulation along the orthorhombic \(b\)-axis. Singh and Pickett \(^2\) have shown that in the presence of the orthorhombic supercell the BiO pockets are smaller, but should still be present. No one has yet calculated the effect of the incommensurate modulations on the pockets, but it is plausible to suppose that they might push the BiO pocket above the Fermi level, thereby explaining the residual discrepancy. However, there remains a problem: the BiO should form an electron pocket, and hence if it is shifted off of the Fermi level, it should reappear in underdoped material (assuming a rigid band filling). Yet curiously enough, the underdoped material has very
low c-axis conductivity, which is greatly enhanced in the overdoped material, suggesting that the latter is more 3D (conducting BiO layer). One possibility is that this is a charging effect – when too many holes are added to the CuO$_2$ planes, additional holes are repelled, and must populate other planes. This could also be a VHS effect, since the CuO$_2$ plane dos drops rapidly in the overdoped regime (see, for example, Ref. [53]).

The incommensurate modulation leads to additional Fermi surfaces produced by zone-folding along the b-direction, which are observed experimentally [3,2,4,57], Fig. 5. A number of detailed features differ between the various experimental groups. This may be partly due to differences in oxygen stoichiometry, and a curious change of the normal-state wave function symmetry has been reported between optimally-doped and overdoped materials [3]. Aebi, et al. [8] have applied a novel modification of the photoemission technique to provide a detailed map of the full Fermi surface. They interpret their data as two sets of Fermi surfaces, the original surfaces, as found in an LDA calculation, plus weak structure due to a set of zone folded ‘ghost’ Fermi surfaces, associated with incipient superlattice formation, Fig. 6. Bansil and Lindroos [88] have pointed out the importance of first principle photo-intensity computations for a proper understanding of how Fermi surface features manifest themselves in an angle-scanned photoemission experiment of the sort reported by Aebi et al. The ghost Fermi surfaces will be discussed in more detail below.

Photoemission experiments on underdoped Bi-2212 have provided striking evidence for pseudogap formation, Section IX.A.2.

2. YBCO, YBa$_2$Cu$_4$O$_8$

a. Extended VHS near Y-Point. Photoemission studies of the Fermi surfaces of YBCO have also been carried out by a number of groups [5,9,10,90,91], including studies of the variation of Fermi surfaces with O stoichiometry [91,92] and Zn and Co substitution [93]. While there is agreement between experiment and LDA calculations, there is considerable disagreement between different calculations, as to whether the X point VHS is bifurcated or merely broadened by coupling to the chains, Fig. 7. Experimentally, Veal, et al. [100] state that this peak is absent along the X axis (perhaps above the Fermi level), while Campuzano and Gofron [101] state that a feature is present, but broadened, perhaps by chain-plane coupling.

Recently, Schabel, et al. [102] have reported results on an untwinned YBCO$_{6.95}$ sample near the X-point. They find a Fermi level crossing similar to that in Bi-2212, but with complications from a strong chain-derived feature. By adjusting the polarization to minimize this chain feature, they found a plane-derived branch with significant dispersion, $\approx 0.5eV$, although a second, flatter band might also be present. This dispersion may be responsible for the absence of a well-defined quasiparticle peak along the $X - S$ line of the Brillouin zone. More importantly, this is the first YBCO sample for which an (anisotropic) gap has been observed, with the largest gap along $X - S$.

b. VHS Near X-Point? Due to the orthorhombic distortion in YBCO, the X and Y point VHS’s need not be degenerate in energy. Unfortunately, the issue of this possible VHS splitting is not well understood. The region near the X-point is very poorly characterized, both experimentally (most high resolution experimental results have been presented only near the Y-point) and theoretically, with considerable disagreement between different calculations, as to whether the X point VHS is bifurcated or merely broadened by coupling to the chains, Fig. 7. Experimentally, Veal, et al. [100] state that this peak is absent along the X axis (perhaps above the Fermi level), while Campuzano and Gofron [101] state that a feature is present, but broadened, perhaps by chain-plane coupling.

c. Complications from the Chains An additional complication in YBCO is the chain layer, which can also be superconducting and can enhance three-dimensional coupling. The chain band crosses the plane band near the X point, which has led to some confusion as to whether the band nearest the X-point is more plane-like or chain-like. Actually, there is no plane-chain coupling in the k$_z = 0$ plane of the Brillouin zone, so the bands simply cross at that point [102]. For arbitrary k$_z$ values, there is a weak hybridization in the immediate vicinity of the point at which they cross, leading to a band anticrossing effect. However, away from this crossing, the 1D band dispersion is predominantly associated with chain electrons, on both sides of the crossing, as illustrated in Fig. 8. Hence, the band nearest the X-point is predominantly plane-like, and there should be a VHS similar to that at the Y-
point.

The plane-chain coupling leads to a larger c-axis dispersion, which could smear out the VHS singularity near X. While the LDA calculations do find significant dispersion near X, the calculations tend to overestimate dispersion, particularly for interlayer coupling, so it would be important to have experimental data.

Chain ordering is also the cause of the orthorhombicity in YBCO, Y-124, which could split the degeneracy of the two VHS’s. For instance, LDA calculations in YBCO find both Y” and X point VHS’s below the Fermi level, but the Y-point VHS is predicted to be 180-200meV(!) below, while the X-point is only 0-20meV below (the spreads in values are due to c-axis dispersion).

3. NCCO

Photoemission studies of Nd$_2$−$x$Ce$_x$CuO$_4$, an electron-type superconductor, find a hole-like and roughly circular Fermi surface, Fig. 10. It is ≈ 200meV from the nearest VHS, and the authors have suggested that this may be why $T_c$ is so low. The apparent simplicity of the Fermi surface is deceptive, since the transport properties imply that the majority carriers are electron-like. This puzzling material will be discussed further in Section XV. The remarkable similarity of the Fermi surfaces of the various cuprates, is well illustrated by Fig. 11, which compares the Fermi surface of NCCO with those of the Bi compounds.

4. LSCO

While there are as yet no photoemission studies on this compound, band structure calculations find the Fermi level coincides with a VHS at the doping of optimum $T_c$, Fig. 12. Positron annihilation studies of the doping dependence of the Fermi surface are consistent with the LDA results, at least near optimal doping.

5. Hg-22(n-1)n

Again, photoemission studies have not yet been successful on these materials. However, Novikov and Freeman have carried out extensive calculations of the band structures, as a function of both stage number $n$ and pressure $p$, comparing them to the infinity phase compounds, Sr$_{1+x}$Ca$_x$CuO$_2$. In all cases, they find that the Fermi level is near one or more VHS’s (there are $n$ VHS’s in a stage $n$ Hg compound), and that the calculated doping (away from half filling) which places the first VHS at the Fermi level corresponds well with the experimental doping of optimum $T_c$. The Fermi surface has the same familiar form at the VHS, Fig. 13. (It would be useful to repeat this analysis for the Tl compounds.)

Pressure causes the apical O’s to move closer to the CuO$_2$ planes, which reduces the Fermi surface curvature, moving the VHS closer to half filling. (This is explained in a tight-binding model in Section V.C.2.) Now the closer the VHS is to half filling, the stronger are the VHS dos and susceptibility divergences. Unless a structural instability intervenes, this should lead to a higher value of $T_c$. Hence, the LDA calculations provide an explanation of why pressure can lead to such a large enhancement of $T_c$ (up to an unprecedented 164K in the 3-Cu-layer compound) and, moreover, in a way which cannot be mimicked by simple charge transfer. It remains to be seen whether this insight can be used to synthesize a chemical substitution which would stabilize these highest $T_c$ compounds at atmospheric pressure.

6. Sr$_2$CuO$_2$Cl$_2$

Many of the cuprate superconductors undergo a Mott-Hubbard transition to an antiferromagnetic insulating state, when the hole concentration is reduced to exactly half filling. So far it has not proven possible to measure angle-resolved photoemission from any of these samples. However, Wells, et al. have measured photoemission from the related insulating cuprate, Sr$_2$CuO$_2$Cl$_2$ (SCOC), Fig. 14a. Attempts to describe the results via calculations of a single hole in an AFM background (tt′J or 3-band models) have found difficulty in reproducing the measured energy dispersion, Fig. 14b, 14c. A good fit is found if the system is instead assumed to be in a flux phase. This is discussed further in Section VII.B.

Some compounds related to SCOC become superconducting when doped, including Sr$_2$CuO$_2$F$_{2−δ}$ ($T_c$=46K) and (Ca$_{1−x}$Na)$_2$CuO$_2$Cl$_2$ ($T_c$=26K). Novikov and coworkers have calculated the LDA band structure, and find a prominent VHS upon doping.

7. BKBO/BPBO

A future research area for the VHS is the exploration of the role of the VHS in 3D materials. Whereas peaks are often found in the dos of 3D metals, they are actually associated with a pair of VHS: the $M_1$ and $M_2$ VHS’s form the onset and terminus of a plateau in the dos, and a peak in the dos is really a narrow plateau. Formally, such a peak can be formed from a 2D saddle point VHS, with a small dispersion in the third dimension. The question is, whether this is an adequate representation of the dos peaks in real materials. The data in this and the following subsections are meant as preliminary hints only, that the Fermi surfaces of some high-$T_c$ materials are suggestive of such a picture.

Figures 15 and 16 show the calculated energy dispersion, dos, and Fermi surface in BaBiO$_3$. Fig-
ure 10) shows a series of cross sections through the Fermi surface, as the Fermi level crosses the VHS. The resemblance to the cuprates, e.g., Fig. 12 and Fig. 13, is striking, as is the fact that the Fermi level is predicted to nearly coincide with the X-point VHS. However, this is a fully 3D band structure, for the high temperature simple cubic phase, and the Fermi surface, Fig. 16b, is fully three-dimensional, with the VHS’s much less in evidence.

In the real material, there is a structural phase transition, presumed to be related to a CDW, which produces a $\approx 1.9$ eV gap at the Fermi level. Angle resolved photoemission studies have reported Fermi surfaces for the doped, metallic phases which are consistent with the calculated surfaces.

8. Fullerenes

Finally, Figure 17 shows a ‘disorder-averaged’ Fermi surface for the fullerene superconductors, $M_3C_{60}(M = K, Rb, Cs)$ [124]. For perfectly ordered buckybals, the Fermi surfaces depend sensitively on the relative orientations of adjacent balls. However, there is strong orientational (merohedral) disorder in these materials, which broadens structure in the dos. By averaging over the disorder, a residual, but smeared Fermi surface is found, which bears a striking resemblance to that of the cuprates. In fact, Mele and Erwin [124] have introduced a disorder-averaged virtual-crystal Hamiltonian model for the bands. They find that the bands reduce to three nearly independent 2D bands, which interact by level repulsion near the points where they intersect (the three bands differ in the choice of dispersing axes, $x, y, z, x, y, z$). The dispersion of the 2D bands is described by Eq. 12 below, with $t_1 = 0$, the simplest band structure used to describe the cuprates.

V. TIGHT-BINDING FERMI SURFACE MODELS

A. 1 Band and 3 Band Models

The LDA or experimental (photoemission) band dispersion can be reproduced by a tight-binding model of the Cu-O$_2$ plane involving three orbitals, Cu $d_{x^2−y^2}$ and one $p$ orbital on each of the planar O’s (the $p$ orbital with a lobe pointing towards the Cu). This is the standard three-band model. The Hamiltonian is

$$H = \sum_j (\Delta d_j d_j + \sum_\delta t_{CuO} [d_j^\dagger P_{j+\delta} + (c.c.)] + \sum_\delta t_{OO} [p_j^\dagger p_{j+\delta} + (c.c.)] + U n_{j\uparrow} n_{j\downarrow}),$$

where $j$ is summed over lattice sites, $\delta$ over nearest neighbors, $\delta'$ over next-nearest (O-O) neighbors, and c.c. stands for complex conjugate. Energies are measured from the center of the O bands, and $U$ is the on-site Coulomb repulsion. In a slave boson calculation, $U$ produces correlations which renormalize the one-electron band parameters. Thus, a simple model is to assume that the one-electron parameters are properly renormalized, and to otherwise neglect $U$. In this case, one need only solve the resulting one-electron Hamiltonian. The energy bands are the zeroes of

$$(E - \Delta)(E^2 - u^2) - 4E^2(s_x^2 + s_y^2) - 8ut^2 s_x s_y = 0 \quad (9)$$

with $t = t_{CuO}$, $s_i = \sin(k_i a/2)$, $c_i = \cos(k_i a/2)$, $i = x, y$, and $u = 4t_{OO} s_x s_y$. The VHS of the antibonding band is at

$$E_{VHS} = \frac{\Delta}{2} + \sqrt{\frac{\Delta}{2}^2 + 4t^2}. \quad (10)$$

For the special case $t_{OO} = 0$, the dispersion simplifies. One O-band decouples, at $E = 0$, the other two bands have dispersion

$$E = \frac{\Delta}{2} \pm \sqrt{\frac{\Delta}{2}^2 + 4t^2(s_x^2 + s_y^2)} \quad (11)$$

and the Fermi surface is exactly square at half filling.

The parameter $t_{OO}$ is important in shifting the VHS away from half filling. The sign is important: $t_{OO} > 0$ shifts the VHS in the direction of larger hole doping, as found in the cuprates.

In the cuprates, two of these bands are filled, and one, the antibonding band, is approximately half filled. For most purposes, it is sufficient to consider only this one band. In this case, it is often simpler in calculations to employ a one band model,

$$E^{(1)} = -2t_0(\bar{c}_x + \bar{c}_y) - 4t_1 \bar{c}_x \bar{c}_y, \quad (12)$$

where $\bar{c}_i = \cos k_i a$, $t_0$ is a nearest-neighbor hopping energy, and $t_1$ a next-nearest-neighbor hopping energy, and

$$E^{(1)}_{VHS} = 4t_1. \quad (13)$$

This model is convenient when only the shape of the Fermi surface matters. Also, it forms the basis of the tJ and t′J models, which include magnetic correlations but simplify the problem by neglecting the oxygens. The parameters of the one and three band models may be interconverted as follows. Let $\tau = t_1/t_0$ and $\bar{a} = 4t_{OO}/E_{VHS}$. Then both models will have exactly the same Fermi surface at the VHS whenever

$$\tau = \frac{-y}{2(1 + y)} \quad (14)$$

with $y = \bar{a} + \bar{a}^2/2$. The parameter $t_0$ can then be chosen to yield approximately the same bandwidth as in the
3-band model. There is considerable flexibility in this choice. One possibility, adopted here, is to make both models have the same curvature near the VHS [specifically, the same value of $(\partial s^2/\partial E)|_{s_{\pm}=0}$]. This yields

$$t_0(1+2\tau) = \frac{\hbar^2}{\sqrt{\Delta^2 + 16t^2}} = \frac{\hbar^2}{8m_\alpha^2a^2}. \quad (15)$$

While the one-band model can exactly reproduce the shape of the 3-band model Fermi surface, the overall dispersion is very different in the two models, so for fitting the angle-resolved photoemission, it is preferable to use the 3-band model. The difference can be seen by comparing Eqs. 10 and 13. $E_{VHS}$ is independent of $t_{OO}$ in the 3-band model, but is proportional to $t_1$ in the one-band case. A large (negative) $t_1$ pushes the VHS close to the bottom of the band, so to fit the dispersion below the VHS (seen in photoemission), a large value of $t_0$ must be assumed, which exaggerates the dispersion above the VHS.

B. Parabolic Bands

For analytic calculations in the vicinity of a VHS, it is convenient to introduce a further simplification by expanding the above dispersion relations near the VHS, and retaining only quadratic terms. This yields

$$E - E_{VHS} = \frac{\hbar^2}{2} \left( \frac{k_x^2}{m^-} - \frac{k_y^2}{m^+} \right), \quad (16)$$

with

$$\frac{\hbar^2}{8m_+^2a^2} = t_0(1 \pm 2\tau). \quad (17)$$

The second VHS has $k_x$ and $k_y$ interchanged.

This can be further simplified to

$$E - E_{VHS} = \frac{2\hbar^2k'_yk'_y}{m^*}, \quad (18)$$

with $k'_y = k_y\sqrt{m^*/m^-}$, $k'_x = k_x\sqrt{m^*/m^+}$, and $m^* = \sqrt{m^+m^-}$, or

$$\frac{\hbar^2}{8m^2a^2} = t_0(\sqrt{1 - 4\tau^2}). \quad (19)$$

Note that the scaling of the $k'$s would involve the opposite effective masses for the second VHS, so Eq. 18 cannot be used to describe inter-VHS scattering. However, it affords a simple approximation for calculating intra-VHS properties.

C. Parameters for the 3 Band Model

1. LSCO: Tight Binding Parameters

It is widely believed that the essential physics of the cuprates should be contained within the three band model of the CuO$_2$ planes. This belief is far more general that the VHS scenario. In Anderson’s model [25], for example, the CuO$_2$ plane bands must be supplemented by an interlayer coupling contribution, but the three-band model still plays an important role. It is thus essential to know the ‘correct’ values to assign to the parameters. The best procedure seems to be to derive parameter values from the LDA band calculations.

However, extreme care must be taken in extracting the parameters, and it is by no means clear whether the best values have yet been found, even for the simplest case of LSCO. In this section, I will discuss some of the problems, and provide a Table of recommended values for LSCO, with suggestions of how these values might change in the other cuprates.

The simplest procedure is to directly fit the LDA-derived Fermi surfaces with a tight-binding model. Unfortunately, the LDA calculations underestimate the role of correlation effects, particularly near half filling, where LDA calculations do not reproduce the transition to the insulating state. For optimal doping, correlation problems are less severe, and a simple tight-binding fit might be adequate. Table I lists tight-binding fits [57,126,103] to the Fermi surfaces for a number of cuprates in the one-band model, Eq. 8. Andersen, et al. [103] also include values for more distant neighbor hopping. Table II lists the corresponding values for the three-band model, Eq. 11. Three sets of values are listed in Table II. Those for LSCO and YBCO are derived from the values in Table I, using Eqs. 14 and 13. This inversion is not unique; however, it is found that $\Delta$ is small, so $\Delta = 0$ is assumed. The values listed for Bi-2212 are the renormalized (via slave boson calculation) parameters which reproduce the photoemission-derived band dispersion of Bi-2212.

In the one band model, it is important to know how the doping $x_c$, at which the Fermi level coincides with the VHS, varies with the parameter $\tau$. This relation is derived in Appendix B.

Many physical properties are given by integrals over the band structure. For example, $\mu$SR results are typically calibrated in terms of $\lambda^{-2} \propto n/m$, where $\lambda$ is the penetration depth, and the factor $n/m$ is derived from a parabolic-band model. What is actually measured is the plasma frequency, which cannot simply represent $n/m$, since it must vanish for a full or empty band. It can be written, for a 2D band, as

$$\omega_{pl,x}^2 = \left( \frac{e}{\pi \hbar} \right)^2 \frac{2c}{\pi} \int d^2k \frac{\partial^2 E}{\partial k_x^2}. \quad (20)$$

For the one-band model, this is illustrated in Fig. 18. Note that $\omega_{pl}$ has a peak near half filling, but not ex-
actly at the VHS. This could help explain the anomalous doping dependence of $T_c$ in overdoped cuprates (the ‘boomerang’ effect), Section VI.D.5.

2. LSCO: Correlation Corrections

More care must be applied if one wishes to include correlation effects in some approximation beyond the LDA. That is because the LDA-derived parameters already include correlation effects in an average way. These correlation effects must first be eliminated to produce bare parameters. A striking example is the transition to a charge-transfer insulator at half filling. This transition occurs when $\Delta/\Delta_{cCuO}$ exceeds a critical value. In LDA calculations, correlations reduce the value of $\Delta/\Delta_{cCuO}$ so much that a correlation calculation, using these starting values, will find a metallic state at half filling. Hence, it is essential to first find the bare, unrenormalized three-band parameters before undertaking a correlation calculation. For LSCO, several groups have provided estimates of these bare parameters, Table III, using LDA or cluster calculations \[127,129\]. Earlier calculations are summarized in Ref. \[130\].

However, even these parameters require further modification: they have been determined as part of a larger parameter set. When this larger parameter set is further reduced to a three-band model, the remaining parameters will have to serve double duty, and the best choice of parameters will be modified from the values found in the larger parameter set. Two examples will be given.

First, at half filling, a hole transferred from a Cu to an O will almost always find that there are already holes on each of the surrounding Cu’s. Hence, it will have an energy $\Delta + 2V$, where $V$ is the nearest neighbor Coulomb repulsion \[131\]. Away from half filling, this is modified to

$$\Delta_{eff} = \Delta + 2V(1 - x - 4r_0^2),$$ (21)

where the term in $r_0$, the mean field amplitude of the slave boson, can play a role in phase separation, as will be discussed further below. Neglecting this term for now, the constant term $2V(1 - x)$ provides a (doping-dependent) renormalization for $\Delta$, for which the $x = 0$ value is listed in Table III. In a three-band model, $\Delta_{eff}$ will provide the best single parameter approximation of the energy difference between adding a hole to a Cu or to an O.

As a second example, it is essential in the VHS model to correctly predict the doping at which the Fermi level coincides with the VHS; within the model, this is also the doping of optimum $T_c$. Now, in the full LDA calculation, this doping is fixed by a rich interplay of many band parameters \[133\], whereas in the three-band model, it is entirely fixed by a single parameter, $t_{OO}$. Hence, in a strictly three-band model, the value chosen for $t_{OO}$ does not coincide with the LDA-derived value of this parameter, but must be taken as an effective parameter which correctly reproduces the location of the VHS. It appears that this value will be considerably smaller than the LDA value. Thus, Aligia \[134\] has shown that the Fermi surface curvature is controlled by two opposing effects, the direct O-O hopping and the Cu $d_{z^2}$-$p^2$-$d_{z^2}$ mixing term, which acts to reduce the curvature. This problem has recently been studied in detail \[136\].

In Ref. \[136\], I attempted to derive an effective value of $t_{OO}$ from a five-band model of the CuO$_2$ planes, including the Cu $d_{z^2}$ and apical O orbitals \[137\]. I found a reduction by more than a factor of two, but due to uncertainties in the parameter values, I do not believe that the final results are quantitatively correct. Hence, I suggest that at present, the best way to choose the value for $t_{OO}$ is empirical: to adjust the value of $t_{OO}$ to reproduce the LDA-value of Fermi surface curvature at optimum doping. This doping is chosen since correlation effects are smaller away from half filling, and the LDA calculations seem to do a good job of reproducing the Fermi surfaces. Clearly, a full derivation of the appropriate $t_{OO}$ is a desideratum, but at present, this seems to be the best available choice. The resulting corrected parameter values are listed in Table IV.

3. Other Cuprates

Unfortunately, such ‘bare’ parameters are available only for LSCO, whereas it is known that the correlated parameters differ significantly for different cuprates.

For other superconductors, there is considerably less information. Only for YBCO are estimates available \[98,103\], Table III, and these have not been corrected for correlation effects. In analyzing other superconductors, two factors enter: first, the values of the three primary parameters may be different, and secondly, additional parameters may be important. These issues will be addressed consecutively. First, since the dominant physics lies within the CuO$_2$ planes, the parameter values would be expected to be fairly similar. However, small changes can be important. For example, $t_{OO}$ seems to be larger in YBCO than in LSCO. This means that the VHS is shifted further away from half filling in the former compound. Correspondingly, the optimum doping is about 0.15 holes/Cu in LSCO and 0.25 holes/(planar) Cu in YBCO. In both cases, the optimum doping brings the Fermi level into registry with the VHS. (In a recent re-analysis of the data \[43\], it has been suggested that the optimum doping is the same for all cuprates, but this result remains controversial. It is further discussed in Section VI.D.5.)

As a second example: the value of $\Delta$ in LSCO is only a little larger than the critical value $\Delta_c$ needed to drive the transition to a charge transfer insulator at half filling. In the Bi- and Tl-based cuprates, it is much harder to find evidence of this insulating phase.
Could this be because for these compounds $\Delta < \Delta_o$? Physically, the parameter $t_{CuO}$ should depend sensitively on the Cu-O separation, $d_{CuO}$, but otherwise may not be sensitive to the chemical environment off of the planes. On the other hand, $\Delta$ depends on the Madelung energy at the Cu and O sites, and hence can differ in different compounds. Similarly, since $t_{OO}$ is modified by additional, off-planar orbitals (particularly the apical O’s, which influence the Cu $d_{z^2}$’s), it can also vary from compound to compound. Ideally, the same detailed procedure should be followed to extract the corrected parameters for all these compounds from the LDA calculations, but in the short term, the simplest procedure is to do a simple tight-binding fit to the LDA data, and then use this to ‘adjust’ the corrected values found for LSCO.

An additional problem is that, for other compounds, parameters beyond the three-band model can be important. A number of examples will be provided in the following subsections.

D. Beyond the 3 Band Model

1. Several CuO$_2$ Layers per Unit Cell

The cuprates behave two-dimensionally because they are layered compounds, and one of the layers is nearly insulating, so that hopping across that layer is extremely improbable. These insulating layers break the material up into cells, such that there can still be strong interlayer coupling within a cell, even though there is very little coupling between cells. While the intercell coupling eliminates the dos divergence at a VHS, intracell coupling does not: it only splits the VHS into several components, each of which diverges logarithmically. In the Bi-compounds, this intracell hopping is so small that it can approximately be neglected. In YBCO, it is quite large, leading to two well-resolved Fermi surfaces, corresponding to symmetric and antisymmetric combinations of holes on the two planes. Liechtenstein, et al. [139] have shown that correlation effects can reduce the intercell splitting by nearly an order of magnitude. These two Fermi surfaces appear to have been resolved in photoemission studies (Fig. 8). Interband coupling can be accounted for by adding a contribution due to hopping along the c-axis. However, the angular dependence of this hopping term is in dispute. To describe the calculated and measured dispersion in YBCO, I have simply added or subtracted a constant term in the energy dispersion:

$$E^{(1)} = -2t_0(\bar{c}_z + \bar{c}_y) - 4t_1\bar{c}_x\bar{c}_y \pm t_z,$$

where $t_z$ is given in Table I. In contrast, Chakravarty, et al. [125] have proposed that the $t_z$ term is proportional to $(c_x - c_y)^2$, which would make the two bands degenerate along the diagonals of the Brillouin zone, in contrast to experiments on YBCO, Fig. 8b, although it may hold for Bi-2212. This issue is discussed in Ref. [103]. For present purposes, the precise shape of the Fermi surface is not crucial. What matters is that, by including a $t_z$ term, it is found that the antisymmetric Fermi surface is considerably larger than the symmetric combination. Indeed, virtually all of the doped holes go into the antisymmetric band, leaving the symmetric band half filled. In optimally doped YBCO, it is the antisymmetric band whose Fermi surface coincides with the VHS.

2. Intercell Coupling and c-axis Resistivity

Since the intercell coupling cuts off the VHS divergence, it can lead to an important restriction on VHS theory. However, the superconducting transition depends only on the integrated dos, within $\sim 4k_B T_c$ of the Fermi level. Thus, if the splitting due to interlayer coupling, $\sim 4t_z$ is smaller than this, the broadening of the dos peak will have no effect. While the calculated values of $t_z$ are already small, there is evidence that correlation effects reduce its importance further, and a strong intracell confinement has been predicted by the spinon-holon theory [140,125]. This same factor is responsible for coherent interlayer conductivity, $\sigma_c$. Yu and Freeman [143] have found that the calculated values for $\sigma_c$ in YBCO exceed the experimental values by over an order of magnitude, and suggest that polaronic effects may be responsible for the difference. Correlation effects may be more important for interlayer coupling – they can reduce intracell interlayer hopping by nearly an order of magnitude [139]. From measurements of the optical conductivity of LSCO, Tamasaku, et al. [142] find that the effective number of electrons contributing to $\sigma_c$ is orders of magnitude smaller than that expected from the theoretical plasma frequency. Indeed, it has been possible to understand the c-axis conductivity of most cuprates below $T_c$ as due solely to Josephson coupling between the superconducting layers [143,144]. Tallon, et al. [145] were able to experimentally vary the interlayer coupling in YBCO by simultaneously doping Ca for Y and removing O, to disrupt the chains while staying at optimal plane doping. They found that $T_c$ actually decreases slightly as the interlayer coupling decreases. This result only means that even for maximal chain coupling, the interlayer hopping is too small to reduce $T_c$ (the residual decrease in $T_c$ is presumably due to a crossover to a 2D Kosterlitz-Thouless type superconductivity).

3. Coupling to Other Layers

The Fermi surface at the VHS illustrated in Fig. 8 is the form most commonly found for the cuprates, but it is not the only possible form. When two Fermi surface sections approach closely in energy, they can hybridize, giving rise to new Fermi surfaces of strikingly different
shape. For instance, LDA calculations of Bi-2212 generally find a Bi pocket just beginning to open near the $X(Y)$ points of Fig. 3 (in the orthorhombic unit cell of Bi-2212, this is referred to as the $M$ point). Since this point coincides with the CuO$_2$ VHS’s, the interaction is very strong. The resulting Fermi surface shapes have been discussed [22]. The VHS’s are not eliminated, but are split and shifted in energy. (Van Hove proved that there must always be at least one saddle point VHS for any 2D electronic band.)

While the LDA calculations find BiO hole pockets crossing the Fermi level, they are not seen experimentally in optimally doped samples, as discussed in Section IV.B.1. However, they should be present just above the Fermi level, and hence will modify the dispersion. Also, doping away from the VHS may push them through the Fermi level.

In addition to distorting the shape of the Fermi surface, these additional layers, if metallic, can also be rendered superconducting via proximity effects. This has been proposed for both the chain layer in YBCO and the Tl layers in the 2-Tl-layer Tl-cuprates [146]. In YBCO, there is evidence that the chains are superconducting (at optimum doping), but do not greatly modify the value of $T_c$ [147]. There is an interesting complication in YBCO: the chains are very sensitive to oxygen stoichiometry, since the O vacancies lie in the chains, and O vacancy disorder quickly disrupts chain conductivity. This strong disorder effect can lead to gapless superconductivity on the chains, with anomalies in many of the superconducting properties [148].

4. Extended and Bifurcated VHS’s

Just as the BiO pocket can push the VHS’s away from the Brillouin zone corners in Bi-2212, interlayer coupling in YBCO is predicted to lower the band energy at the $X$ (and $Y$) points, leading to a camelback band structure. The energy has a local maximum along the $\Gamma - X (\Gamma - Y)$ line, and the change in topology as the energy moves through this maximum leads to a pair of VHS’s, degenerate in energy, Fig. 3c: Andersen et al. [28,103] have provided a detailed calculation, explaining the origin of these bifurcated VHS’s. The bifurcation comes about through a small admixture of the three bands (plus Cu 4s) with a group of c-axis directed $\pi$-orbitals, including the planar O $p_z$ orbitals. This mixing becomes allowed due to the dimpling (or tilting) of the CuO$_2$ planes.

Experiments on YBCO and Y-124 have not found these bifurcated VHS’s, but instead the potentially more interesting extended VHS’s [56]: compare the theoretical and experimental band dispersions found in Fig. 3c. In an extended VHS, the saddle point extends over a finite length of Fermi surface, enhancing the associated dos singularity. There does seem to be a connection between the two types of VHS, in that the length of the extended VHS is approximately the separation between the two bifurcated VHS’s. However, the bifurcated VHS’s are not equivalent to the extended VHS’s: at a bifurcated VHS, the dos always has a logarithmic divergence, even at the point of bifurcation, and indeed it is difficult, in looking only at the dos, to tell when the bifurcation has occurred. Correlation effects can reduce the dispersion, leading to a stronger logarithmic divergence – this is particularly true for interlayer correlations [139]. However, within slave boson theory, correlations will not change the divergence to the power law form, which has been postulated for an extended VHS [24].

An interesting question has to do with (inter-VHS) nesting at an extended saddle point. For the bifurcated VHS’s there is very strong inter-VHS scattering [35]. Since the VHS’s are shifted off of the $X$ and $Y$ points of the Brillouin zone, the inter-VHS scattering is very far from $Q_0 = (\pi/\alpha, \pi/\alpha)$ – for example, see the arrow in Fig. 3a. For an extended VHS, the $Y$-point VHS is stretched along $\Gamma - Y - \Gamma$, but still centered at $Y$; the $X$-point VHS would be stretched at right angles to this. The resulting inter-VHS scattering should be strong over an extended region, centered at $Q_0$. This difference between bifurcated and extended VHS’s should be reflected in the spin susceptibility $\chi$: whereas inter-VHS scattering from bifurcated VHS’s should lead to well-defined incommensurate peaks in $\chi$, extended VHS’s would lead to a broad peak in the spin susceptibility at $Q_0$, the AFM point. Recent experimental evidence on this point will be discussed in Section VI.E.3 (Fig. 3b).

It would be useful to generalize the three band model, to incorporate bifurcated saddle points, and then study how these are modified by correlation effects. Andersen et al. [28] have attempted to produce a set of tight-binding parameters which do just this. Unfortunately, the effects of correlations have not been removed from the parameters, so, just as in LSCO, these parameters cannot be used in slave boson calculations. Thus, when the tight-binding parameters are reduced to a three band model (Table III), the Cu-O splitting is found to be $\Delta = 3.0$ eV. This is better than the situation in LSCO, where neglect of correlations led to estimates of $\Delta \approx 1.4$ eV [149], but $\Delta/t_{CuO} \approx 1.9$ is still too small to lead to an insulating state at half filling – the critical value of this ratio is 3.353, Eq. 17. Since the balance of parameters is so delicate, simply increasing the value of $\Delta$ is found to move the camelback away from the Fermi surface. For more extensive parameter sets, which reproduce the bifurcated VHS’s, the original references [18,103] should be consulted. (Note further that when the model is reduced to three band or one band form, additional interactions arise which are not included in Eqs. 8 and 12.)

The microscopic origin of the extended VHS’s remains unclear, although there are a number of theoretical possibilities. One can generate extremely flat bands by renormalizing the band dispersion near a VHS by, e.g., strong electron-phonon coupling [150], as discussed in Section VIII.D (see Fig. 33) or in the presence of a (magnetic...
pseudogap [111]. However, in both these examples, the actual divergence remains logarithmic, and the extended VHS arises from band narrowing. If one actually wants the dos to change from a logarithmic to a square-root divergence, this can be done only by making the dispersion quasi-1D – e.g., formally, by making the Cu-O hopping parameter anisotropic, $t_x << t_y$. These two situations can be readily distinguished: as the bands become more one-dimensional, the VHS moves closer to a band extremum – either the top or bottom of the band. Note that this is approximately what happens when a gap is opened at the VHS, Fig. 1. The careful study of the dispersion near the VHS in Y-124, where the VHS is 19meV below the Fermi level, would appear to place severe limitations on any quasi-1D model of the extended VHS.

5. Chain Ordering

In YBCO, the CuO chains are also conducting, and must be included in any quantitative model. In addition to proximity-effect superconductivity, discussed above, chains can play a number of roles. First, the chain-ordering transition breaks the symmetry of the X and Y points, and can split the degeneracy of the two VHS’s. This can affect the doping dependence of properties, structural instabilities, and the magnetic susceptibility at $(\pi, \pi)$, important for antiferromagnetism. Unfortunately, the structure near the X point is one of the features in which different LDA calculations are most in disagreement, and more photoemission studies should be made near the X point. Since the chains conduct only parallel to their lengths, along the b-direction, they greatly enhance the in-plane anisotropy of the normal-state transport properties.

6. Ghost Fermi Surfaces

There is considerable experimental and theoretical evidence for the existence of ‘pseudogaps’ (Section IX.A) – an incipient gapping of (part of) the Fermi surfaces of these materials. This may be caused by magnetic effects (incipient antiferromagnetism) or by structural effects. In either case, the gap formation could be associated with an increase in the size of the in-plane unit cell. If so, this would lead to the appearance of additional bands in the Brillouin zone, by a process of zone folding. The gaps are not fully formed, but some residual trace is expected to appear in the photoemission, in the form of ‘ghost bands’ with anomalously large broadening. Such bands are seen in Bi-2212 in photoemission, where they were attributed to short range antiferromagnetic correlations [58], Fig. 1. However, there is no evidence for long-range antiferromagnetic order in Bi-2212, except by substituting Y for Ca [151]. It seems more probable that these ghost surfaces are associated with the known orthorhombic distortion of the Bi-2212 structure [52]: the pseudogap transition temperature is generally found to be close to the superconducting $T_c$ in optimally doped 90K materials, whereas the ghost Fermi surfaces persist up to room temperature in Bi-2212. In other cuprates, the ghost Fermi surfaces may be too smeared out to observe.

7. Spin-Orbit Coupling

Finally, spin-orbit coupling can play an important role in modifying the shape of Fermi surfaces. Thus, in LSCO, the LTO phase transition leads to a doubling of the unit cell, hence to a reduced Brillouin zone, with consequent zone folding. However, because the unit cell contains a glide plane, the energy bands can cross without opening a gap on the Brillouin zone face. (Because of this, the presence of the orthorhombic supercell can often be neglected, as in Fig. 1, above.) However, spin-orbit scattering leads to a coupling between these bands, opening gaps and strongly modifying the topology of the Fermi surface [39]. Since spin-orbit coupling can split the VHS degeneracy, it was originally thought that it might play an important role in structural phase transitions, but the energy involved seems to be too small. Nevertheless, this coupling will have a significant influence on the exact Fermi surface shape, and hence on low-energy transport properties, such as Hall effect and magnetooscillatory phenomena. Spin-orbit coupling also plays an important role in the magnetic properties, opening a gap in the spin-wave spectrum and contributing to the 3D coupling which gives rise to a finite Curie temperature for the antiferromagnetic transition.

VI. PROPERTIES OF A SIMPLE VHS THEORY

A. Divergences in dos and Susceptibility

While the dos and the charge and spin susceptibilities of the VHS model must generally be calculated numerically, some analytical results are possible in the one band and parabolic models. In general, the carrier density is given by the area of the Fermi surface,

$$n = \frac{2ncu}{\pi^2} \int_0^{\pi} \phi_x d\phi_y,$$

(23)

where $\phi_i = k_i a$, $i = x, y$, and $ncu$ is the density of the planar Cu atoms. The dos is then

$$N(E) = \frac{2ncu}{\pi^2} \int_0^{\pi} \frac{\partial \phi_x}{\partial E} d\phi_y.$$

(24)

For the one-band model, in the special case $t_1 = 0$, this can be evaluated exactly.
\[ N(E) = \frac{n_{cu}}{\pi^2 t_0} \int_0^\pi \frac{d\phi_y}{s_x} = \frac{n_{cu}}{\pi^2 t_0} K \left( \sqrt{1 - \left( \frac{E}{4t_0} \right)^2} \right) \]
\[ \simeq \frac{n_{cu}}{\pi^2 t_0} \ln \left( \frac{16t_0}{E} \right). \]  

The density can also be evaluated exactly in the parabolic model,
\[ N(E) = 2 \frac{m^* a^2}{2h^2 k_0^2} \ln \left( \frac{2h^2 k_0^2}{m^* a^2 E} \right) \]
where \( k_0 \) is a momentum cutoff and the first factor of \( \phi \equiv \frac{1}{2} \ln \left( \frac{1 + \delta}{1 - \delta} \right) \ln \left( \frac{\phi_x}{\phi_y} \right) \) if \( A < 1 \) and \( \phi_c \approx \max(T, \omega) \) a small angle cutoff, \( A = \tan \alpha \), and \( \alpha \) defined in Fig. 19.

**B. Estimating Hole Density**

Let \( P \) designate the excess hole doping per CuO₂ plane of a cuprate away from half filling. Experimentally, it can be measured by iodometric titration. In many cuprates, \( P \) can be estimated from the chemical valence. Thus, in LSCO and LBCO, \( P = x \), the number of dopant Sr’s or Ba’s. When the doping is related to added O’s, \( P \) can be estimated from O content, measured, e.g., by thermogravimetric analysis (TGA), but the relation between \( P \) and hole doping must be known. Thus, for YBCO, there is evidence that, when O’s are first added to the chains \((y \equiv 1 - \delta \approx 0)\), the holes remain localized on the chains, up to a critical doping \( y_0 \). Tokura, et al. proposed that \( y_0 = 0.5 \), and \( P = 0.25(y - y_0) \) for larger dopings. However, there is evidence from studying modifications to the Neél temperature, that plane doping starts at \( y_0 \approx 0.2 \). More recently, Tallon, et al. have proposed \( P = 0.187 - 0.21 \delta \), for \( \delta \leq 0.55 \), followed by a more rapid drop for larger \( \delta \), and \( P \approx 0 \) for \( \delta \geq 0.7 \).

In \( La_2CuO_4+\delta \), there is considerable uncertainty about the relation between \( P \) and \( \delta \) (note that in \( La_2CuO_4+\delta \), adding oxygen increases \( \delta \), whereas adding oxygen decreases \( \delta \) in YBCO). Grenier and coworkers found a large discrepancy between TGA and iodometric results, which they could correlate with excess O adsorbed on nonbonding sites from the electrolytic solution. Correcting for the adsorbed fraction, they found that the two measurements would be reconciled if each O contributes two holes to the CuO₂ plane, or \( P = 2\delta \). On the other hand, Radaelli, et al. [157] found better agreement with the relation \( P = \delta \), which would suggest that the interstitial O’s have a partially covalent bonding with the apical O’s, forming the peroxide \( O_2^2^- \). Grenier [158] suggested that he may have overestimated \( \delta \). Chou, et al. [159] find an intermediate result, that the susceptibility of \( La_2CuO_4+\delta \) matches that of optimally doped LSCO \((x = 0.15)\) for \( \delta = 0.11 \). More recently, Johnston [160] found a crossover

\[ P = \begin{cases} \delta & \text{if } \delta \leq \delta_0; \\ \delta_0 + 2(\delta - \delta_0) & \text{if } \delta > \delta_0, \end{cases} \]

with \( \delta_0 \approx 0.06 \), close to the upper limit of the two-phase region. In this paper, I will use this last result, but generally quote the doping in terms of \( \delta \) (note however that Grenier’s group usually measures \( P \) directly by iodometric titration, and converts that into an effective \( \delta \) by the relation \( \delta = P/2 \)). Even lower values of hole doping \(- P \approx 1.1 \delta \) at \( \delta = 0.12 \) – see Ref. [161] and references therein.

**C. Normal State**

There is considerable evidence that the normal state of the cuprates is highly anomalous, particularly in the immediate vicinity of optimum doping. This has led to the notion of a marginal Fermi liquid [162], [163], where the renormalization factor \( Z \) vanishes weakly (logarithmically) at the Fermi energy, so that quasiparticles are not quite well defined. In this section, it will be shown that most of the anomalous normal-state features can be accounted for in the context of the VHS model.

In calculating the properties of the VHS model, a number of complications must be taken into consideration. First, in studying the doping dependence, it is not correct to assume a tight-binding model, since correlation effects pin the Fermi level close to the VHS over an extended doping range, and the dos may actually increase with underdoping.
More importantly, it must be recognized that the Van Hove scenario can actually be subdivided into two classes, the *basic* and the *generalized*. In the *basic* scenario, one analyzes the role of a peak in the dos on superconductivity and the normal state properties, taking correlation effects into account, but neglecting any complications from structural instabilities or phase separation. In the *generalized* scenario, one notes that there are competing instabilities in the vicinity of a VHS, and that these instabilities can profoundly modify physical properties in the vicinity of a VHS. For instance, when a pseudogap opens up, the splitting of the VHS peak will drive the large dos away from the Fermi level. 

In this section, the predictions of the *basic* scenario will be worked out and compared to experiment. The conclusion of this exercise is that while there are some tantalizing correspondences, there are enough differences of detail to suggest that the basic scenario is too simplified to completely describe the cuprates. In particular, recent heat capacity and photoemission studies show that the pseudogap strongly modifies the properties of the underdoped cuprates in ways that are inconsistent with the basic scenario, but that have actually been predicted with the generalized scenario.

In subsequent sections, the complications of the *generalized* scenario will be discussed. These are of two types: (a) strong electron-phonon coupling, which leads to pseudogaps; and (b) a tendency to (nanoscale) phase separation, which produces striped phases. In principle, these are two independent phenomena, and it is possible that some materials may display one without the other (although, within the VHS scenario, the strong electron-phonon coupling stabilizes phase separation). However, in the cuprates, both phenomena appear to coexist, and the greatest challenge lies in understanding how both can be simultaneously present.

### 1. Thermodynamics

#### a. Peak in \( \Delta C \). The peak in the dos associated with the VHS should be directly observed in a number of measurements, such as heat capacity, compressibility, and magnetic susceptibility. These and other thermodynamic properties of a VHS are calculated in Appendix A. Here, the simple VHS model has difficulty in describing the data, since these are dominated by effects of pseudogap formation and/or phase separation. For example, in studying the heat capacity, some groups found it more convenient to analyze the jump in specific heat, \( \Delta C \), associated with the superconducting transition [164-165], due to the difficulty of separating out the phonon contribution to the heat capacity. Theoretically, this should be a measure of the thermally averaged dos:

\[
\Delta C(\delta) = A^2 B^2 k_B^2 T_c <N(\delta)>_{T_c} (1 + \lambda_{ep}),
\]

with \( A^2 = -d[N(\delta)/\Delta(\delta)]^2/d(\delta/T_c)|_{T=\Delta} \), \( B = \Delta(0)/T_c \), and

\[
<N(\delta)>_{T_c} = \int_{-\infty}^{\infty} N(\epsilon)(-\frac{\partial f}{\partial \epsilon})d\epsilon.
\]

This thermal averaging smears out the logarithmic divergence, but still leaves a distinct peak (see Eq. A18). For a weak coupling treatment of the VHS [164] (using the modified parabolic band, Eq. [3]), \( A = 1.74 \) retains its BCS value, while \( B \) varies from 1.84 at the VHS (\( \delta \approx 0 \)) to the BCS value, 1.76, as \( \delta \) increases. The last term in Eq. [9] is included to account for an effective mass enhancement associated with electron-phonon coupling, and must also be calculated in the VHS model [164]. Figure 24a shows the measured [166-169] \( \Delta C \) as a function of oxygen deficiency \( \delta \) in YBCO, compared with both a weak coupling VHS theory (solid line) and a strong coupling version (dashed line). The samples were quenched from high temperatures to minimize problems of phase separation. A clear peak is observed at the optimum value of \( T_c \), which is actually *sharper* than the weak coupling VHS peak. While a strong coupling calculation gives better agreement, this might be evidence for an extended VHS [170]. It is also possible that \( \Delta C \) contains a chain contribution, which is very sensitive to oxygen deficiency. Similar peaks in \( \Delta C \) have been found in LSCO [170], \( \text{Y}_{1-x} \text{Ca}_x \text{Sr}_2 \text{Cu}_2 \text{TiO}_{6-\delta} \), and overdoped T\text{2201} [170,175]. In fact, a reanalysis of the YBCO data [170] finds that when the fluctuations are subtracted, the jump in heat capacity \( \Delta C \) continues to increase, significantly (by \( \approx 45\% \)) in the overdoped regime. The authors suggest that this effect, unique to YBCO, may be associated with chain ordering.

However, the situation is somewhat more complicated. Figure 20b shows that there are two contributions to \( \gamma T \); one associated with the jump \( \Delta C \) at \( T_c \) (diamonds) plus a residual contribution, \( \gamma T \) present in the normal state (open and closed circles are two different measures of this quantity). This is suggestive of phase separation away from the optimum doping, with the two contributions representative of the two phases. The sum of the two contributions (solid line) has a broad peak near the optimum doping, consistent with a broadened VHS peak (for \( x \leq 0.15 \) – the sharp falloff at lower \( x \) is more likely associated with the pseudogap). Hence, the strong doping dependence of \( \Delta C \), Fig. 20a, may be more indicative of the doping dependence of the superconducting fraction, due perhaps to phase separation, rather than the doping dependence of the dos.

#### b. Peak in Heat Capacity, Susceptibility. This conclusion is reinforced by additional studies of the full electronic contribution to the heat capacity [93] and the susceptibility \( \chi [177,178,99] \), which tend to resemble the solid line in Fig. 20a, dominated by a pseudogap in the underdoped regime. At \( q = 0 \), a Pauli-like (T-independent) susceptibility is found only near the doping of optimum \( T_c \) [180] in YBCO; at lower dop-
ing in YBCO, and all dopings in LSCO, a stronger T-dependence is found, which has been attributed to pseudogap effects. Thus, Loram, et al. [181] show that in YBCO, the temperature and doping dependence of $\chi$ is consistent with that of $C_v$, and both are strongly influenced by pseudogap formation.

The influence of the pseudogap on $C$ and $\chi$ will be discussed in Section IX.A.2. Here, I wish to address the question of whether, if the pseudogap could be eliminated, there would be any residual evidence for the VHS. First, the opening of the pseudogap is quite similar to what is expected for VHS nesting, accompanied by the splitting of the VHS degeneracy. Hence, it might be thought that the dos derived from $\chi$ and $C$ should resemble that of a split VHS, which in turn would resemble a single VHS, shifted off of the Fermi energy. Loram, et al. [2] have considered that possibility, and conclude that a gap function produces a considerably better fit to the data: for a shifted VHS, there would still be a substantial (d-wave) gap.

Hence, the remaining question is whether a VHS can be seen to underlie the pseudogap. In LSCO, this appears to be the case [182]. As the hole doping is increased, the pseudogap collapses, revealing a peak in the dos, Fig. 21, open squares, which gradually crosses over to a flat dos at the Fermi level, whereas the data clearly reveal a pseudogap at or near $q = Q_0$, just as predicted for a VHS.

In YBCO – the symmetric plane band and the chain band. In particular, the chain band anticrosses the antisymmetric plane band, with zero gap in the $k_z = 0$ plane. Hence, there will be interband contributions to the dos, which should increase with frequency, or temperature, starting almost from $T = 0$ (not to mention the symmetric plane band VHS’s). Evidence for this explanation comes from Y NMR [183], which gives a measure of the local susceptibility at the Y site, and hence weighs the CuO$_2$ plane bands more strongly. In optimally doped material, the $^{89}$Y NMR shift does indeed have a peak at $T = 0$, open circles in Fig. [21] (here, the Knight shift has been transformed into a susceptibility by assuming that the peak value coincides with the susceptibility of Ref. [19]). There are two simple ways to explain the dos lineshape: in the dashed line of Fig. [2], the data are fit to a broadened VHS, $t_\delta = 20meV$; while the filled circles of Fig. [2] are the susceptibility data after subtracting a constant contribution $\chi_0 = 1.32 \times 10^{-4}$emu/mole, assumed to represent the contribution of the other bands, in particular the bonding plane band. It can be seen that the contribution of the antibonding band (filled circles) is very similar to the susceptibility of LSCO, modified by a larger combined superconducting and residual pseudogap. Since both bands would be expected to make a comparable contribution to $\chi$, and since $\chi$ for YBCO is about twice as large as for LSCO, the latter interpretation is to be preferred. Thus a clear VHS is present in both materials, when the pseudogap closes, while the pseudogap itself can be interpreted as a splitting of the VHS degeneracy, Section IX.A.2.

If, on the other hand, it is assumed that the VHS and pseudogap are two unrelated phenomena, and that the VHS accidentally crosses the Fermi level in the midst of the pseudogap opening, one would expect to see two peaks in the susceptibility, one of which follows the VHS, the other associated with the pseudogap. Two such peaks have not been observed.

The susceptibility also has a strong peak at or near $q = Q_0$, just as predicted for a VHS. In the literature, this is called an antiferromagnetic peak, since $Q_0$ is the wavevector of the AFM superlattice. It is discussed further in Section VI.E.

2. Transport Properties

a. Linear-in-$\omega$ and $T$ scattering rate ($\tau^{-1}$). In a normal Fermi liquid, in any dimension, electron-electron scattering should lead to a resistivity $\rho$ proportional to the square of the excitation energy away from the Fermi energy – hence, $\rho \propto \max(T^2, \omega^2)$. Instead, it was noted that $\rho \propto T$ in optimally doped cuprates, crossing over to $T^2$ in overdoped materials, and to insulating behavior $\propto T^{-1}$ on the underdoped side. Similarly, it was found that $\rho \propto \omega$ in optimally doped material.

Lee and Read [185] first noted that the dos divergence near a VHS should lead to an anomalous scattering rate. They showed that the electron-electron scattering rate $\tau^{-1} \propto T$ when the Fermi level falls at a VHS. For a Fermi liquid, linear in $T$ is equivalent to linear in $\omega$; more
\[ \tau_{ee}^{-1} \propto \sqrt{\hbar^2 \omega^2 + \pi^2 k_B T^2}, \]  
\[ (32) \]

where the factor \( \pi^2 \) is empirical (but c.f. Eq. 4.13 of Ref. [188]).

A number of groups have reanalyzed these calculations, and found significant modifications of the results. There are a number of subtleties, and the final results are not yet clear. The first problem is that the Lee-Read calculation involves inter-VHS scattering, due to a divergence of the inter-VHS susceptibility, \( \text{Im} \chi (q_0, \omega) \propto \ln(\omega) \). Pattnaik, et al. [152] have shown that this divergence is cut off when \( t_{OO} \neq 0 \), and the Fermi surface is not square at half filling, Eqs. [27] and [25] due to weaker nesting (compare Fig. 18a and 18b). They and Gopalan, et al. [188] showed that Eq. [32] still holds, but it is dominated by intra-VHS scattering. The idea is as follows: the scattering rate is calculated from the imaginary part of the self energy, \( \tau_{ee}^{-1} \propto \text{Im} \Sigma \), which in turn is given by an integral (over \( q_1, q_2 \)) of \( \text{Im} \chi (q_1, \omega) \). For a parabolic band, \( \text{Im} \chi \propto \text{sign} (\omega) \), so the integral gives \( \text{Im} \Sigma \propto \omega^2 \). At a VHS, however, \( \text{Im} \chi \propto \text{sign} (\omega) \) for small \( q \) \( (\hbar \omega \geq |E_q|) \) so \( \text{Im} \Sigma \propto \omega \), giving \( \tau_{ee}^{-1} \propto \max (\omega, T) \). A linear-in-\( T \) and \( \omega \) scattering rate was also thought to follow from an extended VHS [189], but this claim has been withdrawn [189]. Figure 22 shows the calculated scattering lifetime as a function of \( T \) or \( \omega \) – good agreement is found with the photoemission line broadening [77,90] and infrared reflectivity [190], even to the magnitude of the scattering. It should be cautioned that the optical data extend into the frequency range of the ‘mid-infrared peak’, and sorting out this contribution could modify the observed frequency dependence. However, a linear-in-\( \omega^{-1} \) optical conductivity is found in Bi-2212 and along the a-axis in YBCO, where there is little sign of the mid-infrared peak [191], moreover, in LSCO the free carrier component has \( \sigma \propto \omega^{-1} \) even after the midinfrared feature is subtracted out [192].

b. Resistivity: theory
Thus, the VHS model predicts a linear-in-\( T \) and \( \omega \) scattering rate, \( \tau_{ee}^{-1} \), in good agreement with experiment. However, experiments also find that the resistivity is linear in \( T \) and \( \omega \). For electron-electron scattering it is non-trivial to calculate the resistivity, both because of the Fermi surface averages and because of the importance of including Umklapp scattering. While the average scattering rate will be dominated by the strong scattering at a VHS, the resistivity can be dominated by those carriers with small scattering, hence far from the hot spots near the VHS. Taking these factors into account, Hlubina and Rice [22] find a \( T^2 \) resistivity near a VHS. (Similar modifications also arise in the calculation of the thermopower [193]). The reason for this discrepancy is not clear at present. There are a number of additional factors which could be included in the calculation. For instance, at a VHS, any scattering at all will lead to a vanishing mean-free path, \( l = v_F \tau \), since \( v_F = 0 \), which suggests that multiple scattering corrections will be large. In particular, since both holes and electrons are simultaneously present at a VHS, there should be strong excitonic effects [29]. Equivalently, Phillips [194] has pointed out that, if the VHS is assumed to cause marginal Fermi liquid behavior, then the renormalization factor \( Z \rightarrow 0 \) at the Fermi level. Since \( \rho \propto Z (E_F) \), a self-consistent calculation of \( \rho \) is required. Newns, et al. [195] have also noted that the Boltzmann equation calculation of the resistivity involves weighted scattering probabilities, and the weighting functions \( \Phi_k \) are not well known. In particular, they may themselves have a logarithmic divergence at a VHS, which would strongly modify the resulting \( T \)-dependence of \( \rho \). A more recent calculation [196], including correlation effects, finds that \( \rho \propto T^2 \) very close to \( T = 0 \), but \( \rho \propto T \) for an extended range of temperatures above \( \sim 0.01B \), with \( B \) the electronic bandwidth. [However, it is not clear if Umklapp scattering was correctly accounted for in this calculation.]

c. Resistivity: experiment
Experimentally, a universal crossover is found in the doping dependence of the resistivity, which is tied to the doping at optimum \( T_c \), \( P^* \). For optimally doped material, the in-plane resistivity is linear in \( T \) down to \( T_c \), except for superconducting fluctuations [197] while for overdoped material, \( \rho \propto T^\alpha \), with \( \alpha \rightarrow 2 \) (Fermi liquid behavior) in strongly overdoped material. For underdoped material, \( \rho \) is sublinear in \( T \) \( (\alpha < 1) \), ultimately developing a semiconducting behavior \( (\alpha < 0) \), and increasing with decreasing \( T \). Batlogg, et al. [198] have found a stronger result at optimum doping: not only do \( \rho (T) \) and the scattering rate \( \Gamma^\ast (\omega) \) increase linearly with \( T \) or \( \omega \), but the slopes \( d\rho /dT \) and \( d\Gamma^\ast /d\omega \) are essentially the same for all families of cuprates studied (LSCO, YBCO, Bi, Tl), even though the \( T_c \) differ. Moreover, for an overdoped sample of LSCO, \( x = 0.34 \), both \( \rho (T) \) and \( \Gamma^\ast (\omega) \) were found to be superlinear functions of their arguments, with essentially the same exponent, \( \alpha \approx 1.5 \sim 1.6 \).

In a rigid band picture there is an approximate symmetry between over and underdoping which is not present in the experimental data. While the crossover from optimal doping to overdoping is consistent with a rigid band model, the anomalous transport in the underdoped material is associated with correlation effects and proximity to an insulating phase. Even so, the small Hall density is hard to reconcile with the large Fermi surface. However, both resistivity and Hall effect can be naturally understood in terms of a percolation picture, if there is a (nanoscale) phase separation between the VHS phase and a magnetic insulator. (See Fig. 2 of Ref. [199] and Fig. 9 of Ref. [200].) Indeed, this observation was one of the initial motivations for postulating the existence of such a phase separation [199,200].

d. Zn and Ni Impurities
A long-standing puzzle in the cuprates has been the specificity of doping effects at in-plane Cu sites – in particular, the fact that non-magnetic Zn depresses \( T_c \) so much more strongly than
magnetic Ni, even though both enhance the resistivity by comparable amounts. Fehrenbacher [204] has been able to explain these results by combining d-wave pairing (see below) with proximity to a VHS. The d-wave symmetry means that potential scatterers (such as Zn) will strongly suppress superconductivity, similar to magnetic scatterers in an s-wave superconductor. The VHS plays several roles: it breaks electron-hole symmetry, so Zn can reduce $T_c$ more than Ni if the two atoms have impurity potentials of opposite signs; it can cause Zn to act as a resonant scatterer, even for not-too-large impurity potentials; and it can explain the varying role of Zn doping as a function of hole concentration, in terms of proximity to the VHS.

e. Thermopower  The thermoelectric power (TEP) $S$ is also found to display a universal behavior in most of the cuprates, Fig. 23a, [209, 202, 203], the TEP has a negative slope, as a function of temperature. Doping leaves the T-dependence nearly unchanged, adding a constant (P-dependent) contribution to $S$. This leads to a universal curve of TEP at room temperature vs. doping, Fig. 23, with $S(290K) > 0$ for underdoped, =0 for optimal doping, and $< 0$ for overdoped material. However, more complicated behavior is found in YBCO, Fig. 23c, [207], presumably due to the chains, which form a nearly 1D electron-like band. Thus, the negative chain contribution changes the sign of $S$ near $O_\tau$, where the chains are nearly perfect, but when oxygen is removed from the chains, the nearly-1D chain electron conduction is rapidly disrupted, leaving a plane contribution to $S$ which resembles the thermopower of the other cuprates. [LSCO with $x > 0.12$ is also an exception 202,206.]

Newns, et al. [207] have calculated how the thermopower should vary near a VHS, assuming rigid band filling. They find that near a VHS, $S \propto (E_{VHS} - E_F)/T$ that is, $S$ changes sign as a function of doping and vanishes at the doping of highest $T_c$, Fig. 23a. This behavior is closer to the anomalous behavior found in YBCO than to the universal behavior of the other cuprates 208. However, if a small, doping-independent term linear in $T$ is subtracted from the experimental normal-state thermopowers, the doping dependence of $S(T)$ is in reasonable agreement with the Newns, et al. model 207. Moreover, the model successfully reproduces the trend of $S(290K)$, Fig. 23a. One residual problem is that the VHS should be associated with zero thermopower, while the optimum $T_c$ is shifted to positive thermopower. Thus, in Fig. 23a, by subtracting curve $b$ from all the curves for Bi-2212 (curve $T_c < 4K$ for Tl-2201), the curves will closely resemble the theoretical curves of Fig. 23d. However, the curves of optimum $T_c$ (curve $d$ for Bi-2212, 84K for Tl-2201) now have a positive thermopower, with the corrected $S(290K) \approx 8\mu V/K$ for both. This is presumably because Newns, et al. [207] employed a simplified model for the VHS, Eq. [18] which has electron-hole symmetry, whereas in the actual bands the VHS is shifted to the hole doped side of half filling. Additional discussion of these calculations is found in Refs. 210. [Alternative interpretations of the thermopower involve strong electron-phonon coupling 211 or (in-plane) Jahn-Teller polarons 212, similar to those discussed in Section VIII.D, below. The calculations of Newns, et al. 207 have been questioned by Hlubina 213, who finds an effect of the opposite sign.

3. Marginal Fermi Liquid Behavior

Noting the anomalous linear-in-T and $\omega$ behavior of the resistivity in optimally-doped cuprates, Varma and coworkers [162] introduced the phenomenological model of a marginal Fermi liquid (MFL): the cuprates can be described by a Fermi-liquid like theory, but the quasiparticle renormalization constant $Z$ vanishes logarithmically at the Fermi level. This follows from postulating the existence of excitations which produce an anomalous contribution to both the charge and spin polarizabilities:

$$\left| \frac{\tilde{P}(\vec{q},\omega)}{\omega^2} \right| \gtrsim \left( \frac{\omega}{\omega + \Delta} \right)^2$$

Exchange of these fluctuations leads to a self-energy of the form

$$\Sigma(\vec{q},\omega) \approx g^2 N(0)^2 [\omega \ln(\omega/\omega_c) - i(\pi/2)z]$$

with $N(0)$ the DOS, $g$ a coupling constant, $\omega_c$ an ultraviolet cutoff, and $z = \max(|\omega|,T)$.

Given this form of $\Sigma$, a number of anomalous features of the cuprates can be explained [162]: $\tau^{-1} \propto \Im \Sigma$, explaining $\rho \propto z$, as well as the broadening of the photoemission peaks with $\omega$. The model can also describe the $\omega$ and $T$ independent background seen in Raman scattering out to $\sim 0.5eV$, the mid-infrared peak in the optical conductivity (although this must be modified [163] in light of the fact that this peak is at least in part due to the chains 211), and several other features.

In searching for a microscopic origin for the anomalous self energy, two early candidates were a conventional Fermi surface nesting 215 and the VHS 217. The VHS model leads to both the self energy correction and the anomalous polarizability, the latter due to excitonic interactions of the holes and electrons simultaneously present at the VHS. While Viroszek and Ruvalds 216 initially chose a model wherein the nesting was well distinguished from a VHS, a more recent calculation 216 finds the strongest effects near a square Fermi surface at half filling – i.e., at a VHS. Moreover, calculations 217 for the Hubbard model also find $Z \rightarrow 0$ only near half filling (i.e., at the VHS). Even this may be an artefact of the calculation technique: in the tJ model, $Z$ is found to be finite even for a single doped hole 215.

3. Marginal Fermi Liquid Behavior

An important difference between the original MFL theory and the VHS and conventional nesting models is that the MFL model assumes a $\vec{q}$-independent self energy, while nesting leads to a strong $\vec{q}$ dependence. However, in order to describe the dynamical structure factor
a $\tilde{q}$ dependent extension of the MFL theory has been introduced \[133,220\].

4. de Haas - van Alphen Effect

At the saddle point VHS, the Fermi surface crosses over from an electron-like Fermi surface centered on the $\Gamma$ point to a hole-like Fermi surface, centered on the Brillouin zone corner $S$. This crossover leads to anomalous transport and thermodynamic properties in a magnetic field. In a strong magnetic field, an electron follows a cyclotron orbit, along a path around the Fermi surface, in a plane perpendicular to the applied field. As the Fermi level crosses the VHS, the cyclotron orbit switches between two branches, Fig. 24. When the Fermi level is exactly at the VHS, there will be a finite probability of switching onto either branch. This orbital switching is analogous to magnetic breakdown \[221\], but is actually a distinct physical effect. It is one of the ‘classical’ (pre-high-$T_c$) VHS effects, and its anomalous properties have been calculated by a number of different techniques \[222\].

The electron orbit need not be localized in $k$-space, but can spread out just as in an open orbit. Hence, the magnetoresistance saturates, and, if scattering is weak, there can be a novel, metallic magnetic band structure, similar to the ‘quantum coherent structure’ proposed by Pippard \[221\]. Unfortunately, dHvA studies have so far only detected some small Fermi surface pockets \[60,61\], and not the larger plane Fermi surfaces where these effects are expected.

The presence of switching orbits at the VHS can also explain the Hall effect anomalies in the cuprate superconductors; whereas photoemission finds evidence for large (‘Luttinger’) Fermi surfaces, the measured Hall density only corresponds to the excess holes beyond half filling of the band. A low-field Hall effect calculation \[200\] suggests that the switching orbit, coupled with strong correlation effects, may be able to account for this anomaly.

5. Excitons

At a switching orbit, the carriers can equally follow either electron-like or hole-like orbits, leading to unusual excitonic effects \[222\]. A carrier localized near one VHS has a positive mass – i.e., behaves like an electron – for certain directions in $k$-space, while in other directions it has a negative, hole-like mass. For a carrier at the other VHS, most of these $k$-directions are reversed. Hence, if these two carriers move together in the same direction, they will usually feel a Coulomb attraction. This may actually lead to an excitonic binding of the pair \[223\]. (I should caution that, while I think the concept of excitonic attraction introduced in this paper is correct, the calculations are wrong, due to an incorrect definition of the excitonic binding energy.) It should be recalled that the CDW/SDW’s can be interpreted as forms of excitonic instability, wherein electron-like and hole-like Fermi surface sections nest into one another (bind into excitons) \[29\].

Recently, Varma \[224\] has explored the consequences of an excitonic instability, without relating it to a particular nesting instability. He suggests that it might give rise to an orbital antiferromagnetic-like instability (Appendix D).

This attractive electron-hole interaction means that the net Coulomb interaction is anomalously small near the VHS. As will be demonstrated below, this can lead to an electronic pairing mechanism.

D. Superconducting State

1. Weak Coupling Theory

The initial interest in the VHS arose because of the possibility that its large dos could substantially enhance the superconducting transition temperature. Indeed, the logarithmic divergence of the dos gives rise to a modified form of the BCS result for $T_c$, \[35,54,225\]. In a weak coupling model, the BCS formula for $T_c$ is

\[
1 = V \int_0^{\hbar \omega_c} \frac{N(E)}{E} \tanh\left(\frac{E}{2k_B T_c}\right) \quad (35)
\]

For the one band model (Eq. 25),

\[
N(E) = \frac{8}{\pi^2 B} \left| \log \left| \frac{2B}{E - E_{VHS}} \right| \right|^2,
\]

where $B = 8t_0$ is the electronic bandwidth, and $N$ is normalized per Cu. Approximating $\tanh(x) \simeq \min(x,1)$, the transition temperature becomes

\[
k_B T_c = eB e^{-1/\sqrt{\lambda}} , \quad (37)
\]

with

\[
\frac{1}{\lambda} = \frac{2}{\lambda_0} + \ln^2 \left( \frac{2B}{\hbar \omega_c} \right) - 1 , \quad (38)
\]

$\lambda_0 = N_0 V$, and $N_0 = 8/\pi^2 B$. This approximation is qualitatively correct, but overestimates $T_c$ by $\approx 15\%$ \[226\]. If $2/\lambda_0 >> \ln^2(2B/\hbar \omega_c)$, Eq. 37 becomes

\[
k_B T_c = eB e^{-\sqrt{2/\lambda_0}} . \quad (39)
\]

At a VHS, $T_c$ is enhanced from the BCS value in two ways. First, the exponent depends only on the square root of $\lambda$, and secondly, the prefactor is an electronic energy, rather than the Debye frequency. However, the first factor is important only when $\lambda$ is small, and in this case, $T_c$ is low. As $\lambda$ increases, the presence of a VHS leads to less of an increase in $T_c$. This can be approximately seen from Eq. 37. For $\lambda_0 = 2$, this predicts $k_B T_c = e\hbar \omega_c/2$. Now with the same approximation of the tanh function,
the BCS equation for a material with a constant dos, $N_0$, would find
$$k_B T_c = \frac{\hbar \omega_c}{2} e^{-1/\lambda_0},$$
so for this value $\lambda_0 = 2$, the VHS enhancement is only a factor of $\sqrt{e}$ = 1.65.

At the same time that $T_c$ is enhanced by a VHS, the Coulomb repulsion is reduced. Bok [227] has calculated the reduced Coulomb repulsion $V_C^*$ due to width of a band with a VHS of width $2D$ plus a flat band of width $2W$:
$$V_C^* = \frac{V_C}{1 + V_C \left[ \frac{\hbar^2}{m^*} (\ln n_{VHS})^2 + n_0 \ln \frac{W}{\hbar \omega_c} \right]},$$
where $n_0$ ($n_1 ln|D/E|$) is the dos in the flat (VHS) band. When $n_1 = 0$, this becomes the usual Anderson-Morel result [228]; when $n_0 = 0$, this shows the enhanced, $\ln^2$, reduction of $V_C$ by a VHS. However, Bok feels that a substantial flat band contribution is necessary to really suppress $\mu^*$.

While the weak coupling VHS model predicts a $T_c$ enhancement and a reduced isotope effect (see below), there are quantitative discrepancies between its predictions and experiment for the magnitude of the isotope effect and of the BCS universal ratios. For instance, the ratio, $2\Delta(0)/k_B T_c$, is only slightly enhanced from its BCS value, 3.53 [226,229], whereas experiments generally find a considerable enhancement, although there is considerable spread in the values quoted. Thus, in photoemission, a ratio of $\sim 6 - 8$ is typically found for the maximum gap value, whereas smaller values $\sim 4 - 5$ are often found for Fermi surface averages (e.g., heat capacity finds a ratio, $\approx 4.8$ [181]). Likewise, the ratio $\Delta C(T_c)/\gamma T_c$ is predicted to be only weakly enhanced from the BCS value, 1.43 [229] (here, $\Delta C(T_c)$ is the jump in specific heat at $T_c$, while $C_N = \gamma T_c$ is the normal state heat capacity at $T_c$). Experimentally, the ratio is close to 5 [229,231], and has an anomalously strong temperature dependence in the superconducting state. Note however that the heat capacity data are for YBCO, whereas smaller values of this ratio are found in other cuprates; hence part of the enhancement may be chain related (although the mechanism is unclear). Larger values for these BCS ratios can be produced by strong coupling (see below) or gap anisotropy [232], or by extended VHS’s.

2. Strong Coupling Theory

Strong coupling calculations [233,234] find that the increase in $T_c$ due to a VHS is slightly larger (a factor of $\sim 2 - 3$ for $\lambda \sim 1$) than predicted by weak coupling theory; for $\lambda >> 1$, the VHS produces no enhancement. A similar result is found for an extended VHS [234]. Since $\lambda$ appears to be close to 1, the VHS could make the difference between a 40K superconductor and a 90K superconductor. Perhaps more importantly, the VHS could be responsible for the large values of $\lambda$, as will be discussed below (Section VIII.C.3,4). Mahan [236] found a related result: he found that essentially the only effect the dos has on the Eliashberg equations is through $\lambda \propto N(E_F)$ – but $\lambda$ has a logarithmic divergence at the VHS, which he suggests may be cut off by additional factors, such as screening. Marsiglio [237] showed that the divergence is not real, but only analyzed the problem at half filling, where the superconductivity is unstable with respect to CDW order. Mahan’s result has been confirmed by Capelliuti and Pietronero [238], who further find that the peak leads to a breakdown in Migdal’s theorem, and that inclusion of nonadiabatic effects can lead to further enhancement of $T_c$. This breakdown of Migdal’s theorem is intimately connected to nanoscale phase separation: at a VHS, the compressibility, which is proportional to the dos (Appendix A), diverges, leading to a divergence in the vertex function (Section VIII.A). In this case, the Migdal self energy should be replaced by a nesting enhanced version, as in Eq. [31].

Straightforward generalization of the VHS model to strong coupling also has difficulty in reproducing the large values of the BCS ratios. However, the strong quasiparticle scattering discussed above acts as a strong and temperature-dependent pairbreaker. In particular, pairbreaking can significantly inhibit the superconducting onset near $T_c$, but has little effect on the low-T values of the gap. Hence, by including pairbreaking effects, the VHS model can generate larger values of $2\Delta/k_B T_c \approx 6 - 8$, close to experimental observations [234].

3. VHS Pairing Mechanism

The presence of both electrons and holes at the VHS leads to an attractive component to the Coulomb interaction. While the net Coulomb interaction is repulsive, it is anomalously small, and its Fourier transform, $V(\vec{q},\omega) = e^{i\vec{q}\cdot\vec{r}}\bar{\epsilon}(\vec{q},\omega)$ has a sharp minimum at $\vec{q} = \omega = 0$, Fig. [24] (with a strong $\vec{q}$ dependence, Fig. [25a]). Newns, et al. [239] noted the similarity between this situation and the usual electron-phonon interaction, Fig. [25a]. In this latter case, the potential is always repulsive, since $V_e > V_{ep}$, but superconductivity is possible since $V_e$ is renormalized to $V^*_e = \frac{V_e}{1 + N(0) V_{ep}(E_f/\hbar \omega_c)}$.

The BCS formula for $T_c$ involves $\lambda - \mu^*$, with $\lambda = N(0)V_{ep}$, $\mu^* = N(0)V^*_e$. In just the same way, the VHS notch in $V_e$ leads to a purely electronic contribution to the pairing mechanism. Neglecting any phonon coupling, the superconducting transition temperature is approximately of the form of Eq. [37], with the substitutions $\hbar \omega_c \rightarrow E^*$, the width of the notch, and

25
\[
\lambda_0 \rightarrow N_0\left(V_e - \frac{V_e}{1 + N_0 V_e \ln^2(2B/E^*)/A}\right),
\tag{43}
\]

with \(V_e\) the depth of the notch. Newns, et al. [239] showed that combining this electronic mechanism with a phonon-mediated pairing could lead to reasonable estimates of \(T_c\).

On the other hand, Mahan [240] has recently shown that in a one-band, tight binding model, the effective potential due to purely electron-electron interactions is always repulsive, and superconductivity is only possible if the gap function changes sign (as in a d-wave superconductor). For electron-phonon coupling, attraction is possible, but “the interaction is most attractive for electrons on scattering to opposite sides of the Fermi surface, and it is repulsive for scattering by small wave vectors.”

In incorporating this behavior into a model calculation, he was able to find nonzero gap functions only near a 2D VHS [241]. A combined phonon-electron coupling mechanism remains possible – at least in the weak sense that the Coulomb repulsion is anomalously small near a VHS.

Liu and Levin [242] have shown that local field corrections to the Coulomb interaction become very important near a VHS, and can lead to an attractive pairing at near neighbor sites due to the ensuing Friedel oscillations (Kohn-Luttinger mechanism [243]). The resulting gap has d-wave symmetry; in this model, there is a competition with electron-phonon coupling, which favors an s-wave gap.

4. Isotope Effect

Experimentally, the isotope effect is found to be extremely small at the doping of optimum \(T_c\), and this was initially taken as evidence against the conventional electron-phonon coupling mechanism. However, in the weak coupling limit, the isotope effect vanishes at a VHS, even for electron-phonon coupling [244]. This result can be seen from Eq. 38. Since \(T_c\) is independent of \(\omega_c\), the isotope effect is identically zero. However, this equation is only valid when \(\lambda_0 \ll 1\), which is not consistent with a large transition temperature. Using the fuller expression, Eq. 57, the isotopic mass exponent becomes

\[
\alpha \equiv -\frac{\partial \ln T_c}{\partial \ln M} = \frac{1}{2} \frac{\ln(2B/\hbar \omega_c)}{2 \ln(eB/k_B T_c)},
\tag{44}
\]

with \(M\) the isotopic mass, and it is assumed that \(\omega_c \propto M^{-1/2}\). While no longer vanishing, this is still significantly reduced below the BCS value, \(\alpha = 0.5\). Moreover, as a function of doping, it is found that \(\alpha\) has a minimum at the VHS, Fig. 26, as found experimentally [244].

However, it is difficult to make \(\alpha\) at the VHS as small as that found in optimally doped YBCO [233,245]. Thus, for the parameters assumed in Ref. [225], \(\alpha_{VHS} \approx 0.2\). If the parameters are adjusted to give a small \(\alpha\) at optimal doping, then the variation of \(\alpha\) with doping is found to be small. The extended VHS also has difficulty in fitting the isotope effect [246]. Carbotte [247] has suggested that strong magnetic pairbreaking in the underdoped material can enhance the doping dependence, and by incorporating this effect, a good fit to experiment can be obtained [233]. Strong anharmonic effects can also produce an anomalously small \(\alpha\) [248,249]. Figure 24 illustrates various calculations for \(\alpha\) in the vicinity of a VHS, comparing them to experimental data [250,251].

In weak coupling theory, \(\alpha\) is found to diverge when \(E_F - E_{VHS} = \hbar \omega_0\) [223,229,253]. This divergence is associated with the sharp cutoff in BCS theory, and should be greatly reduced if a smooth cutoff is assumed. It is not observed in strong coupling calculations [233,239]. It was initially compared to the highly anomalous isotope effect found in LSCO and LBCO in the vicinity of the structural transition to the LTT phase [254]. This is more probably understood as a consequence of the structural instability [255,256].

An interesting finding is that the isotope effect in YBCO is negative for Cu, but positive for O, even though both have a similar doping dependence (very small at the VHS). Franck [257] has pointed out that this sign change can be understood if there is structure in the dos (such as a VHS), and the gap energy falls between the Cu and O phonon frequencies.

Franck [257] has found that the Cu isotope effect in YBCO is small not only at optimum doping, but at a specific underdoping corresponding to the 60K plateau of \(T_c\). He suggests that this might be evidence that a second VHS underlies the 60K plateau.

Some studies have attempted to determine which O’s were playing the main role in the isotope effect. A recent study [258] found that the dominant isotope effect in YBCO is associated with the planar O’s, and concluded: “This suggests that theories of electron pairing in high-temperature superconductors have to consider a phononic contribution, in which the planar tilting or buckling modes in the CuO2 layers play an essential role.”

5. Doping Dependence of \(T_c\)

The universal doping dependence of \(T_c\) was originally revealed in the ‘Uemura plot’ [254,260]. Uemura and coworkers showed that \(n_s/m \propto \lambda^{-2}\) could be extracted from \(\mu SR\) measurements, where \(n_s\) is the superconducting pair density (measured at low temperatures) and \(\lambda\) is the London penetration depth. Furthermore, a plot of \(T_c\) vs \(n_s/m\) displays universal properties, Fig. 27a, particularly in the underdoped regime, where the relation is linear, and all cuprates have essentially the same slope.

The VHS model provides a natural explanation for this universal observation of an optimum doping (i.e., when the Fermi level coincides with the VHS), with \(T_c\) falling off for either under- or overdoping. Figure 28a shows that
the overall trend of the data can be readily reproduced [261]. (In this early work, the phase separation was taken into account approximately. The double peak for YBCO is suggestive of what might happen for a split VHS peak; the arrows represent the approximate dopings at which the Y and X point VHS’s of the antibonding hole band cross the Fermi level in the LDA calculations [27].)

More recently, it has been suggested that there is a universal relation between \( T_c \) and hole doping \( n \) [262], Fig. 28b. While a flat-topped \( T_c(p) \) curve has been suggested [263], most groups find a parabolic form [262,264]. It has further been proposed [138] that, when plotted as \( T_c(p)/T_{c,\text{max}} \) vs \( p \), the curve is universal for all the cuprates! That is, for all the cuprates, \( T_c \) maximizes when \( P = 0.16 \):

\[
\frac{T_c}{T_{c,\text{max}}} = 1 - \left( \frac{P - 0.16}{0.11} \right)^2,
\]

Fig. 28b. It is not clear how to reconcile this with the Uemura plot. It would seem more plausible that \( m^* \) is the same for all cuprates, in which case, the Uemura plot suggests that the optimum doping is different in different cuprates.

If it is further assumed that the main dependence of \( T_c \) on pressure \( p \) or isotopic mass \( M \) comes in through the dependence of \( T_c \) on \( n \), then there should also be universal trends of the isotope effect coefficient \( \alpha \) and the pressure coefficient \( \beta = \partial \ln T_c/\partial p \) as functions of \( T_c \), with both coefficients vanishing at the optimum \( T_c \)! Such universal trends are indeed observed [262]; the isotope effect has already been discussed, while the pressure dependence will be discussed further below.

The overdoped regime also has a universal, but unexpected behavior, Fig. 27b [265,273]. Here, the anomaly is in \( n_s \): instead of growing with doping, it reaches a maximum value, and then decreases with additional doping. This is actually expected near a VHS, as illustrated in Fig. 3 and replotted as Fig. 27c. While the general shapes are in agreement, the experimental points at which \( n_s \to 0 \) are anomalous. In the simple theory, they should lie at the top and bottom of the antibonding band. Instead, they are separated by a much smaller doping. On the underdoped side, this is well understood: this is the correlation-induced Mott-Hubbard insulator at half filling. The point at high doping is somewhat of a surprise, since when \( n_s \to 0 \), the material is a good metal. The suggestion that it is related to a phase separation [260] is consistent with much data discussed in Section XI. Alternatively, it has been attributed to pairbreaking [267]. Strong pairbreaking effects in the overdoped regime are also suggested by heat capacity and IR studies and correlate with increasing Curie terms in \( \chi \) and \( S/T \), where \( S \) is the electronic entropy.

6. Pressure Dependence of \( T_c \)

The pressure coefficient of \( T_c \) shows a nearly universal correlation in the cuprates, when plotted as a function of \( T_c \), normalized to its largest value, with zero coefficient in optimally doped materials, and negative coefficient in overdoped (or electron doped) materials. This is interpreted as due to a pressure-induced doping of the \( \text{CuO}_2 \) planes, along with the parabolic doping dependence of \( T_c \), and is hence consistent with the VHS model [268–270]. Fig. 29 [271,272] illustrates a representative sample of the results obtained. The doping dependence of the pressure coefficient, Fig. 29a, and the isotope effect coefficient, Fig. 29b, are similar [271], while the sign of the effect changes for over doping, Fig. 29c [272]. More direct evidence for the VHS is found in pressure dependences of \( T_c \) for the Hg-cuprates, Fig. 30 [273], where the nonlinear slope of \( T_c(p) \) has been ascribed to the pressure-induced crossing of the Fermi level by a VHS [274].

LSCO provides an exception to the universal scaling behavior: \( dT_c/dp \) is large and roughly doping dependent around the optimum doping [275,276]; in the overdoped phase, it remains positive in the orthorhombic phase, and essentially zero in the tetragonal phase [277,278]. This can be understood readily: most cuprates, the doping of the \( \text{CuO}_2 \) planes is delicately controlled by charge transfer from other layers, and the main effect of pressure is to alter that balance, producing an excess hole doping. On the other hand, doping in LSCO is strictly chemical, replacing La by Sr, and the change of \( T_c \) with pressure is dominated by other effects – related to inhibition/enhancement of the competing structural (tilt mode) instability.

7. Hall Effect Sign Reversal(?)

The detailed analysis of high-\( T_c \) cuprates has called attention to this anomalous phenomenon, which had been observed, but not explained, in conventional superconductors: the Hall effect can change sign on passing from the normal to the superconducting state [279]. This is a material dependent property, found in some superconductors and not in others. In the cuprates, it seems to be present in a limited doping range near the optimal \( T_c \). It is possible that this property also is explained by proximity to a VHS. Thus, in the time-dependent Ginzburg-Landau (TDGL) theory [280], there are two contributions to the Hall coefficient, the normal one, and an ‘anomalous’ one due to vortex backflow, which is proportional to \( \partial N(E_F)/\partial E_F \) – the slope of the dos. If this slope has the opposite sign from the sign of the carrier charge (i.e., if the slope is negative for holes), the anomalous term has the opposite sign from the normal term, and can lead to the sign reversal. Since this slope changes sign at a VHS,
such Hall effect anomalies should be present in some doping range.

In light of this, recent experiments by Jones, et al. [281] on YBCO are interesting. They find a correlation of Hall effect anomaly with TEP. For $S \leq 0$, there is an anomaly, whose magnitude scales linearly to zero as $S \to 0$; for $S > 0$, no Hall effect anomaly is found. This result is consistent with the VHS picture, since the VHS coincides with $S = 0$ in YBCO, thanks to the chain contribution (see Fig. [233]). In LSCO [253], which lacks the chain layer, a Hall effect sign reversal is found in underdoped or slightly overdoped samples, but not in strongly overdoped samples; this was taken as evidence in support of the TDGL theory.

8. $T_1$, Penetration Depth

The nuclear spin-lattice relaxation rate has two anomalous features – the lack of an obvious Hebel-Slichter peak and a power-law T-dependence at low temperatures [283]. The latter feature is suggestive of nodes in the gap, which will be discussed further in the subsection on s vs d wave symmetry (VI.D.11). The lack of a Hebel-Slichter peak can be understood as due to strong pair-breaking quasi-particle scattering near $T_c$ [284,233].

Similar results hold for the penetration depth: the VHS model can explain the T dependence near $T_c$ [233], while there appears to be an anomalous power law temperature-dependence at low temperatures, suggestive of gap nodes [284].

9. $H_{c2}$

The shape of the superconducting $H-T$ phase diagram is also sensitive to structure in the dos. The role of the VHS has been worked out by Dias and Wheatley [286]. The most striking result is that at low temperatures $H_{c2}$ is greatly enhanced, $H_{c2}(0) \propto T_{c}^{2}$, as opposed to the BCS value, $H_{c2}(0) \propto T_{c}^{11}$. Such an anomalous enhancement is indeed a characteristic feature of those cuprates with low-enough $T_c$’s that $H_{c2}(0)$ can be measured [287].

10. Gap Anisotropy

Since the electron-phonon coupling $V$ is enhanced by the phonon renormalization $R$ (Eq. 1) in the denominator, $V$ should have a strong anisotropy, being largest where $R$ is smallest [288]. This can lead to a strongly anisotropic gap, with the largest values near the VHS’s, as found experimentally. It should be noted that, in the calculations of Ref. [288], only an s-like gap was assumed, so the resulting $\Delta$ is of ‘extended-s’ symmetry. It seems likely that, under the appropriate circumstances (e.g., a repulsive on-site $V$), a d-wave gap could be stabilized. Similar anisotropy is found for an extended VHS [28].

11. s vs d Wave

Recently, a number of experiments have found strong evidence that most of the high-$T_c$ cuprates have gaps of d-wave symmetry. The present status of this issue is briefly summarized here, and it is shown that the VHS model is compatible with either anisotropic-s or d-wave gaps.

Several low-temperature properties of the cuprate superconductors have shown anomalous power law dependences on temperature, as if there were nodes of gap zeroes along parts of the Fermi surface. These properties include penetration depth measurements and nuclear spin-lattice relaxation times, $T_1$, discussed above. In the past two years, several experiments have provided more direct evidence that the superconducting gap function has d-wave, or mixed s-plus-d wave symmetry. Thus, while early photoemission experiments on Bi-2212 [7] found an isotropic gap, more recent measurements find large gap anisotropy [72,74,75,76], with the maximum gap along the Cu-O-Cu directions (i.e., near the VHS’s), and a minimum gap, consistent with a zero gap at approximately ±45° to the directions of the maxima. If the gap zeroes fell at exactly ±45°, this would be consistent with pure d$_{x^2-y^2}$ symmetry. While some high resolution studies found the minima off of the 45° line [287,77], this is now understood to be due to interference from a superlattice replica band. The data have now been reanalyzed [290] as a broad minimum gap, consistent with $\Delta = 0$, within ±10° of the 45° angle. However, another group finds a very sharp minimum at 45° – the difference may be an impurity effect. Similar photoemission results have now been reported for YBCO [102]. There is also a report [291] of a highly anomalous temperature dependence of the anisotropy in Bi-2212, which is found to be large near $T_c$, but much reduced at lower temperatures. This could be consistent with a gap of pure d-wave at $T_c$, but with an s-wave admixture at lower temperatures, but it is not clear if this is consistent with other experiments.

Photoemission experiments are insensitive to the sign of the gap function, and hence cannot distinguish d-wave from highly anisotropic s-wave superconductivity, wherein the minimum gap can be very small, or even zero, but the gap function never changes sign. More recently, a number of experiments have been reported which are sensitive to the sign of $\Delta$. There is particularly strong evidence for the existence of $\pi$ junctions [292,293]; in a $\pi$ junction, the sign of the gap changes across the junction, leading to a phase shift of $\pi$ across the junction. For a closed loop containing an odd number of $\pi$ junctions (a $\pi$ loop), there will be a net phase shift of ±$\pi$, which can only be compensated by a spontaneous circulating supercurrent in the loop, in the absence of an applied...
magnetic field. Evidence for such a current, containing a half quantum of flux, is particularly clear in the experiments of Tsuei, Kirtley, et al. [294].

Both theoretical and experimental issues related to possible d-wave superconductivity have been recently reviewed by Scalapino [290]. At this point, the case for a gap which changes sign on different parts of the Fermi surface appears to be strong, although the experimental situation is by no means fully resolved, and some experiments still favor an s-wave gap [297]. A number of theoretical issues must still be settled, however. In particular, it was noted that evidence for π junctions is generally found in bilayer cuprates (cuprates with two CuO2 planes per unit cell), and hence could be modified by interlayer coupling. For example, it is possible that the gap has s-wave symmetry, but the intra- and interlayer gaps have opposite signs [298–300]. However, the squid-ring experiment has now been repeated on Tl-2201, and finds identical d-like symmetry in this single-layer cuprate [301].

Much of the analysis described above assumed s-wave symmetry, and should be repeated for a d-wave gap. Since most of these features are predominantly sensitive to the presence of a peak in the dos, it is not expected that this reanalysis would significantly modify any conclusions. Newns and co-workers [302] have recently generalized their earlier calculations, and find that the experimental results are equally consistent with d-wave pairing. On the other hand, the symmetry of the pairing might reveal something about the nature of the bosons which are exchanged, as discussed below.

12. d Wave Pairing Mechanism

Given that the gap is d-wave, there are two questions: what does this tell about the pairing mechanism, and what about the role of the VHS. The first question is still being debated, but whatever the answer, the VHS can still play an important role. For example, a d-wave gap arises naturally in a model in which the superconductivity is due to spin fluctuations: since the pairing potential is purely repulsive, the gap equation has a solution only if ∆ has contributions of both signs on the Fermi surface [290]. Indeed, the early calculations of Dzyaloshinskii [4] and Schulz [3] showed that the VHS would greatly enhance spin-fluctuation-induced superconductivity in a Hubbard model, leading to a d-wave gap. More recent calculations find a similar result [303].

However, observation of a d-wave gap does not rule out a phonon (or any other) pairing mechanism. All that is required is sufficient anisotropy of the pairing interaction, which follows naturally in a VHS model. Thus, it is known that an anisotropic pairing interaction greatly enhances Tc, while producing an anisotropic gap [304–306]. If the pairing interaction is expanded in terms of a double set of spherical harmonics, and the matrix of coefficients diagonalized, then the highest Tc corresponds to the channel with the largest positive eigenvalue [309], with the gap having the same symmetry. In the present problem, the chief ingredients are the highly anisotropic VHS-coupled pairing and the large on-site repulsion U. By forming a non-s-wave gap, the on-site repulsion is automatically cancelled. A VHS-based electronic pairing mechanism, based on the charge channel [212] also can lead to d-wave superconductivity; moreover, the boson frequency could be substantially higher for the charge modes (plasmons) than for the spin modes.

In conventional superconductors, the electron-phonon interaction is nearly local, due to strong screening effects. In the cuprates, the ionic contribution to the dielectric constant is very large, ~ 40 – 80 [310], so screening is much less effective, leading to a very anisotropic electron-ion potential, and hence to predominantly d-wave scattering [311]. Fehrenbacher and Norman [312] have shown that a gap of d-wave symmetry can appear in a VHS model, as long as V(⃗q) has a symmetry to couple to the VHS – i.e., does not vanish at the VHS’s, $\mathbf{q} = (\pi/a, 0, 0, \pi/a)$. Chan and Plakida [313] have also found (in a model not involving the VHS) that a purely electron-phonon coupling model of superconductivity can still lead to a d-wave gap.

Song and Annett [314] have analyzed the various planar-oxygen-related phonon modes which are most relevant to the cuprates (Section VIII – the breathing and octahedral tilt modes. They found that the breathing mode leads to a repulsive contribution in the d-channel, while the tilt modes lead to an attractive d-wave pairing. (There is a stronger tilt-mode contribution of s-wave symmetry, which is overwhelmed by the Hubbard U repulsion.) However, their calculation found a small net d-wave Tc value. Nazarenko and Dagotto [315] showed that this Tc could be greatly enhanced by fixing the Fermi level at a VHS. Indeed, by using an extended VHS, they were able to reproduce approximately the doping dependence of both Tc and the isotope effect (maximum $T_c \approx 30K$). In their calculation, the extended VHS was introduced via the remnant (‘ghost’) antiferromagnetic superlattice, but since this result depends only on the net dos, it should hold for other mechanisms of extended VHS formation as well. The importance of this same mode has also been pointed out by Bulut and Scalapino [316] and Sakai, et al. [317]. Alternatively, mixed magnon-phonon pairing can lead to d-wave superconductivity with a high Tc, in the proximity of a VHS [318].

E. Magnetic Properties

Originally, a sharp dichotomy was believed to exist between strong correlation and Fermi liquid theories of high-Tc superconductivity. If strong correlations lead to a spin-charge separation, then the physical electron
will be a convolution of spinon plus holon states, and this convolution was believed to wash out the Fermi surface. However, such reasoning does not agree with experiment. It would predict that there are no CDW’s in 1D metals, where correlation effects are strong and spin-charge separation can be rigorously demonstrated. In contrast, CDW’s are almost always found in lower-dimensional materials. A closer analysis of the 1D situation shows a more complicated picture. There is still a well-defined Fermi surface, but it is ‘softer’: the particle distribution function, $n(k)$, has a power-law discontinuity at the Fermi level, rather than the step discontinuity characteristic of a Fermi liquid \[ \text{[31]} \]; equivalently, the renormalization function $Z$ has a power law zero. This more general situation, wherein there is a Fermi surface satisfying Luttinger’s theorem (area of Fermi surface corresponds to number of conduction electrons/holes), but with power-law discontinuities, is known as a ‘Luttinger liquid’ \[ \text{[20,32]} \], as opposed to a Fermi liquid. While Luttinger liquids exist in 1D, their status in higher dimensions is not clear. It has been suggested that a 2D Luttinger liquid exists for an artificial, superstrong Coulomb repulsion \[ \text{[32]} \], but this remains controversial. For more physical interactions the Fermi liquid state is found to be stable. Experimentally, angle-resolved photoemission studies show that the cuprates do have well-resolved Fermi surfaces, and that even for an insulating cuprate, there is a reasonably well-defined energy dispersion \[ \text{[109]} \]. Most theories now find that strong correlation effects in 2D lead to Fermi liquids with renormalized band parameters.

Since the VHS is a topological property, it should still be present in a Luttinger liquid. Anderson has now stressed that in fact nesting effects are enhanced in Luttinger liquids \[ \text{[32]} \]. Indeed, the dos divergence leads to a breakdown of both Haldane’s Luttinger liquid theory \[ \text{[32]} \] and the renormalization group (RG) derivation of Fermi liquid theory \[ \text{[32]} \], in the vicinity of a VHS. The nature of this breakdown remains an open question.

### 1. Spin-fluctuation Induced Pairing

Hence, the VHS can be expected to play an important role in any strong correlation theory of superconductivity, including those in which the pairing arises from spin fluctuations. It was early noted that high temperature superconductivity in the cuprates borders on an antiferromagnetic Mott-Hubbard insulating state of the half filled CuO$_2$ band. This led to a number of suggestions that the superconductive pairing is mediated by magnetic excitations. Most of these theories are based on a peak in the spin susceptibility at the commensurate wavevector, $Q = (\pi/a, \pi/a)$. This peak was initially introduced phenomenologically \[ \text{[32]} \], but in any satisfactory theory, it must ultimately be derived self-consistently — i.e., beginning with a susceptibility derived from the electronic band structure. The only successful attempts to do this have been those which place the Fermi level near a VHS. For instance, Monthoux and Scalapino \[ \text{[32]} \] have found a self-consistent, d-wave superconducting transition in a 2D Hubbard model, with a peak in the magnetic susceptibility near $Q = (\pi, \pi)$, of the form hypothesized for the nearly antiferromagnetic model. From the insert to their Fig. 1, it can be seen that they have chosen a Fermi level close to, but not precisely at the VHS. (Recall that correlation effects generally move the Fermi level even closer to the VHS.)

These calculations would benefit from a more detailed analysis of the role of the VHS. Thus, the reasons for a particular choice of band parameters are not clearly stated, and the resulting Fermi surfaces are often inconsistent with other experiments and/or band structure calculations. Moreover, once an initial set of parameters is chosen, the theories often have difficulty in explaining the doping dependence of various effects. One case in point is the incommensurate neutron diffraction peaks in LSCO, discussed in the following subsection.

In fact, understanding the doping dependencies has proven to be a major problem for the basic Van Hove scenario. My own assessment is that the problem lies not with the VHS, but with the assumption of rigid band filling, which underlies most of these analyses. For instance, consider the role of strong correlation effects. According to the slave boson calculations (Section VII), the transition to a charge transfer insulator at half filling is not a nesting effect, but is driven by a divergent effective mass. Some theories turn the transition into a SDW nesting instability, by fixing the VHS at half filling (e.g., in the Hubbard or tJ model, this happens automatically unless a second-neighbor hopping parameter $t’$ is introduced; it also happens in the three-band model when $t_{OO} = 0$). However, once the VHS is fixed at half filling, the doped material has an electron-like Fermi surface and doping moves it further away from the dos peak; both of these features make it difficult to understand the physical properties of the cuprates.

Shifting the VHS to a finite hole doping (by choosing nonzero values for $t’$ or $t_{OO}$) produces Fermi surfaces in better agreement with band structure calculations and photoemission experiments, but now a strongly non-rigid-band filling is required to simultaneously explain the Mott-Hubbard transition at half filling. Such doping-dependent band structure renormalizations arise naturally in slave boson calculations of correlation effects, Section VII. Unfortunately, even this may not be adequate. There is considerable experimental and theoretical evidence that the doping is not continuous, but involves a (possibly nanoscale) phase separation between the magnetic insulator and the state of optimum $T_c$ (Sections X.XI). These complications should be kept in mind when analyzing the incommensurate neutron diffraction peaks, discussed below.
Neutron diffraction studies have found that in La2CuO4, the antiferromagnetic peaks are commensurate, at \( Q = (\pi/a, \pi/a) \). As the material becomes Sr doped, the peaks split and become incommensurate, at \( Q \pm \delta (\pi/a, 0) \) or \( Q \pm \delta (0, \pi/a) \), with the incommensurability \( \delta \) increasing proportional to the doping \( x \), Fig. [31]. On the other hand, the peak is usually found to remain commensurate in YBCO as \( \delta \) is reduced from 1, although there are indications of anisotropy, consistent with a non-resolved splitting into a four-fold pattern. Thus, in underdoped YBCO \( x \) (\( T_c = 53 \)K), Tranquada, et al. [328] found a pattern with the same symmetry as LSCO, but the unresolved incommensurability was only about half as large. In a nearly stoichiometric crystal, \( T_c = 92.4 \)K, Mook, et al. [329] found a strikingly different result, Fig. [31]. Again, a possible non-resolved four-fold splitting is found, but rotated by \( 45^\circ \) with respect to LSCO. A similar splitting is found in LSCO, Fig. [31]. However, the feature in stoichiometric YBCO is anomalous: this feature is only seen in the superconducting state, and at high energies, \( \approx 41 \)meV, whereas the other peaks discussed above are normal-state, low-energy features. Possible interpretations of this feature are given in the following subsection. A recent reanalysis [330] of a YBCO crystal provides some additional evidence: the lineshape is independent of frequency between 2 and 40meV, and is the same both above and below \( T_c \). It appears to be incommensurate, but whether the spots were oriented as in LSCO or LSNO (or in some other pattern) could not be resolved.

A number of attempts have been made to relate these peaks to nesting of the Fermi surfaces, and to interpret the difference between LSCO and YBCO as due to differences in their Fermi surface topologies [332,333,133]. The Fermi surfaces are calculated using the three band model \( t_{O} \neq 0 \). There are certain difficulties associated with such interpretations, however. In the first place, in a weak coupling calculation the intensity is much larger for inter-VHS scattering (which in these models is commensurate at \( Q \)) than the nesting-associated scattering when the Fermi level is shifted off of the VHS (see Fig. 8 of [334]). In a marginal Fermi liquid model, this VHS intensity enhancement can be greatly reduced by quasiparticle lifetime effects [333]. In the doped material, the model predicts an incommensurate peak in the susceptibility, in accord with experiment; however, the doping dependence is difficult to reproduce [335]. This is because of VHS nesting: the peak is commensurate, at \( \bar{q} = Q_0 \), when the VHS is at the Fermi level. Thus, using the LDA band structure, in which the VHS falls near the doping of highest \( T_c \), the nesting model would predict a commensurate peak at optimum doping, and an incommensurate peak at half filling [333] – the opposite of experiment. Hence, to explain the experimental results, it has been suggested that the LDA calculation is wrong, and that the VHS’s are much closer to half filling [33]. The new slave boson calculations in the three-band \( t_{J} \) model (Section VII.B) will improve the situation, in that a magnetic VHS falls at exactly half filling, leading to commensurate diffraction peaks; however, there will be a second VHS at optimum doping, which will still pose problems.

Finally, the Fermi surface assumed for YBCO locates the VHS far from the Fermi level, in poor agreement with photoemission and LDA results. This is because these calculations either neglect the interlayer splitting parameter, \( t_z \) (Eq. [2]), or match the Fermi surface areas to the early calculations of Yu, et al. [7], which greatly underestimate the hole doping. When the interlayer coupling is correctly included, the major topological difference, which was supposed to explain the experiments, is no longer present: both LSCO and YBCO have VHS’s present very close to the Fermi level, in optimally doped materials (in agreement with experiment). The difference is that in YBCO, this is associated with an extended VHS.

On cooling LSCO into the superconducting phase, the four incommensurate peaks remain at the same value of \( \delta \), but with intensity reduced by \( \approx 60\% \) [336]. This is a potential problem for the above model: the peaks should be washed out for an isotropic, s-wave gap. For a d-wave gap, there can still be magnetic scattering, but only between the gap nodes, where quasiparticles persist at low temperatures. This internode scattering would also lead to a four-fold incommensurate pattern of peaks, but rotated by \( 45^\circ \) with respect to the high-T peaks [337]. This rotation is not observed. The experimental observations can be explained if there is a strong (resonant) impurity scattering [338] which smears out the quasiparticle distribution in \( k \)-space. In a more recent experiment, Yamada, et al. [339] found strikingly different results: in very uniform, high-\( T_c \) crystals, they found that the intensity of the incommensurate peaks completely vanished at low T for \( \omega \leq 3.5 \)meV. Since there was no scattering intensity at the positions of the gap nodes in the normal state, it was not surprising that none appeared in the superconducting state.

A correlation between incommensurate peaks and electronic domain structure has now been clearly established, both for LBCO at \( x \approx 0.125 \), and for the closely related compound, La2-xSrxNiO4. Considerably more evidence for such phase separation is discussed below, in Section XI.

Barzykin, et al. [341], have used a model of discommensurations to resolve a problem with the \( ^{17}O \) spin-lattice relaxation rate. This rate is insensitive to antiferromagnetic effects, which can be understood in terms of a matrix element cancellation, but only if the spin-fluctuation peaks are commensurate. They postulate that the system breaks up into domains, within which the spin fluctuations are commensurate, separated by domain walls. Then the O’s inside a domain see only the commensurate fluctuations, while neutron scattering sees the aver-
age periodicity over several domains, and hence is incommensurate. Walstedt, et al. [343] objected that Cu spins in the domain walls would still spoil the good agreement of the domain model with experiment. However, this assumes that the walls can be treated as incommensurate magnetic states, whereas (in the VHS model), the walls are closer to a second, conducting electronic phase, where the local Cu moments are strongly washed out. In this model, the persistence of the peaks in the superconducting state would follow if the magnetism and superconductivity are associated with different parts of the sample. It should be noted, however, that more recently Zha, et al. [344], have shown that the desired matrix element cancellation can also be achieved by introducing a new term into the transferred hyperfine coupling Hamiltonian, without any necessity for domain formation.

There is still a potential problem for the VHS model here in that no superlattice modulation is expected at optimum doping in the simplest VHS model for LSCO, whereas experimentally the incommensurability remains large [340]. Spin-orbit coupling, by splitting the VHS, can produce an incommensurate diffraction pattern of large [340]. Spin-orbit coupling, by splitting the VHS, whereas experimentally the incommensurability remains large. W alstedt, et al. [342] objected that Cu spins near the susceptibility, Eq. 2, has RPA-like corrections, this result has been confirmed by a number of groups [343–346,329]. Lavagna and coworkers [347] have interpreted this peak as arising from a d-wave superconducting gap. The gap renormalizes the electronic dispersion at the Fermi level. In interpreting these features, caution is advised, since there is some evidence that the gap is related to a pseudogap rather than to the superconducting gap [350].

None of the above calculations suggest why the peak is incommensurate. One possible explanation comes from the band structure predictions of bifurcated (or better, extended) VHS’s, Figs. 3b and 3c. Sections IV.B.2,V.D.4. If the VHS’s in the superconducting state were similarly bifurcated, then they would be split into peaks at \((\pi,0)\) and \((0,\pi)\), so inter-VHS scattering would have four incommensurate peaks at \((\pi,\pi)\) and \((\pi,0)\), which is consistent with the observed symmetry of the diffraction peak, Fig. 3d. (Note that \(\delta_x\) and \(\delta_y\) need not be equal.) The fact that four well-resolved peaks are not found is consistent with the photoemission data, which find extended VHS’s, which spread continuously from, e.g., \((\pi,0)\) to \((\pi,\pi)\), so the resulting inter-VHS scattering should have the form of a smeared-out square, as observed. The size of the square is also in better agreement with the extended VHS: the two bifurcated VHS’s in Fig. 3b are separated by 0.83 of the \(\pi\) distance (length of arrow), whereas the width of the flat region of the extended VHS in Fig. 3b is 0.62, and the edge of the diffraction square in Fig. 3b is 0.46 (all in the same units). The agreement between the latter two is quite reasonable, particularly since the data on the extended VHS are from Y-124, while the diffraction peak is in Y-123.

VII. CORRELATION EFFECTS AND SLAVE BOSONS

The above calculations have all assumed a nearly-free-electron model. How are they modified in the presence of strong on-site Coulomb repulsion? To date, most VHS calculations have included correlations via the slave boson technique. Hence, this section is devoted to a detailed summary of that technique, while alternative ca-

\[ \chi_{\text{RPA}}(\vec{q}, \omega) = \frac{\chi(\vec{q}, \omega)}{1 + J(\vec{q}) \chi(\vec{q}, \omega)} \]
culations, which are just beginning to address the VHS problem, are discussed in Subsection VII.E.

In order to simplify the calculation of correlation effects, the three-band model is often replaced by a single band, Hubbard or tJ model. In this case, the atoms are taken as copper, and the role of the oxygens must be carefully included, via effective hopping and exchange parameters. Zhang and Rice [351] showed that much of the effect of the O’s could be included by hybridizing the Cu d-orbital with a symmetric combination of p-orbitals from the nearest neighbor oxygens. However, in the slave boson approach, the three-band model is not substantially harder to handle. Moreover, there are important electron-phonon couplings involving the O’s, and care must be taken to properly incorporate their effects into a one-band model. For these reasons, one band models of correlation effects will not be discussed, except peripherally, in this review. On the other hand, the oxygen breathing-mode phonon, in which the four O’s adjacent to a given Cu alternately move closer to the Cu or further away, can be thought of as a dynamic Zhang-Rice effect. Since this phonon appears to play a significant role in the cuprates, this analogy will be discussed below.

A. Slave Bosons in the 3-Band Model

On-site Coulomb repulsion $U$ acts to greatly reduce the probability of double occupancy of an atomic orbital. If $U$ is strong enough, this repulsion can lead to a metal-insulator (Mott) transition in a half filled band, where each atom has exactly one electron, and no electron can move without creating a situation of double occupancy. In the cuprates, the Fermi level lies in a predominantly copper-like band, and is near half filling. In this case, the situation is more complicated, since even when $U \to \infty$ the Cu can hybridize with the O’s, and still have a metallic state. However, if there is a large enough energy cost in hopping – that is, if $\Delta/t_{CuO}$ exceeds some critical value – then there can again be a phase transition at half filling, this time to a charge-transfer insulator.

This situation is found experimentally in undoped La$_2$CuO$_4$ and in YBCO, $\delta = 1$, where the insulating phase is also found to display antiferromagnetic order. It cannot be reproduced by LDA calculations, even if the magnetic order is included [352]. Hence, a variety of techniques have been applied to the problem, to try to incorporate the strong on-site correlations more accurately. One popular technique, for both cuprates and heavy-fermion materials, has been the slave boson technique [353]. This method involves self-consistent renormalization of the hopping parameter, and leads to a charge-transfer insulator ($t_{CuO} \to 0$) at half filling, above a critical value of $\Delta/t_{CuO}$.

The simplest version of the theory assumes $U \to \infty$, where $U$ is the Cu Coulomb energy, while the O Coulomb energy $U_p$ can be neglected. (Near half filling, very few holes are on the O’s, so the probability of double occupancy is already small.) The earliest slave-boson calculations on the cuprates [354] neglected direct O-O hopping, but this has been included in more recent calculations [355, 356]. The theory is formally a large-N theory, where N is the degeneracy of the electron states on a Cu site, and the calculation is usually carried out only to lowest order in $1/N$. At this order, no magnetic effects are included. Moreover, $N \simeq 2$ for the cuprates, so it is doubtful whether the lowest-order predictions of the theory are quantitatively correct. Nevertheless, detailed calculations are important – for example, to see how close the cuprates are to the metal-insulator transition, for a ‘realistic’ choice of parameters.

Taking $U \to \infty$ is equivalent to forbidding double occupancy of the Cu’s. In a slave boson calculation, this constraint is enforced by introducing a boson to occupy the second orbital of each singly occupied site. By satisfying the constraint in mean field, it is possible to reduce the calculation to a self-consistent renormalization of the bands. The Cu-O hopping parameter is reduced by the renormalization, while $\Delta$ is renormalized to a lesser extent, so the antibonding band becomes more Cu-like.

The equations of self-consistency can be written

$$r_0^2 = \frac{1}{2} [1 - \sum_k u_k^2 f_k(E_k)],$$

$$\Delta_0 - \Delta = \frac{1}{2r_0^2} \sum_k u_k^2 f_k(E_k)(E_k - \Delta),$$

where the renormalized parameters are $t_R = r_0 t_{CuO}$ and $\Delta$, $f_k(E_k)$ is the Fermi function, and $u_k$ is the d-wave amplitude of the wave function. $E_k$ and $u_k$ are calculated using the renormalized parameters, and it is assumed that $t_{CuO}$ is not renormalized. Only the case $T = 0$ will be considered in the present paper. As written, Eqs. [47] and [48] are valid for a hole picture, so $f_k(E_k) = 1$ for $E_k > E_F$, and = 0 otherwise. An equivalent electron picture can be constructed, but some care must be taken, since the above sums are then over all three occupied bands [356]. The sums are normalized per Cu atom, so for example

$$\sum_k (1) = 6,$$

that is, that there are three bands (spin 1/2), and

$$\sum_k f_k(E_k) = 1 + x.$$

Equations [47] and [48] can be generalized to include spin-orbit and electron-phonon coupling [359]. These equations are solved self-consistently by guessing initial values for the renormalized parameters and numerically performing the double integrals to allow calculation of the corresponding bare values, then readjusting the initial guesses until the known values of the bare parameters
are recovered. If \( t_R \) is small enough, however, the equations simplify to a scaling form, for which only a single parameter, \( \Delta \), need be varied. Details are given in Ref. [136].

One subtle point of the slave boson calculations must be briefly discussed. In order to have a well-defined parameter, \( \Delta \), need be varied. Details are given in Ref. [136].

The reasoning is that the Cu degeneracy is 2 for spin and \( N/2 \) for orbital states, and Eq. (51) is consistent with the assumption that the Cu-O hopping does not involve spin flip. This factor of two will be assumed throughout the rest of this paper. A search of the literature shows that this factor underlies much of the controversy about whether the slave boson calculation produces a metal-insulator transition (MIT) at half filling, for reasonable parameter values. Those papers which include the factor of two find a MIT; those which neglect this factor do not. In the following sections, the good agreement with experiment, and with other theoretical approaches, only holds when Eq. (51) is assumed. A fuller discussion is found in Ref. [136].

**B. Exchange Corrections**

1. Inclusion of Exchange

A failing of the conventional slave boson theory is that it does not predict the antiferromagnetic properties of the insulating phase at half filling. This is because the theory is valid in the limit \( U \rightarrow \infty \), and in this limit, the exchange coupling, \( J \propto 1/U \), vanishes. In a systematic \( 1/N \) expansion, exchange terms only appear in order \( 1/N^2 \). However, both experiment [103] and theory [111][112] (Section IV.B.6) have revealed the importance of these terms. Thus, whereas the slave boson calculations predict that the bandwidth collapses (effective mass diverges) at the Mott transition when \( J = 0 \), for finite \( J \) the dispersion remains finite, even in the presence of a charge transfer gap, Fig. 14.

A finite \( U \) can be incorporated into a slave boson calculation by going to a four-slave-boson approach [359], assigning separate slave bosons for each empty or doubly occupied or singly occupied site, with two bosons in the latter case to account for the electronic spin. Alternatively, exchange can be approximately included by introducing a Heisenberg \( J \) term [360][362],

\[
H' = J \sum_{j,\delta,\sigma,\sigma'} d_{j,\sigma}^d d_{j,\delta,\sigma'}^d d_{j,\delta,\sigma}^\dagger d_{j,\sigma'}^\dagger
\]

with a mean-field decoupling of the \( d^\dagger \)-term. Caprara and Grilli [361] have called this a three-band \( tJ \) model. They find that the dispersion remains finite at half filling, even though the optical conductivity has a gap.

2. Magnetic Phases

A variety of magnetic phases are possible, including uniform, flux [363], and Néel phases. In the uniform and flux phases, there is a non-zero value of

\[
\Delta_{ij} = \sum_{\sigma} <d_{i\sigma}^d d_{j\sigma}^\dagger> = \Delta_{1} e^{i \phi_{ij}}.
\]

If the phases \( \theta_{ij} \) around a plaquette add up to zero (modulo \( 2\pi \)), Eq. (53) describes a uniform phase; in the flux phase, the phase around a plaquette is \( \pi \) (again, modulo \( 2\pi \)). For the uniform phase, the self-consistent equations are as follows: Eq. (13) remains unchanged; in Eq. (15), the term \( \Delta \) on the right-hand side of the equal sign should be replaced by \( \Delta = \Delta - 2\Delta_{1}(\bar{c}_x + \bar{c}_y) \); and there is a third equation,

\[
\Delta_{1} = -\frac{J}{2} \sum_{k} u_{k}^{2} f_{j}(E_{k})(\bar{c}_x + \bar{c}_y).
\]

The resulting energy dispersion is given by Eq. 3 with the substitution \( \Delta \rightarrow \Delta_{1} \). At half filling, for \( \Delta > \Delta_{c} \), there is an insulating phase with \( \Delta_{1} = 0 \). In the uniform phase, there is no phase transition: \( \Delta_{1} \) is non-zero for all temperatures, but monotonically decreases in magnitude as \( T \) is raised – and also as the system is doped away from half filling [364] (in agreement with four-slave-boson calculations [367]). In the insulating phase, the energy dispersion is

\[
E = \Delta + 2\Delta_{1}(\bar{c}_x + \bar{c}_y),
\]

Fig. 22a.

Introduction of a phase change of \( \pi \) around an elementary plaquette opens a gap over most of the Fermi level, with the gap vanishing at one point (actually, at a set of symmetry-equivalent points). In these flux phases, the partitioning of the net phase change among the four links of the plaquette is a gauge degree of freedom; surprisingly, the particular choice modifies the electronic energy dispersion. For instance, if the full phase change of \( \pi \) is allocated to a single bond along \( x \), this changes the sign of \( J \) for that bond \( (e^{i \pi} = -1) \), leading to a dispersion

\[
E = \Delta + 2\Delta_{1} \sqrt{\Delta_{x}^{2} + \Delta_{y}^{2}}.
\]

Fig. 22b. On the other hand, if the phase change is distributed equally, with \( \pi/4 \) on each bond, the dispersion becomes

\[
E = \Delta + 2\Delta_{1} \sqrt{\Delta_{x}^{2} + \Delta_{y}^{2}},
\]

34
Fig. 32. The contrast of these two cases is instructive: the former gaps the flat part of the energy dispersion, but leaves the VHS ungapped; the latter gaps the VHS, while having a zero gap in the middle of the flat bands, at \((\pi/2a, \pi/2a)\). Yet both gaps produce the same dos, and hence the same energy lowering. Thus, in the flux phases, \(VHS\) \textit{nesting is equivalent to conventional nesting}. Despite this formal equivalence, \textit{only the VHS nesting is observed experimentally}, Fig. 14a.

How can this symmetry breaking be understood? One possibility is a term like \(t_{OO}\), which breaks electron-hole symmetry, and weakens the flat band nesting. However, at half filling, \(t_{OO}\) should not affect the dispersion, so a second-neighbor exchange, \(J'\), would be needed. Alternatively, I suspect a spin-Peierls interaction: it is the tilting of the \(CuO_4\) octahedra which introduces spin-orbit coupling and Dzyaloshinskii-Moriya exchange, thereby stabilizing a long-range magnetic order. A detailed understanding of this process does not yet seem at hand, but a discussion of the issues involved is in References \[366\]. It seems likely that the resulting spin-phonon coupling will favor a particular flux phase.

There can also be a Néel phase, quite similar to the \(SDW\) phase of Kampf and Schrieffer \[367\], but with the energies scaled by \(J\) instead of \(U\), with gap function

\[
\Delta_2 \equiv (-1)^{i+x} \sum_{\sigma} <\sigma d_{i\sigma}^\dagger d_{i\sigma}>. \tag{58}
\]

Note that \(\Delta_1\) and \(\Delta_2\) may be simultaneously non-zero at mean field level, both in the uniform and flux phases, Fig. 32i-f. When a small Néel gap is added to the uniform phase, the resulting dispersion matches that found for a single hole in the \(tJ\) model \[10,11\], Fig. 14a, but is in poor agreement with the dispersion found experimentally in the insulator SCOC, Fig. 14a. On the other hand, the dispersion of the flux phase matches that found in SCOC, Fig. 14b.\[13,14,15\]. This is somewhat surprising, since the flux phase is generally found to be stable away from half filling, whereas the experiments are in the Mott insulating phase, at half filling. Since 2D fluctuations are known to eliminate the spin wave gap in the AFM phase, it has been hypothesized that the fluctuation-corrected AFM phase will resemble the gapless flux phase \[368\], but so far fluctuations have not been included in the theory. More recently, a good fit to the dispersion has been obtained in the model of a single hole in an antiferromagnetic background \[369\]. However, this model involves a mixture of hopping and exchange parameters, whereas the 3-band \(tJ\) model would suggest that only the exchange parameters affect the dispersion near half filling.

The magnitude of the predicted bandwidth can also be estimated. Using the mean field decoupling, the equilibrium value of \(\Delta_1\) in the uniform phase is \[361\]

\[
\frac{2J}{\pi^2} = 0.203J, \text{ which is smaller than that found in Ref. 10.} \tag{11} \Delta_1 \approx 0.55J. \text{ However, if Eq. 2} \text{ is instead decoupled via a Jordan-Wigner transformation} \[362\], \(\Delta_1/J = (1/2 + 2/\pi^2) = 0.703\), in better agreement. (In attempting to reproduce the calculation of Ref. 361 I found \[364\] \(\Delta_1 = 4J/\pi^2 = 0.406J\).)

The consequences of these novel magnetic phases for a VHS model have yet to be worked out; to understand the competition between magnetic and structural instabilities, it will be necessary to include a spin-Peierls coupling, Section VIII.E.

C. Numerical Results

A charge transfer insulating phase can occur only at exactly half filling, just as in the one-dimensional Hubbard model \[370\]. The transition occurs only if \(\Delta_0\) exceeds a critical value \(\Delta_c\). For \(t_{OO} = 0\), \(\Delta_c\) can be found analytically \[371\]

\[
\frac{\Delta_c}{t_{CuO}} = 4\sqrt{\frac{1}{2} + \frac{2}{\pi^2}} = 3.353, \tag{59}
\]

or \(\Delta_0 = 4.36eV\) when \(t_{CuO} = 1.3eV\).

For \(t_{OO} \neq 0\), the critical value must be evaluated numerically \[376\]

\[
\Delta_c = 3.353t_{CuO} + 2.94t_{OO}. \tag{60}
\]

For \(\Delta_0 > \Delta_c\), the Fermi level jumps discontinuously as \(x\) passes through zero, with the discontinuity being the charge-transfer gap. Away from half filling, renormalization pins the Fermi level close to the VHS \[356,358,372\].

These results are illustrated in the numerical calculations of Fig. 32, assuming \(t_{OO} = 0.25eV\), as \(\Delta_0\) increases from 4eV (solid lines) to 5eV (dashed lines) to 6eV (dotted lines). Figure 32a shows that \(t_R\) renormalizes to zero exactly at half filling (\(\Delta_0 = 5eV\) is just below the transition, so \(t_R\) has a small but finite value at half filling). Near half filling, the Fermi energy changes rapidly (Fig. 32b), from a value near \(\Delta_0\) (Cu-like carriers) when \(x < 0\) to a much smaller value (more O-like) for \(x > 0\). This change is discontinuous above the Mott transition; this is the charge-transfer insulator gap \[354\], and should be compared to the one-dimensional Hubbard model (see Fig. 3 of Ref. 16).

This result is consistent with the results of other, non-slave boson calculations of the three-band model. Thus, the studies that produced the parameters of Table III \[127,131\] also explored the low energy sector of the three-band model, and all find an insulating state at half filling with a large charge transfer gap, comparable to experiment. See also Refs. \[373\], which find similar results.

As \(x\) increases, \(t_R\) grows \(~\sqrt{x}\) while \(\Delta\) decreases, ultimately becoming negative. At the VHS, \(\Delta\) is small and positive. This is consistent with LDA calculations, suggesting that the LDA calculations should be reasonably accurate away from half filling. Note the importance of self-consistency. By extracting parameters from the LDA calculations which are not renormalized by correlation effects, a large \(\Delta\) value is found. Using these parameters in
the slave boson calculation, it is possible to explain both
the MIT at half filling and the small renormalized value of
$\Delta$ near the VHS. If, on the other hand, one had merely
chosen tight-binding parameters which reproduced the
band structure near the VHS, a slave boson calculation
utilizing those parameters would have found a metallic
state at half filling.

When $\Delta$ becomes negative, the Fermi level falls di-
rectly in the O-like band. In this regime, the three-band
model should not be trusted, because of the proximity
of the $d_{z^2}$ band to the Fermi level. Indeed, in this dop-
ing step an enhanced $d_{z^2}$ character is often observed
experimentally [374].

The quasi-pinning of the Fermi level to the VHS is illus-
trated in Figs. 33c and d. In a rigid-band filling picture,
the bandwidth and the position of the VHS would both be
independent of doping, so the separation between the
VHS and Fermi level would smoothly track the variation
of the Fermi level with doping. This is not what happens
in the presence of strong correlation effects. Figure 33c
shows that the position of the VHS (defined by the hole
doping $x_{VHS}$ at which the VHS would coincide with the
Fermi level) actually changes with doping, while Fig. 33d
shows the energy separation between the Fermi level and
the VHS, $\Delta E = E_F - E_{VHS}$. Note for example the case
$\Delta_0 = 6eV$: over the doping range $x = -0.1$ to $x = +0.3$,
the Fermi energy varies by $4eV$, while $|\Delta E| \leq 10meV$!
In general, the pinning range extends from half filling to
a finite doping where the VHS again intersects the
Fermi level, Fig. 33d. This doping, which in the VHS
model corresponds to optimum doping, is fixed by some
electron-hole asymmetry parameter, $t_{OO}$ or $t'$. In the
limit $t_{OO}, t' \to 0$, this second point collapses to half fill-
ing. The pinning is further illustrated in Fig. 33e [355],
which shows the dos vs energy for several different dop-
ings. Clearly there is a large shift in the absolute Fermi
level, $E_F$, while $E_F - E_{VHS}$ has a much smaller change.
Thus, correlations strongly pin the VHS near the Fermi
level, especially when a Mott transition occurs at half fill-
ing. Note further that the shift $\Delta E$ is not a monotonic
function of doping, but actually vanishes a second time
at a finite $x$ (Fig. 33f).

In these calculations, part of the pinning is due to a
genuine renormalization of the shape of the Fermi surface
with doping, but part simply arises from the collapse of the
bandwidth to zero at half filling. In this sense, the
results of including exchange in a three-band tJ model
are even more interesting, Fig. 33g [204]. A strong pinning
of the Fermi level to the VHS is still found. But here, the
bandwidth remains finite at half filling, so the pinning is
mainly due to changes in the shape of the Fermi surface.
Indeed, from Eq 5 it can be seen that the VHS falls exactly
at the Fermi level in the uniform phase at half filling.
The double crossing of Fermi level by the VHS
(Fig. 33h) is also found in the present case, now associated
with a crossover from magnetically-dominated behavior
(bandwidth $B \sim J$) at half filling to a more metallic
behavior ($B \sim t$) in the doped material.

This strong pinning of the VHS near the Fermi level
has been found in a number of slave boson calculations
[356,358,372], as well as in infinite-dimensional calcula-
tions [377,380] correlation calculations [374,377] which
do not involve slave bosons, and renormalization group
calculations [35,375]. Recent 4-slave boson calculations
of the one and three band Hubbard models find even
stronger pinning [374]. This pinning can be described as
an effective mass renormalization $\Delta E = \Delta E_0/m^*$, where
$\Delta E_0$ is the bare splitting and $m^*$ an effective mass.
If there is a charge reservoir, this pinning can even alter
the hole density in the CuO$_2$ planes [3]. This may ex-
plain some anomalous results, such as the absence of BiO
pockets in the Fermi surface of Bi-2212, which disagrees
with band structure calculations.

D. How Good are Slave Boson Calculations?

1. Comparison with Monte Carlo Calculations

A number of objections have been raised to the slave
boson approach for calculating correlation effects. The
main problem is that the constraint of no double occu-
pancy is satisfied only on average. Zhang, et al. [380] have
suggested that, if the constraint is satisfied exactly, then
the metal-insulator transition would arise for all $\Delta > 0$,
rather than only above a critical threshold, $\Delta > \Delta_c$. It
is therefore important to test the predictions of the slave
boson theory, particularly near half filling, where corre-
lation effects are strongest.

One test is to compare the predictions of slave boson
theory with predictions of correlation effects by other
means. A particularly attractive comparison is with
Monte Carlo calculations on finite sized clusters, since
these calculations are essentially exact, except for be-
ing limited to finite size and not-too-low temperatures.
These calculations assume $t_{OO} = 0$, and a large but finite
value for the on-site Coulomb repulsion, $U_d = 6t_{CuO}$.
Figure 36 shows a comparison of the Fermi energy vs
doping, for several different values of $\Delta$, for both cluster
calculations (symbols) [381,382] and slave boson calcu-
lations (lines). Since this is theory vs theory, the com-
parison has essentially no adjustable parameters. The
agreement is fairly satisfactory. Both theories find evi-
dence for an insulating gap at half filling, above a crit-
ical value of $\Delta$. The cluster calculations find a smaller
$\Delta_c \simeq 2t_{CuO}$. The critical value $\Delta_c$ in the slave boson
calculation would be reduced slightly by including ex-
change corrections [36]. Both calculations display the
same overall doping dependence. The present compar-
ison would therefore tend to validate both calculations
(the cluster calculation, in that finite size and finite tem-
perature effects do not seem to limit their validity).
2. Comparison to Experiments

A separate test of slave boson theory is to compare its predictions with experiment. An important test is to see how well theory fits the photoemission-derived energy band dispersions. Estimating the bare parameters from LDA calculations, Fig. 37a compares the experimentally-determined dispersion for Bi-2212 with both the bare band dispersion, and the slave boson corrected dispersion, assuming the bare parameters are the same as those found for LSCO. The overall reduction in bandwidth is well reproduced by the slave boson calculation, but it cannot account for the extreme flatness of the bands in the immediate vicinity of the Fermi level (the extended VHS).

Since the extended VHS’s have much stronger singularities, it is important to try to understand just how they might be produced. One possibility is that this is due to interlayer coupling. For instance, in Bi-2212 there is a Bi-derived Fermi surface pocket immediately above the Fermi level at the VHS. In principle, level repulsion from this pocket could make the VHS anomalously flat. However, tight-binding models are unable to reproduce such a feature: the dos always has a logarithmic divergence, independent of the position of the second band, and the magnitude varies smoothly and monotonically as the degree of overlap between the two bands is varied [32].

Also, since the extended VHS seems to be a common feature of many high-T_c cuprates, it would be preferable to have an explanation which depends on the CuO_2 planes only. Fig. 37b suggests one such explanation: a polaronic renormalization of the electronic bandwidth within a Debye frequency of the Fermi level [150]. Somewhat surprisingly, the polaronic enhancement is found to be pinned to the VHS, and not to the Fermi level. Hence, it can also explain the case of YBa_2Cu_3O_8, where the extended VHS is found 19meV below the Fermi level.

3. Doping Dependence of Photoemission in YBCO

The doping dependence of angle resolved photoemission spectra was studied early on in YBCO [92], and recently in Bi-2212 [58-80]. The results in these two experiments are strikingly different. In Bi-2212, the spectra are dominated by the opening of a pseudogap in the normal state above the superconducting transition temperature, while such effects are not seen in the experiments on YBCO. With recent improvements in sample quality and photoemission resolution, I would strongly urge that the experiments on YBCO be reproduced (note that in these experiments, a feature associated with the VHS was not identified). However, it is striking how well the data on Bi-2212 agree with the VHS theory of pseudogap formation, while the YBCO data are for the most part consistent with slave boson calculations in the absence of a pseudogap. The former data will be discussed in Section IX.A.2, and the latter in this section.

Photoemission in YBCO provides strong evidence for the pinning of the Fermi level to the VHS. Indeed, there is virtually no shift of the Fermi surfaces with doping! Experimentally, it is found [28] that a strong feature near the X and Y points ≈1meV below the Fermi level shifts by 200meV as the oxygen is reduced from O_{6.9} to O_{6.3}, Fig. 38. At the same time, the saddle point feature near the X(Y)-point is within resolution limits locked to the Fermi level, shifting by less than 10meV over the same doping range. Figure 39 shows the actual photoemission spectra along Γ – Y(X), both for Y-124 (a), YBCO_6.9 (b), YBCO_6.5 (c), and YBCO_6.3 (d) [28]. It can be seen that the VHS is nearer to the Fermi level in YBCO than in Y-124, but that there is no evidence for a shift in this feature with doping in YBCO. While the intensity is largely lost by O_{6.3}, there is still a clear shoulder which has the same dispersion as in the more highly doped samples.

This pinning of the Fermi level near the VHS is predicted by the slave boson calculations, Fig. 33a. Figure 33 shows the expected band dispersion for LSCO as x is varied from the VHS to half filling. The total shift of the Fermi level from the VHS is only 16meV – quite comparable to experiment. However, experimentally it is also found that the bandwidth is nearly independent of doping, which is not reproduced by the slave boson calculations of Fig. 33b (the bandwidth is proportional to \( t_R^2 \)). This can be very nicely explained by the inclusion of exchange corrections. Figure 33 shows the band dispersion calculated self-consistently at a number of doping levels assuming the uniform magnetic phase (Eq. 33). All curves are referenced to the Fermi level, taken as \( E_F = 0 \). For electron-doped samples (dashed lines) the calculated bandwidth changes rapidly with doping, decreasing as half filling is approached, signalling the transition to an insulating phase. However, at half filling, a finite bandwidth remains, due to the magnetic excitations, with bandwidth \( \Delta_1 \approx J \). On the hole doping side, the band dispersion of the filled states is nearly doping independent out to a doping beyond the VHS, while the dispersion of the unoccupied states (not visible in photoemission) increases rapidly with doping. This behavior is in quite good agreement with photoemission in the metallic regime in YBCO. Experimentally, removing oxygen leads to negligible change in the band dispersion, until \( \delta \approx 0.65 \), at which point the conduction bands abruptly vanish [11,22]. While I am comparing the theory for LSCO with experiments on YBCO, this is not expected to make any qualitative difference in the band dispersions.

In the slave boson calculation, the absolute position of the Fermi level, Fig. 33b, is calculated with respect to an assumed zero in the predominantly oxygen-like nonbonding band – the calculation of the absolute position of the Fermi level, with respect to all the other bands in the crystal is beyond the scope of slave boson theory. However, the general feature of relatively weak variation in
the hole doped phase, with a strong/discontinuous jump at the insulating state at half filling, would be expected to persist. The sudden vanishing of the dos for YBCO would be consistent with this opening of the Mott gap – recall from Section VLB that the hole doping of the planes vanishes near O₆. However, a photoemission peak at the gap energy was not observed in these experiments, and another motivation for repeating the experiments on YBCO would be to identify a feature associated with the charge transfer gap, and study how it varies with doping.

Similar experiments have been performed near the metal-insulator crossover, in a number of d=1 Mott-Hubbard systems including Cu₃, Sr, VO₃, and Pb(5d) core level all shift by different amounts with doping. Thus, it is difficult to evaluate the significance of the finding that the Fermi level is nearly unchanged in absolute value between hole-doped LSCO and electron-doped NCCO. While one would initially expect that the Fermi level would shift by the charge transfer gap, the complete elimination of the apical O’s should partially compensate for the shift, in a way which lies beyond the realm of slave boson calculations. An attempt to analyze these level shifts in terms of bond-valence sums is presented in Ref. 89, but the dominant effect in Bi-2212 seems to be a chemical potential shift.

There is one interesting observation which might find an explanation in the slave boson calculations. In LSCO and NCCO, there is very little shift of the chemical potential with doping, whereas in Bi-2212, there is a small shift in the metallic regime, but a substantial shift as the insulating phase is approached. This behavior should be compared with Fig. 3b: when there is a Mott transition at half filling, the Fermi level is very weakly dependent on doping in either the hole-doped or the electron-doped regimes, but with a discontinuous change at exactly half filling. However, this discontinuity requires a critical value of the Cu-O energy separation, \( \Delta \geq \Delta_c \). For \( \Delta \) slightly less than \( \Delta_c \), there is no discontinuity in the chemical potential, so it varies rapidly in the immediate vicinity of half filling. This is consistent with the suggestion that the AFI phase is harder to produce, is much more strongly related to the Cu-O energy separation, and can lead to flat (doping independent) segments of \( \mu \) for isolated CuO₂ planes. However, nanoscale phase separation is actually more correctly viewed as a charge-bunching phase (as in a striped phase, Section X.B.3); as such, \( \mu \) can still depend on doping. Indeed, even these measurements of \( \mu \) find indications of phase separation. Thus, van Veenendaal et al. in studying the Cu 2p⁵/₂ core level of Bi-2212, found a broadening which could indicate such an inhomogeneity, but only in the CuO₂ planes! This is precisely what would be expected from the models of hole-driven phase separation discussed in Section X below. Furthermore, there is evidence for two Sr environments in LSCO.

4. Chemical Potential

Several groups have measured the doping dependence of the chemical potential \( \mu \). However, comparison of the experimental results with slave boson calculations is non-trivial since the calculations ignore Coulomb effects. In an elemental material such as Si, the approximation can be justified since the dopant ions are assumed to form a uniform background, keeping the material neutral on average. In a layered material, however, this is a more severe approximation, since the doping counterions are located on different layers, so changing the hole doping shifts the overall potential of the CuO₂ planes with respect to the other planes, in ways which are ignored in slave boson calculations. Moreover, additional screening can be produced by polarizing atoms on other layers. For instance, the apical O’s move closer to the planes with increasing hole doping, and in overdoped materials part of the holes go to the apical O’s rather than to the planes.

Experimental evidence for this is seen in Bi-2212, where there is clear evidence for non-rigid-band filling: the valence band, the Bi(5d) core level, and the Pb(5d) core level all shift by different amounts with doping. Thus, it is difficult to evaluate the significance of the finding that the Fermi level is nearly unchanged in absolute value between hole-doped LSCO and electron-doped NCCO. While one would initially expect that the Fermi level would shift by the charge transfer gap, the complete elimination of the apical O’s should partially compensate for the shift, in a way which lies beyond the realm of slave boson calculations. An attempt to analyze these level shifts in terms of bond-valence sums is presented in Ref. 89, but the dominant effect in Bi-2212 seems to be a chemical potential shift.

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5. Effective Mass Divergence

Another experimental observation also points to the possibility of phase separation. The slave boson calculation predicts that the Mott-Hubbard transition involves the collapse of the electronic bandwidth as Cu-O hybridization is eliminated. Experimentally, this should show up as a divergence of the effective mass, and hence of the DOS, as half filling is approached. Such a divergence is indeed observed in the linear-T coefficient of the specific heat, $\gamma$, for La$_{1-x}$Sr$_x$TiO$_3$ and Y$_{1-x}$Ca$_x$TiO$_3$ [17], but is not found in the cuprates.

E. Other Theories of Correlations

As discussed above, slave boson calculations predicted that correlation effects produce a strong doping dependence of the electronic bandwidth, in particular, with hopping $t \to 0$ as half filling is approached. Despite this, the holes have a well-defined dispersion, and there should be an enhanced VHS, pinned near the Fermi level. Recent Monte Carlo calculations of the tJ and Hubbard model have substantially confirmed these predictions, and verified the important role played by auxiliary parameters such as $t_{OO}$ or $t'$ which break the electron-hole symmetry. These calculations have further shown the importance of magnetic effects near half filling, which provide a finite residual bandwidth $\approx 2J$ in the insulating limit. Such magnetic effects can be incorporated in the slave boson scheme via the 3-band tJ model.

Dagotto, et al. [11] have shown that when there is an antiferromagnetic gap, each of the subbands has a well-defined VHS; they call their theory, which combines spin fluctuations with the VHS, “the best of both worlds”. They find that the resulting bands are particularly flat, and can give rise to an extended VHS – which in turn can generate a high-$T_c$ d-wave superconductor from a phonon-mediated pairing mechanism [315]. However, Ioffe and Millis [396] have pointed out a problem: to generate the requisite superlattice, the antiferromagnetic fluctuations must be quasistatic, with energies less than $k_BT$. This in turn would lead to long-range AFM order in the limit $T \to 0$. In contrast, near optimum doping, NMR finds spin fluctuations only at energies larger than $k_BT_c$. On the other hand, there is ample evidence (Section IX) for the short-range structural disorder, which can also produce extended VHS’s and pseudogaps.

VIII. ELECTRON-PHONON INTERACTION

The role of electron-phonon interaction in the high-$T_c$ cuprates has been vigorously debated. There is considerable experimental evidence for structural instabilities and other phonon related anomalies; of particular interest are anomalies near $T_c$. However, anomalies at $T_c$ are always expected, and do not necessarily indicate that the electron-phonon coupling is strong enough to cause the elevated transition temperatures. Moreover, structural instabilities are common to a wide variety of mostly non-superconducting perovskites, and can be due predominantly to phonon anharmonicity, with little or no electronic contribution [397]. The purpose of this chapter is to show theoretically how electron-phonon coupling could play a strong role in the cuprates; the following chapter will present experimental evidence that this is indeed the case.

A great number of theoretical models of electron-phonon coupling have been applied to the cuprates – some involve particular phonons, most often breathing mode or apical oxygen related, while others are more generic models of polaronic or bipolaronic coupling. Several conferences have been devoted to this topic [398].

In this section, I will concentrate on the electron-phonon couplings associated with the VHS – in particular, VHS nesting or Jahn-Teller effects.

As discussed in Section VI.A above, the VHS leads to $ln$ or $ln^2$ singularities in the charge and spin susceptibilities. In this section, the singularity in the charge susceptibility will be explored. In principle, this can lead to both structural phase transitions and an enhanced electron-phonon coupling parameter $\lambda$.

This is a long and important chapter because the phonon coupling has proven to be more subtle than expected. In conventional superconductors, it will be recalled, there is a strong competition in the charge channel between superconductivity and structural instability in the form of a combined CDW Peierls instability. In LSCO, the evidence for a CDW was ambiguous. The LTO phase was initially identified as a CDW phase [4,59], but this identification was abandoned when it was realized that the VHS degeneracy is not split in the LTO phase [400]. No more promising candidates appeared in the other cuprates.

A first hint came from the discovery of the LTT phase in La$_{2-x}$Ba$_x$CuO$_4$, which was found to strongly suppress $T_c$ [101], and the subsequent realization that this phase does split the VHS degeneracy [102,403]. Based on this idea, the model of a Van Hove – Jahn-Teller (JT) effect was introduced [102,407], and it was postulated that both the LTO and HTT phases could be dynamic JT phases, with important short-range order. It was gradually realized that the main transition, corresponding to a CDW in other systems, was the onset of short-range order in the HTT phase, which could be identified with the experimentally observed pseudogap phase. A similar phase is found in YBCO. Experimental evidence for the pseudogap is presented in Section IX.A.

Analysis of the LTT transition is complicated because the soft mode, the tilting of the CuO$_6$ octahedra, couples quadratically to the electrons (non-Migdal behavior) [408,406,314]. A detailed analysis [150] of the ionic model finds that there is strong linear coupling to a variety of in-plane modes, but as these soften, they couple
to the lower frequency tilt modes, and drive them soft. These planar modes, discussed in Subsection D below, can display strong polaronic coupling effects. Indeed, the extended VHS’s may be generated by polaronic band narrowing.

This section will attempt to discuss these features in detail. Subsection A discusses the special features of VHS nesting which are responsible for the pseudogap and for nanoscale phase separation. The various phonons which can couple to a VHS are discussed in Subsection B. Subsection C describes the quadratic coupling to tilt-mode phonons, and the interpretation of the LTT and LTO phases of LSCO as static and dynamic VHS-JT phases, respectively. In Subsection D, it is shown that, in the ionic model, there is a linear coupling to planar stretch modes with ensuing polaronic effects. Complications due to correlation effects are pointed out in Subsection E, while an alternative structural-instability model, involving an apical oxygen double well, is briefly discussed in Subsection F. Following this, Section XI provides a growing.

A. VHS Nesting

1. Pseudogap Formation

Early calculations of VHS-induced structural distortions assumed the presence of a zone-boundary ($\vec{Q}$-point) phonon which has a strong linear coupling to the VHS. While no specific phonon was assumed, the gap $\vec{q}$-dependence is consistent with that of an O-O stretch or bending mode with ensuing polaronic effects. Complications due to correlation effects are pointed out in Subsection E, while an alternative structural-instability model, involving an apical oxygen double well, is briefly discussed in Subsection F.

Following this, Section XI provides a summary of experimental data, particularly in regard to pseudogaps, short-range order, and anomalies near $T_c$. The nesting which are responsible for the pseudogap and for nanoscale phase separation away assuming that the structural instability is related to the dos, and hence diverges at a VHS – this is the fundamental basis for nanoscale phase separation away from the VHS (see discussion in Appendix A). But in Fermi liquid theory, a divergence in the compressibility is related to a divergence in the static vertex function [411], and hence a breakdown of Migdal’s theorem [238].

In the adiabatic approximation (neglecting $\Omega R$ in the energy denominators), and high-\(T\) limit, the self energy becomes

$$\Sigma(\vec{k}, \omega) \simeq \frac{2 k_B T}{N} \sum_q |g(q)|^2 \frac{\omega_q R}{\Omega_q R} \left[ 1 - f(E_{\vec{k}-\vec{q}}) + n(\Omega_q R) \right] \left( \frac{\omega}{\omega + \mu - E_{\vec{k}-\vec{q}} + \Omega_q R + i\delta} \right),$$

where $\chi$ is the bare susceptibility, $\Omega_0^2$ is the renormalization factor at the VHS (see discussion in Appendix A). But in Fermi liquid theory, a divergence in the compressibility becomes

$$\Omega_{q R}^2 \simeq \omega_{q R}^2 \left[ R + \xi^2(T) \right] |q - q_0|^2,$$

where $\xi(T)$ is a coherence length [412] and $R \equiv (\Omega_{q R}^2/\omega_{q R}^2)^2$ (Eq. [3]) is the renormalization factor at the nesting vector which vanishes at the structural instability temperature $T^*$. Within the VHS model there is a pseudogap instability at a finite temperature at both half filling and at the VHS due to VHS nesting, but as soon as the material is overdoped, nesting becomes considerably worse, so the structural instability (pseudogap) $T^*(x)$ will rapidly vanish at some critical doping $x^*$. This is a quantum critical point (QCP) since, when $T^*$ is low, quantum corrections become important. From the observed pseudogaps, Fig. 42 below, the doping of optimum superconducting $T_c$ falls close to this critical point in YBCO, and further away in LSCO. Recently, Perali, et al. [413] have explored the consequences of introducing such a critical point in the overdoped regime, but without assuming that the structural instability is related to VHS nesting.

2. Phase Separation

Phonon-induced phase separation was adduced from a somewhat different formalism, commonly used in studying alloy phases and structures [23]. Here, the electronic
ground state energy is expanded in a power series in the single ion pseudopotential \( w(\mathbf{q}) \):

\[
E_e = E_0 + E_1 + E_2 + \ldots,
\]

(65)

with \( E_0 \propto w^w \) (Eq. 2.12 of Ref. [26]). The term \( E_1 \) depends on the ionic density, but not the arrangement of the ions, so the leading structure-dependent term is \( E_2 \), which can be written as

\[
E_2 = \frac{1}{2N} \sum_{\mathbf{q} \neq 0} \frac{\chi(\mathbf{q})}{\epsilon_r(\mathbf{q})} |w(\mathbf{q})|^2 |S(\mathbf{q})|^2,
\]

(66)

where \( \epsilon_r \) is the dielectric constant, defined below Eq. [3], and \( S(\mathbf{q}) \) is the structure factor of the ions in a unit cell. In the theory of Hume-Rothery phases (discussed in Section 7.2 of Hafner [2]), the series of structural phase transitions as a function of doping is explained by writing the electronic energy up to order \( E_2 \), and then noting that each phase has a Kohn anomaly (coming from \( \chi \)), and hence a minimum in the free energy when the Fermi surface intersects the Brillouin zone boundary. When the free energies are calculated for a series of different structures as a function of doping, it is found that the Kohn anomaly minima all occur at different dopings depending on the particular Brillouin zones. This leads to a phase separation, with regions of two phase coexistence determined by the common tangent construction (as in Fig. 58 below).

When the above formalism is applied to the cuprates [41], the logarithmic divergence in \( \chi(\mathbf{Q}) \) ensures that \( E_2 \) will have a minimum at the VHS, making this a very stable phase, so that either under- or overdoping will lead to phase separation. Note that the formalisms for \( \Sigma \) and \( E_e \) above are not exactly equivalent. However, by identifying \( g(\mathbf{q}) \approx w(\mathbf{q}) \), then expanding Eq. (65) to lowest order in \( w(\mathbf{q})^2 \) yields an expression approximately equivalent to Eq. (64). In Appendix C, some tight-binding realizations of this formalism are discussed, showing that similar results hold for both conventional and VHS nesting.

### B. ‘Umklapp’ vs. ‘Jahn-Teller’ limits

Given that the splitting of the dos peak associated with a VHS can stabilize a CDW, the question arises as to which phonons are involved. There are a number of phonons which can couple to the VHS, but sorting them out requires some effort. In principle, there are two different ways to split the VHS degeneracy, associated with the ‘Umklapp’ and the ‘Jahn-Teller’ limits of the theory. The starting point is the high temperature tetragonal (HTT) phase in which the \( X \) and \( Y \) point VHS’s are assumed to be degenerate. The ‘Umklapp’ limit involves a phonon of wave vector \( Q = (\pi/a, \pi/a) \) which condenses to produce an orthorhombic cell. Here, the \( X \) and \( Y \) points remain degenerate, but Umklapp coupling introduces equivalent gaps at both the \( X \) and \( Y \) points – this is the direct 2D analog of the usual 1D Peierls distortion. Umklapp scattering leads to period doubling, with associated zone folding, leading to ‘ghost’ Fermi surfaces and ‘shadow bands’, Fig. [11]. The stronger the umklapp splitting, the more intense the ghosts. The ghost Fermi surfaces are similar to those observed in Bi-2212 photoemission experiments, Fig. [11b] [88], although these ghosts may be associated with the ordinary orthorhombic distortion. Curiously, the distortion which produces the low-temperature orthorhombic (LTO) phase in LSCO does not split the VHS – there is an additional, glide symmetry which prohibits umklapp splitting of the VHS degeneracy. Spin-orbit scattering can produce a splitting, but this is believed to be a relatively small effect [114,136]. Magnetic long-range order can also lead to an umklapp gap.

In the ‘Jahn-Teller’ (JT) limit, the structural distortion splits the degeneracy of the two VHS’s, driving one below and the other above the Fermi level. The two cases are illustrated in Fig. [42] and compared to the experimentally-derived dispersion in underdoped Bi-2212 [117], Figs. [42a] and b. In the ‘Umklapp’ limit (Fig. [42d]), there is an energy gap, whereas the ‘Jahn-Teller’ limit (Fig. [42c]) only breaks the degeneracy of the dos at the \( X \) (solid line) and \( Y \) (dot-dash line) points in the Brillouin zone without producing a true gap. This Jahn-Teller type distortion is easy to recognize from its symmetry-breaking property: if the equivalence under a symmetry operation of the two in-plane oxygens is broken, the corresponding distortion splits the two VHS’s in energy. Thus, the distortion of the low-temperature tetragonal (LTT) phase, Fig. [13a], is a JT distortion. However, the LTT tilt mode only couples quadratically to the holes, whereas the accompanying in-plane shear mode has a linear coupling. The comparison with experiment will be discussed further in Section IX.A.2.

From Fig. [13] it can be seen that the LTO and LTT distortions both involve octahedral tilts, and differ only by tilting in different directions: along the Cu-O-Cu bond in the LTT phase, and at 45° to this direction in the LTO. In some related compounds, tilting at intermediate angles is also possible, leading to a Pccn phase. Since the Pccn tilt can be considered as a superposition of the LTO and LTT tilts, it also leads to a (reduced) splitting of the VHS degeneracy. Other phonons can be similarly classified. Thus, both Cu-Cu and O-O stretch modes can lead to an orthorhombic distortion, Fig. [14], and both distortions produce a gap at the Fermi level. However, the Cu-Cu stretch mode does not couple to the VHS, and the energy gap shrinks to zero at that point, whereas the O-O mode does couple to the VHS, and has a finite gap throughout the Brillouin zone (an Umklapp gap). Particular forms of the electron-phonon coupling for these modes are discussed in Appendix C.
C. Tilt-mode Instabilities and Dynamic JT Effects

The tilt mode which drives the LTT instability also splits the VHS degeneracy. Hence, this may be the structural distortion that competes with superconductivity. That interpretation is discussed in this section, and it is shown that the LTO and HTT phases can be interpreted as dynamic JT phases with the pseudogap corresponding to the dynamic JT onset. However, there are still complications. Whereas conventional strong coupling models involve only linear coupling due to Migdal’s theorem, the LTT and LTO distortions in LSCO involve a tilting mode phonon which only couples quadratically to electrons. A number of recent models have explored the role of this quadratic coupling \[^{408,414,406}\].

This subsection also briefly describes an analogy to the dynamic JT phases in ferroelectrics like BaTiO\(_3\), presents an interpretation of the dynamic JT phase in terms of solitonic moving domain walls, and points out that these anomalous low frequency modes could play a role in superconducting pairing. In the following subsection, it will be shown that there is a linear coupling (probably to O-O stretch modes) which underlies the instability.

1. Rigid Unit Modes

Most perovskite structures are sensitive to structural distortions – principally either ferroelectric or associated with octahedral tilt-mode instabilities. The low-temperature distortions of LSCO and LBCO (LTO, Pccn, LTT) are associated with octahedral tilts, and there is some evidence of a pyramidal tilting instability in YBCO. Similar instabilities are found in BPBO, BKBO, Section XVI. In undoped SrTiO\(_3\), there is an antiferrodistortive instability associated with the tilting of the TiO\(_6\) octahedra, while doped SrTiO\(_3\) is superconducting – one of the first known members of the family of high-T\(_c\) perovskites. Ferroelectric phenomena play a minor role in the cuprates, and are briefly discussed in Subsection C.5. The tilting instabilities are part of a much larger class of phenomena. Heine and coworkers \[^{417,411}\] have developed the concept of ‘rigid unit modes’ (RUM’s), originally in the framework alumino-silicate compounds, to describe their structural instabilities. In these structures, there is an array of weakly coupled rigid units (e.g., the CuO\(_6\) octahedra in LSCO); there are a certain number of vibrational modes of these units which do not distort the units, but flex the coupling between them. Some of these modes (the RUM’s) have a very low frequency – they differ from zero-frequency modes only by quadratic coupling terms. These modes are sparse in the phonon spectra of these materials, but their locus in \(\vec{q}\)-space can be worked out from simple symmetry considerations \[^{111}\]; these modes are ‘natural candidates for the soft modes that typically drive displacive phase transitions.’ The octahedral tilt modes of the cuprates fall into the category of RUM’s.

Dove, et al. \[^{419}\] list four forces important in driving the structural phase transition. The most important is the polarizability of the oxygen ions, which also plays a large role in the cuprates. Another is that Si-O-Si bond angles prefer to be bent, \(\approx 145 – 150^\circ\), rather than straight \((180^\circ)\); the analogous result may also be important in the cuprates. Most interestingly, they note that in special cases, electronic instabilities can play an important role.

2. Tilt-modes in the Cuprates

The strong anharmonicity of the tilting modes in LSCO is known from LDA frozen phonon calculations. Pickett, et al. \[^{403}\] have carried out extensive numerical calculations of the phonon energy surfaces in LSCO and LBCO, particularly near the soft modes of the LTO and LTT phases. They analyzed undoped La\(_2\)CuO\(_4\), but with lattice constants appropriate to La\(_1.96\)Ba\(_0.04\)CuO\(_4\), to approximate the effects of lattice strain. They found that the HTT structure is unstable and the HTO structure metastable, with energy minima associated with the LTT phase, Fig. \[^{45}\]. The HTT is actually at a maximum of the energy surface, \(\approx 46\text{meV}\) above the LTT minima, while the LTO phase lies in a shallow local minimum, \(\approx 14\text{meV}\) above the LTT minima. This result is consistent with the double well potential derived from the experimental temperature dependence of the LTO soft mode phonon in LSCO \[^{416}\], Fig. \[^{46}\].

Given this large anharmonicity, the LTO and LTT transitions can be understood in a purely ionic model without any electron-phonon coupling \[^{397,420}\]; there are large interlayer strains due to the lattice mismatch between the CuO\(_2\) and the LaO planes \[^{422}\], which can be relieved by tilting of the CuO\(_6\) octahedra. However, the question arises as to whether electron-phonon coupling can play a role in these transitions. Thus, frozen phonon calculations automatically include electron-phonon coupling effects, and a Landau theory of the transition \[^{422}\] cannot distinguish between ionic and electron-phonon models since the Landau theory parameters are chosen phenomenologically. In a model which simultaneously incorporates both anharmonicity and electron-phonon coupling \[^{408,436}\], it is possible to explore the competition. While a certain amount of anharmonicity appears to be necessary, it is possible to fit both the phonon softening and the doping dependence of the transitions either by purely ionic models, or by models with a strong electron-phonon coupling, Fig. \[^{40}\].

3. Tilt-stretch Mode Coupling

However, a purely ionic model cannot provide a self-consistent explanation of the doping dependence of the
LTO transition in the cuprates [150]. Detailed analysis of the model shows that the dominant effect on doping is the change of the Cu-O bond length which, in an ionic model, is due to a large decrease of ionic size with valence, as $O^{2-} \rightarrow O^{-}$ [123, 124, 150]. Such a large hole-induced variation of an ionic size is known to lead to strong electron-phonon coupling terms, so that a model which neglects these terms cannot be correct. Hence this linear electron-phonon coupling should be included in the model, via the length dependence of the hopping parameters, in which case the VHS will play a dominant role in the physics of the transition. A model combining strong VHS-related electron-phonon coupling plus interlayer-strain-induced anharmonicity can explain both the temperature dependence [106] and the doping dependence [150] of the LTO transition. Nd-substitution experiments [125] rule out a pure electron-phonon model since the Nd changes the atomic size without providing any charge transfer; hence, a pure electron-phonon model would predict no change in the transition temperature. On the other hand, photodoping (Section XI.A.5) changes the hole content without modifying the ions, and this too can drive the LTO-HTT transition [126], thereby ruling out a purely ionic model. An important result of this analysis is that there must be coupling not only to the tilt modes, but to in-plane modes which change the Cu-O bond length.

The mode coupling is most easily seen at the ionic level: an oxygen with an excess hole, $O^-$, is much smaller than $O^{2-}$. Hence, an isolated $O^-$ will cause the two adjacent Cu’s to approach as in a Cu-Cu stretch mode. A coherent pair of O’s sharing the hole will lead to an O-O-type stretch mode. If the hole further delocalizes along one direction, say along $x$, then the $x$-axis will shrink (more $O^-$-like) while the $O^{2-}$-$y$ axis will expand, coupling to the shear mode. Finally, since the CuO$_2$ layer is under lateral compression due to interlayer misfit, the larger $O^{2-}$’s may buckle out of the planes, thereby giving rise to the LTT-type tilting distortions. This would explain the curious feature that the lattice constant along the tilted axis is actually larger than that along the transverse axis.

While the combined influence of two phonon modes – high-frequency bond stretching and low-frequency tilt modes – complicates the analysis, it does provide one simplification. Whereas the tilt modes couple quadratically to the holes, the stretch modes have a strong linear coupling. This means that the coupling can be analyzed in terms of conventional polaronic effects [150]. In fact, the Holstein and Holstein-Hubbard models can also play a role [427, 430, 229, 21, 407], since the associated Umklapp scattering can also split the VHS degeneracy. Note that, while these modes are not condensed in the macroscopic LTO or LTT phases, they could play a role in a dynamic JT or local polaronic picture. Polaronic effects are discussed in Section VIII.D.3.

4. VHS JT Effect and the LTT Phase

The Jahn-Teller (JT) effect was initially developed for molecules and applied to isolated impurities in solids. In molecules, the JT theorem states that whenever a molecule has an electronic degeneracy, there is a molecular distortion which splits the degeneracy. Since the electrons can repopulate into the lower of the split energy levels, the distortion produces an electronic energy lowering, which overcomes the potential energy of the distortion. The net result is that a molecule with an electronic degeneracy can lower its energy by distorting spontaneously. A static distortion is referred to as a static JT effect. However, if the energy barrier is small, the molecule can tunnel between several equivalent distortions, giving rise to a dynamic JT effect [43].

A similar effect can arise in a crystalline solid – the 1D CDW with accompanying Peierls distortion being the most familiar example. In this case, the electronic degeneracy is associated with the two Fermi surface points. In the cuprates, there are a number of candidates for JT effects. The distortion of the CuO$_6$ octahedra in LSCO resembles a classical molecular JT effect: in the undistorted molecule, the Cu $d_x^2-y^2$ and $d_{3z}^2-r^2$ orbitals are degenerate – the elongation of the Cu- apical O distance is the JT distortion which splits the $d$ hole degeneracy. However, a similar distortion is found in La$_2$NiO$_4$, even though Ni is not a JT molecule. Hence, the distortion may instead be a purely static ionic effect. A number of theories have been proposed wherein this distortion, in dynamic or static JT form, contributes to the high $T_c$ values [432]. Alternative dynamic JT models for the cuprates have been proposed by a number of groups [434, 435] – indeed, the double well models for the apical O’s can be a variant of this idea – while dynamic JT models have also been proposed for other novel superconductors, particularly the fullerenes (Section XVII.C), and for a number of perovskites (Section XI.H).

The VHS-JT effect is distinct from these models in that the electronic degeneracy is associated with the two VHS’s, at $X$ and $Y$. Any structural distortion which splits that degeneracy will drive a VHS-JT effect. This was initially pointed out in 1977 by Friedel [130], and more recently applied to the cuprates [402, 407]. Now in LSCO and LBCO, the lowest energy phonons which split the VHS degeneracy are the LTT-type tilting modes (out of the plane) of the CuO$_6$ octahedra, which are anomalously low frequency rigid-unit modes, further softened because the tilting relieves some of the interlayer strain. While these phonons differ from conventional CDW modes, they do behave like Jahn-Teller phonons. In the low-temperature tetragonal (LTT) phase, the apical oxygen tilts toward the $x$ or $y$ axis, splitting the VHS degeneracy [102, 404]. Fig. 43h. Hence, the LTT phase can be considered as a static JT phase.

Pickett has found that the splitting of the VHS degeneracy can lead to a significant enhancement of the LTT...
phase stability \[^{404}\]. It has been pointed out \[^{437,438}\] that his assumed LTT tilt angle is too large, by about a factor of 2, and that the VHS splitting effects would be much smaller if a more realistic angle is assumed. In fact, there is now clear evidence that there is a critical tilt angle below which the electronic anomalies are greatly reduced \[^{139}\]. There are several considerations which could enhance the VHS splitting over the LDA value. Thus, LDA calculations generally overestimate electronic bandwidths by \(~\) a factor of two; a smaller bandwidth, due to correlation effects, would enhance the importance of the VHS splitting. In fact, LDA probably overestimates the c-axis dispersion by an even larger factor \[^{441}\], and it is this factor which smears out the logarithmic singularity of the VHS. Polaronic effects (Section VIII.D) considerably enhance the sharpness of the VHS peak, possible explaining the observed extended VHS’s. Moreover, if the tilting is partly dynamic, the macroscopic average tilt angle will underestimate the maximum local tilt angles. Indeed, recent EXAFS measurements on LSCO, at \(x \geq 0.15\) \[^{440}\] report evidence for incredibly large tilt angles, \(\Phi \approx 14 - 18^\circ\). Finally, the distortion which drives the LTT instability is not a pure tilt, but includes an in-plane O-O stretch mode which leads to a \textit{linear} splitting of the VHS degeneracy.

Due to the strong effect it has on \(T_c\), there have been many experimental investigations of the LTT phase, both in LBCO and in LSCO. Substitution of La by other trivalent ions (especially Nd) greatly extends the range of hole doping over which the LTT phase is stable. This phase has turned out to be surprisingly complex. No strong electronic anomalies are found when the octahedral tilt is less than a critical value, \(\Phi_c \approx 3.6^\circ\), but when the tilt exceeds this value, there is a metal-insulator transition at the LTT transition. At lower temperatures \(T_c\) is suppressed, being replaced by a magnetic transition \[^{469}\]. The exact relation between these three transitions has been studied in detail, but remains controversial. Since nanoscale phase separation also seems to play an important role in this phase, a detailed discussion of the LTT phase will be deferred until Section XIII, after phase separation has been discussed.

\section*{5. Dynamic JT and the LTO and HTT Phases}

In a uniform low-temperature orthorhombic (LTO) phase the apical oxygen tilts along the [110] direction, Fig. \[^{13}b\], leaving the two planar O’s equivalent \[^{109}\]. Hence, the uniform phase is not JT-related in the absence of spin-orbit coupling, and in the cuprates spin-orbit coupling is a small effect \[^{107,136}\].

Magnetic effects offer an interesting possibility. In the mean-field theory, long-range antiferromagnetic order opens an energy gap which also splits the VHS degeneracy. However, fluctuations eliminate this gap in a strictly 2D material, and the residual gaps observed experimentally are again too small (indeed, they are partly induced by spin-orbit coupling). Moreover, the long-range ordered (3D) antiferromagnetic phase is restricted to lower temperatures and smaller doping than the LTO phase. It is possible that short-range magnetic order could help stabilize an LTO phase, particularly in the presence of nanoscale phase separation. At present, there are no calculations of this effect.

Another possibility is that the LTO phase is a \textit{dynamic} JT phase in which the LTT tilt direction hops back and forth between x and y directions, giving an average macroscopic orthorhombic symmetry. Thus, the local symmetry differs from the global one, stabilized by a dynamic splitting of the VHS degeneracy \[^{407}\]. In such a phase, the macroscopic symmetry is orthorhombic, but locally the octahedra have a predominantly LTT-like distortion, with tunneling between adjacent minima. This is consistent with frozen phonon calculations, which find that the LTO distortion is unstable with respect to an LTT configuration \[^{404}\], Fig. \[^{15}\].

Moreover, the pronounced double well structure in Fig. \[^{12}\] is strong evidence that \textit{even the HTT phase cannot be a simple uniform, untitled phase, but must involve local octahedral tilts}; the existence of the LTO phase must also be due to strong ‘entropic effects’ – i.e., due to the extreme softness of vibrations in the direction of the LTT tilts. Thus, as a function of temperature, the sequence of transitions \(\text{LTT} \rightarrow \text{LTO} \rightarrow \text{HTT}\) can be understood as a series of JT phases, Fig. \[^{17}\], in which the system progresses from being trapped in a single potential minimum, to hopping between two minima, to hopping between all four. At still higher temperatures, all tilting is lost. This onset of tilting seems to correlate with the experimentally observed pseudogap transition, Section IX.A. There is now considerable experimental support for such local LTT order which will be discussed below, Section IX.B.

If the HTT and LTO phases are both dynamic JT phases, then the transition between the two would be due to long-range strain forces, but would have relatively little effect on the Fermi surfaces. This would explain why the HTT-LTO transition has so little effect on the in-plane resistivity \[^{441}\]; however, the transition drives a \textit{metal-insulator transition} in the c-axis resistivity \[^{442}\], with \(\rho_c\) increasing with decreasing T in the LTO phase.

Experimentally, there are hints that the LTO phase has a different character in undoped and doped LSCO (Section XI.I). This would be consistent with the picture of a nanoscale phase separation (Sections X and XI) in which the phase near half filling is dominated by the Mott-Hubbard instability, and that in doped material by proximity to the VHS. Thus, while a static LTO phase near half filling could be stabilized by magnetic effects, that phase in the doped material could be a dynamic JT phase.
6. Analogy with Ferroelectrics

In BaTiO$_3$, there is a series of structural phase transitions as a function of temperature which are analogous to the proposed sequence HTT$\rightarrow$LTO$\rightarrow$LTT in LBCO, Fig. 48. In the titanate, at very low temperatures the structure is rhombohedral, with the Ti distorted off of the cube center, pointing toward one of the eight surrounding O’s. This appears to be a simple, static distortion, with net ferroelectric moment. As the temperature is raised, the symmetry switches to orthorhombic, as if the Ti were now pointing towards the center of a cube edge, halfway between two O’s. But microscopically, this is not what is happening. Instead, the Ti still points toward one of the O’s, instantaneously, but *dynamically hops from one distorted position to an adjacent one*, in such a way that the average distortion is orthorhombic. At higher temperatures, there is a transition to a tetragonal phase, in which the Ti hops among four adjacent minima. Finally, at room temperature the material is in a ‘cubic’ phase, but the Ti is still distorted off-center, but now hopping among all eight possible positions. This last phase has no net ferroelectric moment.

The dynamic nature of these phases was first detected from streaking of X-ray diffraction spots, which showed that the Ti was tunneling between equivalent energy minima in all but the lowest-T phase. EPR experiments on BaTi$_{1-x}$Mn$_x$O$_3$ found that the Mn$^{++}$ were on the distorted Ti positions in the rhombohedral phase, but no EPR signals were found in the higher-T phases due to the rapid reorientation of the ions. It should be cautioned that this ‘eight-site’ model is not universally accepted, and that recent Rietveld refinements of the neutron diffraction pattern do not find evidence for the proposed Ti displacements. On the other hand, recent femtosecond Raman measurements have provided strong support for the model, in that the relevant phonons are found to obey a strongly damped, soft-mode dynamics (consistent with an order-disorder transition with small energy barriers). Additional low frequency modes following relaxational dynamics, which would have been inconsistent with the eight-site model, are not observed.

The microscopic origin of the effect is not yet clear, although a dynamic JT phase is not ruled out. Although BaTiO$_3$ is an insulator, a JT effect is still possible if the Fermi level lies in a hybridization gap – a gap between two bands which are strongly hybridized. This appears to be the case in BaTiO$_3$, where the Ti and O hybridize. Indeed, the sequence of phase transitions has been interpreted as a pseudo-JT effect. Regardless whether the microscopic mechanisms are identical or not, BaTiO$_3$ provides an example of a material with dynamic local order – and a perovskite at that. Many of the properties of domain wall dynamics, of long range ordering, etc. would be expected to be qualitatively similar in the two systems. Unfortunately, much remains to be learned about the perovskite phases, although there is still considerable interest in them.

The analogy with LBCO can be best understood by comparing Fig. 48 with Fig. 49, which illustrates the tilting mode instabilities of LBCO, interpreted as a dynamic JT effect.

Recent studies are stressing the analogy with the cuprates. It is found experimentally that the Debye-Waller temperatures (which give a measure of local distortions) are very similar for the cations in BaTiO$_3$ and the cuprates. Recent band structure calculations note the importance of Ti-O hybridization in BaTiO$_3$ and similar covalency in KNbO$_3$ and KTaO$_3$. Photoemission studies find indications of covalency in the reduced valence of the Ti. The same problem of electron-phonon interaction in the presence of strong correlation effects is being studied (1D model) for the perovskite ferroelectrics as for the cuprates. It is found that, near the point of crossover between a Mott and a charge transfer insulator, there is a strong enhancement of electron-phonon coupling.

7. Solitons

The dynamic JT phase could be realized as a pattern of LTT-type domains, separated by dynamic domain walls which can be described as solitons, Fig. 49h. Static versions of these solitons are found in transmission electron microscopy (TEM) studies of the LTO-LTT transition. It was initially thought that, since the LTT phase is tetragonal, this transition should be clearly marked by the disappearance of twinning in the LTT phase. Instead, there appeared to be no change in the pattern of twins at the transition. In fact, the LTT phase has orthorhombic symmetry within a single CuO$_2$ layer, but the global symmetry becomes orthorhombic due to the interlayer stacking. Thus, the single-layer twin boundaries are equivalent to antiphase boundaries (APB) of the 3D structure, Fig. 49b. A careful TEM study of the LTT-LTO transition showed that the LTT APB’s readily transform into APB’s and twin boundaries of the LTO phase by a simple O tilting, without changing their locations. Thus, the microtwinning, which is typically observed in doped LSCO, may be a direct manifestation of the dynamic JT effect. In another TEM study of the LTT phase, Zhu, et al. find a domain pattern which they interpret in a similar fashion, Fig. 49i.

Bianconi and Missori have applied a variant of the above model to explain their EXAFS observations in Bi-2212. They find two in-plane Cu-O bond lengths, and assume that the longer one is associated with LTT domains. From the relative fraction of long bonds, they estimate the LTT fraction, and by assuming that these domains give rise to the incommensurate modulation in Bi-2212, they can reconstruct the striped phase ‘polaronic CDW’, Fig. 49j. Similar EXAFS data have now
been reported \cite{440} for LSCO ($x = 0.15$) and again interpreted in terms of alternating LTO and LTT stripes. Bianconi further assumes that the LTO stripes contain all the doped holes. I would have expected the opposite: that the LTO stripes are the remnant of the undoped AFM phase at half filling, while holes are added to the LTT stripes. In LSCO, the LTT domains correspond to $\approx 32\%$ of the stripes, suggesting that the hole doping in the LTT stripes is $0.15/0.32 \approx 50\%$. This seems rather high. If, however, the domains are dynamic, the LTT percentage could be underestimated. Thus, if the tilting octahedra have long bonds only about half of the time, the LTT domains would be $\sim 64\%$ of the population, with $\sim 25\%$ hole doping.

### 8. Low-Frequency Modes

The possibility should, of course, not be overlooked that these dynamical Jahn-Teller oscillations, being very low frequency, could themselves be playing an important role in the superconductive pairing. Indeed, as early as 1946, Teller suggested that the dynamic JT effect could be responsible for ordinary superconductivity \cite{16}. Hardy and Flocken \cite{162} showed that, if octahedral tilting leads to a double well, electron-phonon coupling with such a double well could greatly enhance $\lambda$ due to anharmonic effects. Variants of this double well model have often been applied to the cuprates; usually, however, one assumes that the double well is associated with the apical oxygen $\lambda \sim 0.25$. Similar dynamic Jahn-Teller effects have been predicted in the Buckyball superconductors \cite{464}, and the anomalous properties of ‘Berrynic matter’ are just beginning to be explored \cite{465,466}. These will be discussed further in Section XVII.C.

### D. Linear coupling to Stretch or Breathing Modes and Polaron
d

#### 1. Which Modes are Coupled?

As discussed in Section VIII.C.2, the strong doping dependence of the LTO transition temperature is due to the large variation of the oxygen ionic radius with valence. This variation is a manifestation of a strong linear electron-phonon coupling to those phonons which modulate the Cu-O bond length. A number of in-plane phonon modes can be involved, most importantly the O-O and Cu-Cu stretching modes, Figs. 44a and b. The O-O stretch modes are particularly strongly coupled, because they split the VHS degeneracy, and can open a full gap at the Fermi level, Fig. 44c. However, at half filling, correlation effects weaken coupling to the O’s, so spin-Peierls coupling mainly involves the Cu-Cu stretch mode. This latter mode does not split the VHS degeneracy (due to matrix element effects), but does open up a conventional nesting gap over the rest of the Fermi surface, Fig. 44c.

Understanding which modes dominate the linear coupling is still an unresolved question. One problem is that the electron-phonon interaction depends not only on the phonon mode, but also on the nature of the coupling (Appendix C). For instance, the above analysis assumes that the coupling arises through the phonon modulation of the Cu-O separation, which leads to a modulation of the hopping parameter $t$. In this case, when the calculation assumes coupled O-O stretch modes along both $X$ and $Y$, the coupling produces two modes: a breathing mode, where one Cu has 4 short O bonds, and the other 4 long bonds, and a quadrupole mode, where each Cu has two long and two short bonds, but for one sublattice the long bonds are along $X$, and for the other along $Y$. For $t$-modulation coupling, it is found that the gap of Fig. 44c is doubled for the breathing mode, and vanishes for the quadrupole mode – the coupling is to a charge modulation of the ‘effective Cu atom’, the Zhang-Rice hybridization of Cu with the symmetric combination of nearest-neighbor O’s. As discussed below, this appears to be the opposite of what is seen in neutron diffraction: the quadrupole mode has an anomalous softening, the breathing mode does not. This strong coupling to the quadrupole mode suggests that a different coupling mechanism is more important, but its particular form has not yet been determined. Perhaps a true molecular JT effect involving coupling to the Cu $d_{z^2}$ orbitals would work. A similar coupling has been proposed in the related La$_{1-x}$Sr$_x$MnO$_3$ compounds \cite{467}, Section XI.H.5; indeed, in the manganates, the charge-ordered phase is accompanied by a combined tilt-mode JT distortion $\lambda \sim 1$.

Why the breathing mode does not show strong softening remains a puzzle. Perhaps correlation effects are strong enough to suppress this $t$-modulation coupling. Nevertheless, a number of groups \cite{468,473} have recently found theoretical evidence for strong electron-phonon coupling to the breathing modes, leading to possible CDW or striped phase instabilities. Inhomogeneous Hartree-Fock calculations \cite{469} on small clusters find that Cu-O stretch modes can play an important role in modifying the one-hole state near the AFI at half filling. If the electron-phonon coupling to this mode is strong enough ($\lambda \sim 1$), the one hole state crosses over from a ferromagnetic polaron to a dielectric (spin-quenched) polaron. The latter state is closer to what is found experimentally in lightly-doped LSCO, Section XI.B.

#### 2. Experimental Evidence

Neutron diffraction studies \cite{476} find tantalizing evidence that the high-frequency O-O stretch modes soften...
anomalously in the doped cuprates, LSCO as well as YBCO, Figures [47] and [51]. These figures illustrate the dispersion of three O-O stretch modes of different symmetry. The breathing mode (Fig. 50a, top) is the highest $\Sigma_1$ modes in Figs. [50], c, and d, while the linear stretch mode (Fig. 51, bottom) is the highest $\Delta_1$ mode. The dispersion of the planar quadrupolar mode is illustrated in Fig. 51. No softening is found for the breathing mode in either LSCO (Fig. 50b) or YBCO (Fig. 50a) or in the related but non-superconducting compound La$_2$NiO$_4$. [While Fig. 50a] shows softening of the $\Sigma_1$ mode, the sample had poorly defined modes, and more recent work [176] at lower temperatures find that the $\Sigma_1$ mode has a dispersion very similar to that of the cuprates. Infrared studies by Ohbayashi, et al. [178] do find an anomalous decrease in the intensity of the breathing mode (around 670 cm$^{-1}$) when LSCO and LBCO are doped into the superconducting regime.

The planar quadrupolar mode should split the VHS degeneracy, although it appears that coupling to the Cu JT effect is necessary to open a gap (Appendix C). This mode was also predicted to be important in several other strong electron-phonon coupling theories which do not involve the VHS [47]. Figure 47 shows that this mode has an anomalous dispersion suggestive of a very strong softening for a wide variety of perovskites [178]. However, this mode does not have a strong doping dependence, and a similar softening is found in many non-superconducting perovskites. The lack of doping dependence may be more apparent than real due to mode coupling. As the mode frequency softens, it pushes down other phonon modes with which it couples until the ultimate instability is associated with the very low frequency tilt modes. Due to anticrossing phenomena, the planar quadrupolar branch may be pinned above the next lower branch, and the doping dependence appears mainly in the lower branches. Recently, Araji, et al. [47] have noted that at $T_c$ there are anomalous changes in the neutron scattering of a number of zone center and $(\pi/a, \pi/a)$ phonon modes, including the planar quadrupole and breathing modes, and they have suggested that there is a correlation between these high-energy phonons and the low-frequency buckling modes of the LTO distortion [48].

The really strong, doping-dependent softening is found for the planar O-O stretch mode, Fig. 51a, lower frame. Note that the softening is greatly enhanced in the doped material. In the same regions of $q$-space, there is considerable smearing of the phonon modes. In a recent study, the signal of the Cu-O stretching mode was lost near the $X$ (or $Y$) point, with its intensity shifted to lower frequencies [48]. The origin of this softening is unclear. Splitting of the VHS degeneracy requires a nesting along the diagonal coupling the two VHS’s, while a linear O-O stretch mode leads to nesting along $(\pi/a, 0)$. It has been suggested that these anomalies are associated with inter-VHS nesting of the bifurcated VHS’s [49]. However, bifurcated VHS’s are not found experimentally in YBCO and are not expected to arise in LSCO and LNO, which show equally strong mode softening. It is tempting to relate this mode softening to the domain structure associated with the striped phases. From the incommensurate neutron diffraction peaks, these stripes are aligned along $(\pi/a, 0)$ in LSCO. However, the stripes are tilted by 45° in LNO, and possibly also in YBCO, Fig. 47.

The importance of electron-phonon coupling in the Cu-O bond stretching modes at $q = 0$ (which are related to both Cu-Cu and O-O stretching) is revealed by optical studies of a series of related, perovskite-like structures, which show an anomalously strong dependence of this mode frequency on Cu-O bond length [48]. Neutron pair distribution function (PDF) analyses have been an important probe of local order in the cuprates. So far, however, most of the anomalous behavior has been found to be associated with c-axis displacements, and not in-plane motions. However, this may be because the planar motion is at a higher frequency – out of the energy window of previous PDF analyses; new experiments are planned [45]. Curiously, a low-frequency Cu-O stretch mode has been observed only in LSCO near $x \simeq 1/8$, where the material is close to the LTT instability which suppresses $T_c$ (the stretch mode was not observed at the higher doping $x = 0.15$) [48].

3. Polaron

A number of theories have suggested the importance of polaronic effects in the cuprates [48]. Moreover, these calculations naturally give rise to a polaronic renormalization of the electronic bandwidth which is pinned to the VHS (even when this falls away from the Fermi level). This could explain the experimental observation of extended VHS’s. Fig. 51b. To fit this extended VHS requires an electron-phonon coupling constant $\lambda \simeq 3$; this is in good agreement with the values found from analyzing the mid-infrared absorption band in LSCO as a polaronic band, $\lambda = 4.8$ (for $x=0.1$), and $\lambda = 2.4$ (for $x=0.15$) [48], while $\lambda \simeq 2$ is estimated from point-contact spectroscopy [48]. A similar renormalization of the VHS is found in a generalized Migdal-type diagrammatic approach to the Holstein-Hubbard model [49]. The flattening of the bands leads to a large enhancement of the electron-phonon coupling parameter $\lambda$. However, the narrow peak is rapidly washed out as $T$ increases, and it may be hard to observe any enhancement of $\lambda$ above $T_c$. A related result was found by Salkola, et al. [48]: in the presence of a charged striped phase of arbitrary origin, there will be a tendency to flatten the dispersion near a VHS since the energy gap structure has its largest effects where the dispersion is weakest – i.e. at a VHS. It will be interesting to analyze polaronic effects further within the Van Hove scenario to see, for instance, whether the polarons are large or small, or if there are bound bipolarons.
E. Phonons and Correlations

Correlation effects at half filling modify the nature of the electron-phonon coupling in the cuprates. Slave boson calculations find that for modes which involve modulation of the hopping parameter $t$, the coupling is renormalized to zero $[49, 139]$ since Cu-O hopping is itself suppressed. However, this conclusion is not consistent with the results of Anderson $[229]$ who found that correlations actually enhance nesting effects, and Eliashberg $[491]$ who finds that electron-phonon coupling can remain strong in the presence of strong correlation effects. Just as in a 1D system, coupling via a modulation of $t$ can be replaced by a coupling by a modulation of the exchange energy $J$, leading to a possible spin-Peierls transition. In the one-band Hubbard model, the two-dimensional spin-Peierls interaction was analyzed by Zhang and Prelovsek $[492]$ and by Tang and Hirsch $[493]$. They found that (1) in the very strong coupling limit, the spin-Peierls phase is suppressed by Néel ordering up to a critical electron-phonon coupling $\lambda_c \simeq 1.175$ $[492]$. Within the Van Hove scenario, the electron-phonon coupling parameter is expected to be $\lambda \geq \lambda_c$; therefore, even in this extreme limit a spin-Peierls transition should exist. (2) However, this strong coupling limit sets in only for $U \geq U_c \simeq 15t_{\text{Cu-O}}$ $[493]$, which is considerably larger than the on-site Coulomb repulsion $U$ in the cuprates. For $U \leq U_c$, the structural transition temperature is virtually unchanged from the $U=0$ Peierls transition. This behavior is very different from the one dimensional case, where correlations actually enhance the Peierls transition up to some $U_c$. Note moreover that the magnetic instability itself (flux or Néel phase) can split the VHS degeneracy, Section VII.B.2.

Thus, in the presence of strong correlations, there should be a striking crossover in the nature of the electron-phonon coupling $[113]$. In the doped material, the electron-phonon coupling is Peierls type due to modulation of $t_{\text{Cu-O}}$ with strong coupling to O-O bond stretching modes. Near half filling, the VHS can be split by the magnetic instability, and there can be an additional spin-Peierls coupling due to modulation of the exchange $J$, with strong coupling mainly to Cu-Cu stretching modes. Such a crossover arises naturally in the context of the three-band TJ models discussed above, which involve a spin ($J$ dominated) to charge ($t$ dominated) crossover as a function of doping. This crossover may have been seen experimentally in underdoped Bi-2212, Section IX.A.2.

There is one additional factor which can enhance electron-phonon coupling near a VHS. Grilli and Castellani $[494]$ have shown that correlation effects reduce electron-phonon coupling only when $\vec{q} \cdot \vec{v}_F$ (or more generally $(E_{F_k} - E_{F_{k-q}})/\hbar$) is $> \omega_q$. Near a VHS, the opposite limit holds since $v_F \to 0$, so that the bare coupling should be used. Note, however, that this applies to dynamical phonons. For a static structural distortion, the phonon frequency $\omega_q$ is renormalized to zero, and correlation corrections remain important.

F. Apical Oxygens

In addition to the tilting modes, there have been a number of reports in the cuprates of other structural anomalies, also associated with possible (dynamic) JT instabilities. Perhaps the most persistent candidate has been the apical O for which it has been suggested that the potential has a double well for motion perpendicular to the planes. This was originally suggested from EXAFS anomalies, including changes in Cu EXAFS at $T_c$ $[496]$.

However, frozen phonon calculations find no evidence for an apical O double well potential $[496, 497]$, neutron diffraction studies fail to observe the splitting of the apical oxygen position $[495, 182]$, and the Cu-O c-axis vibrations are much stiffer and display much less anharmonicity $[170]$ than would be expected from the proposed double well potential. In fact, neutron diffraction thermal factors for the apical O are much larger in-plane (associated with octahedral tilting) than along the c-axis (related to the proposed double well) $[495, 500]$. Alternative explanations for the EXAFS observations have been proposed in terms of either an experimental artifact $[501]$ or a phase separation $[502]$. In the latter picture, the apical oxygen acts as a source of holes for doping onto the CuO$_2$ planes, and the Cu – apical O bond length decreases with increasing hole doping of the planes (see the discussion in Müller $[503]$). In the presence of a nanoscale phase separation (Section X), there will be local domains of alternating high and low hole density. Hence, an EXAFS experiment will observe two different Cu – apical O lengths associated with the two types of domain, the shorter length correlated with the higher hole density. Recently, this picture has been confirmed; the 500cm$^{-1}$ phonon mode, associated with c-axis vibrations of the apical O, was observed to split in an O-doped LCO crystal with a clear macroscopic phase separation (staging) into hole rich and hole poor regions $[484]$. Neutron pair distribution function studies also find evidence for local (dynamic) phase separation in several of the cuprates with one domain characterized both by the planar O’s having an enhanced out-of-plane displacement, and by a reduced Cu-apical O distance $[484]$.

Brandow $[501]$ has suggested that the Cu-apical O distance $d_A$ modulates the Cu-planar O energy splitting $\Delta$; the smaller $d_A$, the smaller is $\Delta$. If so, this could be an additional role played by the apical O. Since $\Delta$ is close to the critical value needed for the Mott-Hubbard instability, small changes in $d_A$ could locally shuffle the planes between an insulating (long $d_A$) and a metallic (short $d_A$) state; this correlation is consistent with the PDF analyses $[484]$.
IX. ELECTRON-PHONON INTERACTION: EXPERIMENTS

The VHS-JT model makes a number of predictions concerning the structural phases, which have nothing to do directly with the superconductivity. Hence, experimental confirmation would be a strong support for the VHS model as a whole. Recent photoemission experiments directly relate the pseudogap to the magnitude of the VHS splitting, while other experiments provide highly suggestive evidence for local order in the lanthanum cuprates similar to that proposed for the dynamic JT state. The potential importance of these findings, coupled with the difficulty of probing short-range order, means that additional experiments would be most welcome. Confirmation of this aspect of the model would constitute a major predictive triumph of the VHS theory, and would confirm that the VHS is playing a crucial role in the low energy physics of the cuprates.

A. Pseudogap

1. Experimental Observations

The Van Hove – Jahn-Teller model predicts a competition between structural instability and superconductivity. However, the fundamental structural instability involves the onset of a tilting of the CuO₆ octahedra (in LSCO), which, as a dynamic JT effect, may involve only short-range order. An analogous situation is common in 1D conductors, where pseudogaps are often found (see p. 38 of Ref. [503]). Due to strong fluctuation effects, long-range order cannot exist in a 1D system. Hence there is typically a wide temperature range between the mean-field transition temperature $T_{MF}$ and the temperature of true 3D order $T_{3D}$, driven by weak interchain coupling. However, below $T_{MF}$, there are large fluctuations into the localized state, which are reflected in the dos, producing a pseudogap, Fig. 11. – the dos is strongly reduced, but does not equal zero until a true gap appears below $T_{3D}$. A similar situation arises in a 2D system, which again cannot display long-range order. Figure 41 illustrates a CDW-like pseudogap in the cuprates, while Fig. 11 shows a magnetic pseudogap – the strong similarity follows because this latter is calculated in the (weak coupling) SDW limit, which is virtually indistinguishable from the CDW theory.

In this subsection, I will discuss the experimental evidence for the tilting onset, with concomitant appearance of a pseudogap. Recently, a ‘pseudogap’ phase was found within the HTT phase of LSCO. At a temperature $T^*$, Fig. 23a, the susceptibility peaks and the anomalous temperature dependence of the Hall coefficient $R_H$ begins [504], in good agreement with prediction [209]. While there is no long-range order associated with $T^*$, there is a correlation with the LTO phase, in that, as the doping is varied, $T^* \sim 2T_{LTO}$.

A similar ‘pseudogap’ phase is found in YBCO, Figs. 2b and c: the magnetic susceptibility $\chi_Q$ peaks at a finite temperature [307] and then decreases at lower temperatures, as if a gap (the ‘pseudogap’) were opening up in the dos. This pseudogap is also observed in the dynamic structure factor [508], the resistivity [209], and the heat capacity [510], showing that this is not simply a magnetic effect, but is consistent with a dos change. Moreover, the magnetic susceptibility shows a pseudogap not only at the ‘antiferromagnetic’ wave vector $(\pi/a, \pi/a)$, but also at $\vec{q} = 0$ [511]. The pseudogap transition temperature is also correlated with the onset of the anomalous T-dependence of the Hall coefficient [512], just as in LSCO. It has also been suggested that there is an enhancement in the TEP below the pseudogap onset [513], but this claim has been disputed [514]. The similarity of the pseudogap in YBCO to that in LSCO has been emphasized by Batlogg, et al. [515]. Fig. 24. While there is no long-range structural phase transformation associated with the pseudogap, recent neutron diffraction data is suggestive of a local tilting instability [496], consistent with a dynamic JT model.

YBa$_2$Cu$_4$O$_8$ (Y-124) is underdoped, and similar in many of its properties to YBCO$_{6.67}$, but additional doping, provided by substituting Ca for Y can enhance $T_c$ to $\approx 92K$. It also shows evidence for a pseudogap in Knight shift measurements [516], spin-lattice relaxation times [510], and resistivity and Hall coefficient [517]. Neutron pair distribution functions [518] find local distortions of both planar, apical, and chain related O’s, which have the same temperature dependence as the pseudogap. When the hole doping in Y-124 is varied by cation substitution, the doping dependence of the pseudogap is found to be similar to that found in YBCO [519]. Whereas no elastic or heat capacity anomalies are found in pure YBa$_2$Cu$_4$O$_8$ near the pseudogap, in Ca substituted samples there are clear anomalies in both properties at 150K, strongly suggestive of a second-order phase transition (520,521). A curious feature of the resistivity in Y-124 is its anisotropy [517]: a clear pseudogap dip is observed below 160K, in good agreement with prediction [200]. The authors suggest that it is associated with enhanced c-axis coupling, which could shift the whole phase diagram to higher temperatures.

In YBCO and Y-124, the optical conductivity shows direct evidence for a pseudogap, both in the a,b plane [522,214] and along the c-axis [524,143]. For example, in optimally doped YBCO ($T_c = 93K$), the a-axis conductivity starts to decrease near $T_c$, as if a gap is opening up. At low T, $\sigma_a$ is close to zero for $\omega \lesssim 400 cm^{-1}$, and is depressed up to $\approx 1000 cm^{-1}$ (the b-axis behavior is similar, but complicated by the presence of an extra chain contribution). This was initially taken as evidence for
the superconducting gap, but it was found that as the oxygen content is reduced, the conductivity continues to decrease over the same frequency range, but the falloff begins at a higher temperature. Indeed, $\sigma_{\text{c}}$ has the same temperature and doping dependence as found from the NMR relaxation, $1/T_1 T$ — showing that the pseudogap couples to both spin and charge degrees of freedom. Furthermore, in both YBCO$_{0.7}$ and Y-124 at low frequencies, the c-axis conductivity $\sigma_{\text{c}}$ is also depressed with decreasing $T_c$, again closely following the T-dependence of the Knight shift. This pseudogap has a flat bottom out to 200cm$^{-1}$ in YBCO$_{0.7}$ (180cm$^{-1}$ in Y-124), independent of $T_c$, and the zone of depressed $\sigma$ persists out to about 400(350)cm$^{-1}$.

The normal state Raman spectrum of most cuprates shows evidence for a broad electronic continuum which can be understood in a marginal Fermi liquid picture. Cooling optimally doped materials below $T_c$ leads to the opening of what appears to be a gap at low frequencies, but with a substantial spectral weight persisting in the gap at low $T$, suggestive of d-wave pairing. Just as with the optical gap, this was initially interpreted as a superconducting gap, but was found to persist at higher temperatures in underdoped material. Thus, in YBCO, the gap terminates in a broad electronic peak which in $B_{1g}$ symmetry is centered near 500cm$^{-1}$ ($\approx$60meV). Even in optimally doped YBCO$_{1.02}$, the peak starts to appear about 40K above $T_c$,[22], while in underdoped materials, it begins to grow at even higher temperatures [24,27], suggesting that the peak corresponds not to the opening of a pseudogap above $T_c$.

Furthermore, the frequency shift of several infrared and Raman phonons, which begins at $T_c$ in optimally doped YBCO, actually starts at temperatures higher than $T_c$ in YBa$_2$Cu$_4$O$_8$ and oxygen-deficient YBCO, close to the (pseudogap) temperature at which the susceptibility peaks [28,29].

Most recently, neutron scattering revealed yet another feature which appears to give a sharp indication of the superconducting gap onset in YBCO. A broad, weak magnetic feature at $Q_0$ sharpens into a well-resolved peak near 41meV just below $T_c$.[34,36,28,29]. Perhaps not surprisingly, in Zn doped samples, this sharpening is found to occur at a higher temperature, even though the Zn suppresses $T_c$.[35].

The $T^*$ phase boundary can be estimated within the VHS-JT model as a function of doping [403], in this calculation, it was assumed that the VHS remained pinned to the Fermi level at all dopings. This was intended to approximate the effects of nanoscale phase separation. However, when strong correlation effects near half filling are included via the three-band $tJ$ model (Section VII.B), it is found that this condition is automatically satisfied, without assuming phase separation. There is a crossover from spin dominated to charge dominated response, with the VHS intersecting the Fermi level at two different dopings, and remaining very close at intermediate doping.

Accompanying this crossover, the electron-phonon coupling crosses over from spin-Peierls-like at half filling to ordinary Peierls-like (this is a mean field approximation to the dynamic JT phase) in the doped material. Since the nesting is better at half filling, the structural transition temperature is highest there, and superconductivity is suppressed. As doping increases, the nesting worsens, and the structural transition temperature decreases. At the same time, the superconducting transition is less sensitive to nesting, so that the $T_c$ increases until the two transitions meet at the VHS phase. The resulting calculations give a good description of Loram’s heat capacity data, Fig. 52, and also explain the fact that the superconducting $T_c$ increases as the LTO transition temperature decreases.

One further prediction relates the $T^*$ transition with the pseudogap onset in YBCO. Based on the Uemura plot, Figs. 27 and 28a, the doping at optimum $T_c$ is higher in YBCO ($\approx$ 0.25 hole per planar Cu) than in LSCO ($x \approx 0.16$). Within the VHS model, this suggests that the bare VHS is closer to half filling in LSCO, which in turn implies better nesting and hence a higher tilting instability onset temperature. This is what is found experimentally, and may explain why additional long-range ordering transitions are found in LSCO, but not in YBCO. Since the tilting instability competes with superconductivity, this may in turn explain why $T_c$ is so much lower in LSCO than in YBCO. (Note that this interpretation is not consistent with the alternative finding, Fig. 28b, that the optimal $T_c$ occurs at the same hole doping in both YBCO and LSCO.)

In Y-124, Zn doping is found to strongly suppress $T_c$, and to inhomogeneously fill in the gap states of the pseudogap, but without affecting the gap energy [35]. This seems to occur by a local suppression of the pseudogap, affecting primarily Cu’s which are nearest or next-nearest neighbors to a given Zn.

Clear evidence for a pseudogap is also found in Tl-2212 from a peak in the susceptibility. The variation of $T^*$ with O-doping is remarkably similar to that found in YBCO, even though O-doping does not give rise to long-range antiferromagnetic order. Similar effects are found in Bi-2212 [33].

2. Pseudogaps in Photoemission

While Fig. 1 shows that the VHS’s are close to the Fermi level in all the cuprates, the separation $E_F - E_{VHS}$ is rather larger than expected for the Van Hove scenario. In this subsection, I explore the possibility that the feature observed in photoemission as the VHS is actually a pseudogap-split VHS, as in Fig. 11. For instance, in NCCO, if $E_F - E_{VHS}$ is identified as $\Delta^*$ for the pseudogap, while the pseudogap transition temperature is estimated from Fig. 12b as that of LSCO for $x \rightarrow 0$, then $\Delta^* \approx 220$meV, $T^*_c \approx 1050 K$, and $2\Delta^*/k_B T^*_c \approx 4.9$.
A similar calculation for Y-124 yields $\Delta^* \approx 19\text{meV}$, $T^* \approx 120\text{K}$, and $2\Delta^*/k_BT^* \approx 3.7$. Both numbers are comparable to (but smaller than) the corresponding ratio for the superconducting transition.

It is not clear why a similar pseudogap is not seen in underdoped YBCO (Section VII.D.3). In underdoped Bi-2212, it is found that the separation $E_F - E_{VHS}$ systematically increases with underdoping [384,385,386] (Figs. 42a and b) as predicted by the VHS model of the pseudogap. Recent studies [385,386] have found two remarkable features: the splitting (or shifting) of the VHS increases monotonically with underdoping, while a true gap $\Delta^0$ (reduced photoemission intensity near the Fermi level) of $d$-wave symmetry is found in all samples below a pseudogap transition temperature $T^*$. The two features are clearly distinct; the maximum gap is $\approx 25\text{meV}$ [385,386], while the peak shifts by $> 200\text{meV}$ from the Fermi level [386].

Remarkably, $T^*$ scales with the VHS splitting, whereas the pseudogap features (gap energy and anisotropy) are virtually indistinguishable from sample to sample, and indeed coincide with the feature identified as the superconducting gap in optimally doped Bi-2212. Evidence that the pseudogap has $d$-wave symmetry has also been found in heat capacity [27] and NMR [35] studies. There are some differences in these studies; for several cuprates, NMR finds two $d$-wave gaps – a pseudogap which varies strongly with doping, and a superconducting gap with a zero temperature limit $\Delta^0(0) \approx 8T_{c,max}$ which is independent of doping (where $T_{c,max}$ is the maximum $T_c$ in a given compound, as a function of doping). This latter is similar to the second photoemission gap. On the other hand, heat capacity sees a single $d$-wave gap with its peak coincident with the VHS.

As illustrated in Fig. 12, the VHS splitting can be understood as the opening of a (possibly dynamic) gap, with a crossover from a structural gap near optimum doping (Figs. 12a and d) to a magnetic gap near half filling (Fig. 12b). The key feature is that, in the absence of a gap opening, the VHS would be pinned to the Fermi level over the full doping range from half filling to optimal doping, consistent with slave boson predictions (Fig. 33d). Note that if the photoemission peak at $X$ is associated with the onset of a gap, then there must be a corresponding pileup of DOS above $E_F$. This constitutes a strong prediction of the model, and I would greatly encourage any inverse photoemission or equivalent studies to search for such a feature. While angular resolution is not necessary for detecting the dos pileup, the theory makes very definite predictions about where in $k$-space this dos should reside. Much additional information can be extracted from direct photoemission studies about the nature of the pseudogap phase by a careful comparison of the $X$ vs $Y$ points of the Brillouin zone.

In principle, two different types of gap-opening are possible, which can be associated with the ‘Umklapp’ (Fig. 24) and the ‘Jahn-Teller’ (Fig. 12c) limits of the theory. The theory has been analyzed for the tetragonal phase, assuming a degeneracy of the $X$ and $Y$ point VHS’s in the absence of a structural distortion. In the ‘Umklapp’ limit, the degeneracy is maintained, but Umklapp coupling introduces equivalent gaps at both the $X$ and $Y$ points: this is the direct 2D analog of the usual 1D Peierls distortion. In the ‘Jahn-Teller’ limit the structural distortion splits the degeneracy of the two VHS’s, driving one below and the other above the Fermi level.

Such a splitting is expected for the orthorhombic distortion in YBCO, where the VHS is clearly seen along $Y$, but not along $X$. However, the magnitude of the splitting is not clear due to complications associated with the chain Fermi surface, which is expected to interact strongly with the plane Fermi surface near $X$. Such a splitting would be a clear signature of a JT-like effect. However, if the experiment averages over many domains (as in a dynamic JT effect), the photoemission would appear to be a superposition of the two Fermi surfaces, with $x$ and $y$ axes interchanged, thereby complicating the interpretation.

In the ‘Umklapp’ limit, there is a true gap [105] with the maximum gap (at $X$ or $Y$) equal to the VHS splitting, in agreement with the heat capacity data [32]. Note that the ‘Umklapp’ form of the dispersion due to O-O stretch modes (Fig. 42d) gives a good description of the experimental data (Figs. 42a and b) including the camelback curvature. As discussed in VIII.E, correlation effects are expected to lead to a striking crossover from charge-dominated behavior at optimum doping to spin-dominated behavior at half filling. This crossover was taken into account in the model calculation of the pseudogap, Fig. 12a, 105. Hence, it is gratifying to note that with increased underdoping the electronic dispersion, including VHS splitting, evolves smoothly into the form found in the AFM insulator, SCOC, Fig. 12a.

The interpretation of the other gap-like feature, $\Delta^0$, is much more problematic. The maximum gap falls at the same point of the Brillouin zone as the VHS splitting, but is much smaller, $\approx 25\text{meV}$, and doping independent. This gap does not appear to be associated with a conventional structural instability; the gap seems to open over the entire Fermi surface, which would require an exactly filled band below the gap – i.e., the gap must fall at exactly half filling of the band, which is not the case here.

I suggest two possible explanations. First, there could be a ‘dynamic JT’ gap: the static JT tilt does not produce a gap, but leads to a 4-fold degeneracy of the symmetry-broken state. Quantum tunneling between these states can lead to a dynamic restoration of the ground state symmetry – this is the dynamic JT effect. While in the molecular limit there should be a true gap [40], the nature of the broadening of this gap in the solid state is less clear. It is plausible to suppose that such a gap should be of $d$-wave symmetry; positive along $Y$ and negative along $X$, to preserve the JT distortion. This would explain why the gap is so much smaller than the VHS splitting.

Alternatively, if it turns out that there are really two $d$-wave gaps simultaneously present, one due to a pseud-
dogap and the other to superconductivity, an interpretation in terms of phase separation might be possible. (For a uniform system with two competing s-wave gaps, once the pseudogap wins out, the superconducting gap is reduced to zero \[505\].) For d-wave gaps, both could coexist, if the one had maxima where the other had minima; however, in the present case, both gaps seem to maximize near the location of the VHS's.) The fact that the zero-T superconducting gap remains constant \[534\], while \[505\] near the location of the VHS's.) The fact that the zero-

Moreover, within this RVB model, fluctuations were found to eliminate the pseudogap phase \[533\], and it was suggested that the pseudogap might be caused by interlayer coupling \[300\]. This was originally proposed in the nearly-antiferromagnetic Fermi liquid model of the cuprates \[539\]. The idea is that there are major differences in the magnetic properties of bilayer cuprates, such as YBCO, which have two CuO\(_2\) planes per unit cell, and single layer cuprates, such as LSCO. Some properties, such as the pseudogaps, would be associated with interlayer exchange coupling, and hence would be absent for single layer cuprates. However, this result is inconsistent with the experimental observation of the pseudogap in LSCO. Barzykin and Pines \[540\] have recently reanalyzed the experimental situation, and find that the pseudogap onset depends only on hole doping, and “bi-layer coupling plays little or no role in determining spin pseudogap and scaling behavior”. They find that the pseudogap onset can be found from a scaling argument in the nearly antiferromagnetic Fermi liquid model. Ioffe and Millis \[396\] have shown that the fluctuation problem can be overcome if the Fermi level is close to a VHS. In a weak-coupling calculation, the pseudogap is also found to be VHS-related \[541\]. On the other hand, Vilk \[542\] finds that the shadow bands cannot be understood as precursors to the AFM band.

3. Magnetic Models of the Pseudogap

a. General Considerations These pseudogaps have been alternatively interpreted in terms of a spin gap, arising within a purely magnetic model of the cuprates. A number of inequivalent magnetic calculations have been applied to this pseudogap, which are summarized in Ref. \[396\]. Thus, Kampf and Schrieffer \[367\] used a weak coupling SDW approach to model the effect of quasi-long-range AFM fluctuations, Fig. 11. In RVB-like, or gauge field calculations, a spin-charge separation is assumed, and it is found that there should be two independent transitions in mean-field, one at \(T_{BE}\) associated with Bose condensation of the holons and the other (\(T_D\)) with the appearance of a finite RVB order parameter on the spinons \[31,537\], Fig. 53. Only when both spinons and holons are condensed will there be a long-range superconducting order. The onset of the spinon pairing is taken as the pseudogap onset, \(T^*\). This onset is higher than the superconducting transition in the underdoped regime, and coincides with it in the overdoped regime. While this reproduces experimental observations in the underdoped regime, Tallon, et al. \[513\] find that the pseudogap temperature is clearly below the superconducting temperature in the overdoped regime, Fig. 52c; although other groups find a variety of behaviors; see the data of Hwang, et al. \[506\], Fig. 52a and of Chen \[512\], et al., Fig. 52 (the filled triangles are from overdoped samples). The frequency shift of the 340 cm\(^{-1}\) phonon also begins considerably below \(T_c\), in overdoped YBCO \[529\].

In all of this, there is one important caveat; if one adds a d-wave symmetry gap to a structureless, parabolic band, then the point of the maximum gap automatically becomes a saddle-point VHS! Hence, it is important to distinguish whether the VHS exists in the underlying band structure or not. Evidence for this was discussed in Section VI.C.1. Note that, to explain the pseudogap, the VHS must be pinned to the Fermi level over an extended doping range, as predicted in the presence of strong correlation effects.

b. Interpreting the Underdoped Cuprates It is instructive to see how the recent photoemission and heat capacity results on underdoped cuprates can be understood in the magnetic model. I claim that the data constrain the theory in two ways: (1) the pseudogap is driven by a splitting of the VHS degeneracy and (2) the experimental observations require VHS pinning, and therefore a nonzero \(t'\) in the one-band model. (In all of this discussion, I am concerned with the observation of the VHS splitting, which is the large energy in the problem; I do not understand the origin of the smaller \(\Delta^g\).)

In the VHS model \[105\], correlation effects renormalize \(t \to 0\) at half filling so the residual dispersion is magnetic, with perfect nesting (square Fermi surface). In this case, the pseudogap arises from a nesting instability, as in the flux phase or a spin-Peierls transition \[40\]. \[11\]. Fig. 52a. In contrast, the RVB model interprets the pseudogap as a Bose condensation of holons, which should have nothing to do with a Fermi surface. However, in their recent work, Wen and Lee \[11\] show that their gauge-field model is closely related to the flux phase, and hence produces the same VHS splitting, Fig. 42c.

Given this, the magnetic model becomes virtually in-
distinguishable from the present VHS model (based, e.g., on the 3-band tJ model) at half filling. However, the models diverge away from half filling. In particular, since the RVB calculations are based on a simple tJ or Hubbard model with electron-hole symmetry (t′ = 0), there is no pinning of the VHS to the Fermi level. Thus, with doping the Fermi level moves away from perfect nesting, and the gap will quickly close. Moreover, when the gap just closes, the VHS will be far away from the Fermi level. Thus, the model cannot explain the experimental results that the VHS is close to the Fermi level near optimum doping. To be definite, consider the results of Fig. 21 for LSCO: when the pseudogap just closes, for x ≈ 0.26, the VHS is at the Fermi level. We can compare this with the expected result for the tJ model. At this doping, the dispersion should be dominated by t. Assuming t = 0.125eV, then for x = 0.26 the VHS would be 70meV away from the Fermi level. This is clearly incompatible with observations. Hence point (2) above: to pin the VHS near the Fermi level requires a nonzero value of t′.

At this point, the magnetic model looks more and more like the VHS model. Indeed, the only possible difference lies in the role of phonons. The data that I have assembled in this section strongly suggest that phonon effects play a large role, particularly away from half filling. The remaining question is how large a role do magnetic effects play near optimal doping. Since the magnetic Fermi surface nests at half filling, magnetic effects would be expected to decrease rapidly with doping, and there is theoretical (Section VII.B.2, Refs. 383,384) and experimental (Section XLD, Fig. 60) evidence that this is the case. Moreover, Tranquada and coworkers 543,544 have shown very clear evidence for magnetic and charge-stripe phases in Nd substituted LSCO, and provided strong circumstantial evidence that the stripes exist as fluctuations in the Nd-free materials. The evidence is that the striped phases compete with superconductivity, with the magnetic and (presumably) charge ordering temperatures increasing with decreasing doping – just like the pseudogap temperature! Such a result does not follow naturally from the gauge-field models, but was indeed predicted in the VHS model, while such a magnetic-to-charge crossover has already been incorporated in the theory for the pseudogap 407.

While a magnetic model 407 can explain the anomalous susceptibility, it seems difficult in such a model to explain evidence for a simultaneous gap in the charge excitations 506,512 and the direct modifications in the phonons, unless there is (at the minimum) a strong spin-Peierls coupling 545. Hence, a model combining strong correlations and strong electron-phonon coupling is required – as in the Van Hove – Jahn-Teller model.

Finally, it should be noted that a similar pseudogap is found in the C60 superconductors 510. A phononic, nesting-related gap can be easily generalized to describe this case, whereas a magnetic gap seems improbable.

B. Short-range Order and the Dynamical JT Phase

Beyond the presence of a pseudogap, a number of recent experiments have provided highly suggestive evidence for local order in the lanthanum cuprates very similar to that proposed for the dynamic JT state. Thus, by studying La NMR, Hammel, et al. 547 have found that in La2CuO4+δ there is not a single, well-defined octahedral tilt angle in the LTO phase, but rather an extremely broad distribution, from essentially zero tilt up to some maximum value, Fig. 54. The experiments could not distinguish static from dynamic disorder, but are consistent with dynamically tilting octahedra. (The dynamic JT effect is likely to be sensitive to disorder, so that the local tilt angles may be pinned by impurities.) Comparable results are found in LSCO: the Cu NQR line width increases by a factor of ≈20 from its value in undoped La2CuO4 548.

Similar spectral broadening effects are found in studies of the e-axis polarized phonons in underdoped YBCO 549 and in Y-124 549. In YBCO6.6, the optical conductivity displays three sharp features at room temperature (Fig. 55) which are associated with an O(2)-O(3) plane bending vibration (315cm−1) and the apical O(4) vibration (570 and 610cm−1 – the mode is split in underdoped samples due to chain O vacancies). When cooled below 150K, these three peaks weaken, particularly the 315cm−1 mode, and are replaced by an extremely broad feature at ≈400cm−1. The inset shows the T-dependence of the intensity of the 400cm−1 feature. The curve has a point of inflection close to Tc. In Y-124, this feature seems to appear at a temperature (∼100K) significantly below the pseudogap onset near 180K. It must be kept in mind that these e-axis phonon anomalies are not universal in the cuprates – they are not found in optimally doped YBCO, nor in LSCO 142 or Bi-2212 550, but similar anomalies are found in Pb2Sr2Ru3O8 (R = rare earth) 551.

Billinge, Egami, and coworkers 552,553 have developed the technique of studying pair density functions (PDF’s) derived from neutron powder diffraction data as a means of probing details of local order in the cuprates. These PDF’s have supplied evidence for (possibly dynamic) local tilting in Tl-2212 554, LSCO 554, NCCO 552, and the infinity-phase compound, Ca0.85Sr0.15CuO4 555. Billinge, et al. 556, have used this technique to determine the local tilt of a single CuO6 octahedron in LBCO. They found that there was no change in the local tilt direction in crossing the LTT-LTO phase boundary (Fig. 56) – the tilt in both phases was found to be consistent with that expected for the LTT phase! Above the transition, the LTO order builds up over an extended cell of dimensions ≈ 10Å. These findings have since been confirmed by XAFS analysis in LSCO 557, and are in good agreement with the present dynamic JT model. Also, in measurements of the elastic moduli near the HTT-LTO transition, the critical fluctuations could only be under-
standing if there were deviations from pure $Bnab$ symmetry in the LTO phase, suggested to be associated with local deviations of the tilt axes from $[1,1,0]$ or $[1,\bar{1},0]$ directions [568]. PDF’s also find that the local symmetry in the HTT phase has finite octahedral tilts with random directions [554,555,484].

Electron diffraction experiments find similar results. In LBCO, $x = 0.125$, LT superlattice spots are found up to the LTO-LTT transition at 70K, but diffuse spots, associated with local LTT order, persist in the LTO phase almost up to the HTT phase boundary at 180K [560,561]. In La$_{1.875-\delta}$Sr$_{0.125}$CuO$_4$, long-range Pccn (or LTT) order is found for $0.2 \leq x \leq 0.4$ (the highest doping studied), but short range Pccn/LTT order was seen, as either diffuse spots or streaks, over the entire range $0 \leq x \leq 0.4$ and up to room temperature [562]. In this material, there is again a strong anticorrelation between Pccn/LTT order and superconductivity. Neutron diffraction studies of the HTT phase has finite octahedral tilts with random directions [558]. PDF’s also find that the local symmetry in the HTT phase has finite octahedral tilts with random directions [558].

C. Anomalies at $T_c$

Given the above picture of a dynamic JT effect competing with superconductivity for the VHS dos, it is hardly surprising that, when the superconducting transition occurs, the loss of dos would lead to striking modifications in the local structure – in particular, modifications of the local tilting structure. Thus, in the Bilbro-McMillan theory for A15 compounds [12], the onset of superconductivity freezes in, or even reduces the order parameter of the competing structural instability. A similar effect is predicted for the cuprates (Fig. 4 of Ref. [105]). There is considerable experimental evidence for such structural anomalies in the immediate vicinity of $T_c$, which will be briefly reviewed here.

These experiments do not necessarily imply that electron-phonon coupling plays a dominant role in superconductivity. Anomalies at $T_c$ are expected due to very general thermodynamic relations because the free energy in a superconductor depends on strain. Small anomalies are found in conventional superconductors, and these should be larger in the cuprates since they scale with $N(0)/\hbar\Delta$. Thus, when the superconducting gap opens, the linewidths of most phonons will be affected. If the phonon frequency $\hbar\omega_{ph}$ lies below the gap energy $\Delta$, the normal-state electron-phonon scattering will be cut off, and the phonon width will decrease. But, if $\hbar\omega_{ph} \geq \Delta$, there will be additional scattering associated with pair-breaking [471]. This change in scattering has been observed, and used to estimate the superconducting gap [572]. However, it does not require a very large electron-phonon coupling to explain these results, $\lambda \approx 0.6$ is adequate. (This result is based on analysis of c-axis polarized phonons, which may only have a quadratic electron-phonon coupling.)

On the other hand, some phonon anomalies observed at $T_c$ in the cuprates [573] are so large that they cannot be explained by conventional Eliashberg theory [574] unless nesting effects are included [575]. Alternatively, some of the following anomalies may be associated with the pseudogap, which generally falls at a temperature close to $T_c$ in optimally doped cuprates. Whether the superconducting or the pseudogap dominates can be determined by studying underdoped samples, where the two gaps are well separated.

A summary of these studies is as follows: (1) in most of the cuprates, there is a local, probably dynamic order, which is different from the average, long-range order. (2) This local order consists predominantly of deviations of the oxygen (those in the CuO$_2$ planes and those adjacent to these planes) from their equilibrium positions. (3) These planar oxygen motions are predominantly tilts and shears, which change local O-O distances while leaving Cu-O distances fairly constant. (4) At $T_c$, there is a sudden decrease of this local disorder. (Within the VHS model, superconductivity ‘eats’ part of the dos peak which was driving the dynamic JT effect.)
Evidence for these effects has been summarized by Egami and coworkers [585,574], and is briefly recapitulated here. PDF analysis finds evidence for dynamical tilting, which decreases at $T_c$ in Tl-2212 [553] and NCCO [577,552]. Electron diffraction studies in Tl-2223 find diffuse scattering that increases dramatically below $T_c$ [578]; the symmetry of the scattering is consistent with LTT-type tilts. There are also anomalies in thermal expansion coefficients, which may be associated with local structural distortions [577,580]. In LSCO, the anomalies in the (anisotropic) thermal expansion coefficients are consistent with a freezing in of the octahedral tilt below $T_c$, whereas above $T_c$ the tilt angle is changing significantly with temperature [580]. In O-doped La$_2$CuO$_{4+x}$, a shift of the La NQR frequency near $T_c$ has been interpreted as a sudden change of tilt angle [581]. A similar freezing in of local tilt disorder also appears to be found in YBCO; thermal expansion measurements find an anomaly in the orthorhombic strain, associated with freezing in of the orthorhombic deformation [582], while a similar freezing in is inferred from the temperature dependence of the Debye-Waller factors in a neutron diffraction study [498], and from changes in the Cu-Ba distances observed via EXAFS [601]. Indeed, in an untwinned single crystal, there is striking evidence that the orthorhombicity is greatly reduced immediately below $T_c$ [583]. Neutron diffraction measurements of the phonon density of states in LSCO [584] find an anomalous sharpening of the O-related peaks below $T_c$, as if a dynamic fluctuation were quenched; Zn doping is found to have the same effect as increasing $T$. Related effects are found in YBa$_2$Cu$_4$O$_8$ and YBa$_2$Cu$_{3.5}$O$_{7.5}$ [580], where the $b$-axis length becomes $T$-independent below $T_c$. Finally, Arai, et al. [181], in an inelastic neutron scattering study of YBCO, found evidence for a local $<110>$-type buckling distortion, with a dynamic correlation length which diverges at $T_c$; similar anomalies are found in LSCO [480].

Some ion channeling studies [587] find a sudden increase in ordering below the superconducting transition in YBCO and Bi-2212, associated predominantly with a,b-plane vibrations of Cu’s and apical O’s; in an O-deficient sample, the anomalies were absent [588]. However, while a second group also reported channeling anomalies [589], the two studies are not mutually consistent. A more recent study on films found no evidence for channeling anomalies [590]. Clearly, more work is required to resolve this issue.

An intriguing possibility arises from a study of the c-axis optical conductivity of LSCO [591], below $T_c$, a sharp plasma edge appears, which is associated with superconducting carriers. That is, since the c-axis plasma frequency is smaller than the superconducting gap, the reflectivity is controlled by the former. For present purposes, the relevant point is that the observation of the plasma frequency signals a coherent c-axis charge transport which is absent above $T_c$. Such normal-state incoherent c-axis transport was predicted in connection with spin-charge separation models [140]. Within the present model, this could be associated either with nanoscale phase separation or with the dynamic JT effect. If this is purely 2D, then the tilts in different layers will be uncorrelated, preventing coherent c-axis hopping. At $T_c$, the tilting is frozen out, and coherent c-axis transport appears. Alternatively, if the holes are confined to domain walls, Coulomb repulsion will cause walls in different layers to avoid one another, leading to a very incoherent c-axis transport.

Mössbauer studies [592] of YBa$_2$Cu$_3$O$_8$ find motional narrowing of the nuclear resonance above $T_c$ due to dynamically fluctuating EFG’s, associated with vibrations of the planar and apical O’s. Below $T_c$ there is significant line broadening associated with greatly reduced fluctuations. This is in striking agreement with the present model of dynamic JT fluctuations, which are partially quenched below $T_c$. It may also provide an explanation for a puzzling feature of EFG measurements in the cuprates. The asymmetry parameter $\eta$ should be proportional to the orthorhombic splitting in the LTO phase; instead NQR measurements find an anomalously small $\eta \approx 0$ [590,594]. This result would be consistent with motional narrowing. Below $T_c$, an excitation energy of 9.3meV is found; this is comparable to the inter-(LTT)-well excitation energy $\approx 15$meV calculated by Pickett, et al. [604] for octahedral tilts in LBCO.

In Bi-2212, Mook, et al. [573] used neutron resonance absorption spectroscopy (NRAS) to measure the average kinetic energy of the Cu related to the phonon density of states. They found a significant softening just above $T_c$ of the O-related peaks below $T_c$, and it is assumed that the DOS is given by a 2D density of states in the same temperature range for both Cu and O modes [590]. Below $T_c$, the oxygen breathing modes are broadened over a large range of $q$ space near $(\pi/a,\pi/a)$ [498], suggestive of strong electron-phonon coupling, perhaps enhanced by nesting effects [597]. No anomalous NRAS softening was found for Cu in YBCO [588] (although, due to the presence of chain sites, the expected change is close to the limits of resolution of the measurement); below $\approx 100$K, the Cu kinetic energy stopped changing with $T$, similar to Bi-2212. A similar softening occurs here of the elastic constant $(C_{11} - C_{12})/2$ - is found in LSCO $(x \approx 0.14)$, which is replaced by a mode hardening below $T_c$ [599]. The symmetry of the softening is consistent with an incipient LTT or Pccn phase. The superconducting $T_c$ was reduced by an external magnetic field, and it was found that the mode softening persisted to $T_c(B)$, Fig. 57. The solid line is fit to the theoretical expression

$$\Delta (C_{11} - C_{12})/2 = -2d^2 \int_0^\infty N(E)(-\partial f(E)/\partial E) dE,$$

where $d$ is the deformation potential, $\Delta E_k = 2d(\epsilon_{xx} - \epsilon_{yy})$, and it is assumed that the DOS is given by a 2D VHS. This anomaly is much larger, and begins at a higher
temperature (≈50K) in optimally doped LSCO than in either underdoped ($x=0.09$) or overdoped ($x=0.19$) material [276]. The magnitude of the effect is much larger than in conventional superconductors, but that is expected since $\Delta C_{\text{p}}/C_{\text{p}} \propto (\Delta(0)/E_F)^2$. What is unconventional is the sign of the effect; for conventional superconductors, the lattice usually softens below $T_c$ [276]. As we have seen, the stiffening can be a signature of a competing structural instability. A similar hardening is found in $Y_{0.9}$Cu$_{0.1}$Ba$_2$Cu$_4$O$_8$; however, it is displaced about 10° below $T_c$ and resembles a first-order transition [607].

Measurements of the elastic properties of the cuprates find a large number of anomalous changes in sound velocities and attenuation peaks, but there is tremendous variability in the results of different groups. In polycrystalline samples, the results may depend on grain size or on void fraction. Recent reviews [558,602–604] have concluded that there is considerable evidence for a structural instability a few degrees above $T_c$ in both the La- and the Y-cuprates. For some elastic constant studies [578,605], there appears to be an anomaly at a temperature corresponding to the optimum $T_c$ for LSCO, extending over a wide composition range, including insulating samples. The form of the anomaly – a minimum in the sound velocity – is suggestive of a low-frequency relaxation process, such as domain wall motion [607]. A resistive anomaly is found in the same regime (≈37K) in overdoped LSCO [276]. Similar anomalies are reported above $T_c$ at 95K in LSCO ($x=0.2$) and at 120K in YBCO [606]. In high-resolution dilatometry studies of twinned and untwinned LSCO crystals, instabilities in the range 40-60K (not reproducible in detail) were found in the twinned samples only, reinforcing the suggestion that these features are ‘related to the relaxation of twin-induced internal stresses’ [276]. The Cu NQR frequency also displays an anomaly at $T_c$, suggestive of a structural modification [607,608,610]; however, such anomalies are found in conventional superconductors [607], although their origin is not understood.

Besides the evidence for a structural anomaly just above $T_c$, additional information can be gleaned from a study of the discontinuities in elastic parameters at $T_c$. Millis and Rabe [609] provided a detailed analysis of the experimental data as of 1988 – unfortunately mostly on polycrystals. They found that, whereas the first strain derivatives of $T_c$ were comparable to those of conventional superconductors, some second derivatives are anomalously large. They suggest that $T_c$ is extremely sensitive to some form of shear distortion, which by symmetry cannot couple to $T_c$ in first order. An analogous case occurs in $V_3$Si, where superconductivity couples to a CDW which reduces the lattice symmetry from cubic to tetragonal. In the cuprates, this mechanism could also work, but only if “the transition is ... not the observed orthorhombic-tetragonal transition but instead a potential transition to a still lower symmetry phase, which is inhibited by the presence of the superconductivity” [609].

In light of the evidence that, at optimum $T_c$, the pseudogap and superconducting transitions virtually coincide, it is important to analyze the data on local structural anomalies away from optimum doping to see which of the two transitions they are associated with.

D. Anomalies at $T_N$

In the VHS model for the pseudogap, it is suggested that near half filling the pseudogap and LTO transitions are of a spin-Peierls nature, involving a modulation of the exchange coupling $J$ [118]. In this case, it might be expected that there should be some structural anomalies at the Néel transition. There appears to be some experimental evidence for such anomalies. Thus in LSCO:Gd, Rettori, et al. [611] used Gd EPR to detect the local magnetic field near the Néel transition. For a quantitative fit to the field dependence, they were required to assume that, below $T_N$ there is either a lattice distortion or a Heisenberg-type interaction between the Cu and Gd spins. In $La_2CuO_4+\delta$, there are enormous transport anomalies near $T_N$ at small $\delta$, which show prominent hysteresis and are correlated with thermal expansion anomalies [611]; however, these anomalies are probably associated with phase separation, and not with the Néel transition. Clear phonon softening at the Néel transition is also found in the related compound CuO [612].

E. Transitions off of the CuO$_2$ Planes

1. VHS Related

As described in Section VIII, the VHS-JT model is considerably more flexible than the conventional CDW model in that a large number of phonon modes – any mode which splits the VHS degeneracy – could be involved. In this subsection, I briefly note that the cuprates often display structural instabilities involving atomic displacements completely off of the CuO$_2$ planes, often involving quite complex (incommensurate) distortions, and yet these distortions also split the VHS degeneracy. Thus for instance, in YBCO, the chain ordering splits the degeneracy of the $X$ and $Y$ point VHS’s. In $Tl-1201$ and $Tl-1212$, the structural distortions have been analyzed in detail [613]. The O-atoms show a very large displacement from their nominal positions, and this distortion breaks the symmetry of the two in-(CuO$_2$)-plane O’s, thereby lifting the VHS degeneracy. However, these off-CuO$_2$ plane distortions do not show any sudden changes at $T_c$, as opposed to the in-plane (dynamic) distortions [184]. Since Bi-2212 has a different symmetry from LSCO, it may be that the orthorhombic distortion splits the VHS degeneracy – certainly the ‘shadow Fermi surfaces’ seen in photoemission [25] are exactly those which would be produced by VHS nesting.
These distortions can have two different roles in VHS theory: (1) it is possible that the transitions are driven by the VHS instability; (2) they could have independent origins, but by splitting the VHS degeneracy, they could weaken CDW-like instabilities of the CuO$_2$ planes which compete with superconductivity.

In a related vein, Phillips [194] has suggested that defects off of the CuO$_2$ planes can act collectively to enhance the strength of a dos peak associated with the VHS.

2. CDW’s on the Chains

In assessing the importance of electron-phonon interaction in the cuprates, it is important to not overlook the clues offered by the CuO chains in YBCO. There are certainly many differences: the chains are far from half filled, so correlation effects are weaker; the chains are nearly 1D, so the theory should be easier; the chains are very sensitive to oxygen disorder. Moreover, it is only recently that the use of untwinned single crystals has allowed the unambiguous extraction of the chain contribution to transport. Hence, the signs that there are CDW’s on the chains are most intriguing, and should be followed up with further study. The most striking results are Edwards, et al.’s STM studies [614] of in-situ cleaved surfaces of YBCO. They found a modulation along the chains with wave vector close to the expected value of 2$k_F$ for the chains. They also found evidence of a $\approx 20$ meV energy gap; this seems to be more consistent with an induced superconducting gap (albeit rather large). Near an oxygen vacancy, the modulation amplitude increases, as if the CDW is pinned, but the gap is reduced. This would be expected for superconductivity since oxygen vacancies or disorder quench superconductivity. However, the question then arises as to why no CDW gap is seen. A neutron diffraction study [615] has now found evidence for incommensurate fluctuations with wave number consistent with the chain 2$k_F$.

In analyzing transport properties of untwinned YBCO, Fehrenbacher [610] assumed that the difference between the conductivities along the $b$ and $a$ axes could be identified with the chain conductivity, $\sigma_{cb}$. [One note of caution: the VHS dos peaks are associated with quasi-1D motion along the respective Cu-O-Cu links in the plane. Even if the chains were insulating, the conductivities along $a$ and $b$ could differ simply because the $X$ and $Y$ VHS’s can be shifted by different amounts from $E_F$.] He found that he could describe $\sigma_{cb}$ in terms of disorder scattering, but only by postulating an unreasonably large disorder. A much more satisfactory fit was found in terms of a strong polaronic coupling to the chain Cu-O stretch modes. Near half filling, he found evidence that the chains form incommensurate CDW’s with the charge motion associated with moving domain walls. The similarity of this picture with the model I have described for the planes is striking.

There has also been evidence that the chain O’s have a double-well potential with two minima displaced off of the chain axis in the $a$ direction [617]. This is consistent with frozen phonon calculations of Cohen, et al. [618], which find such a potential. It has been proposed that some low temperature phase transitions identified in elastic constant measurements could be related to ferroelectric or antiferroelectric ordering of these O’s [605,521]. However, inelastic neutron scattering finds no anomalous or anharmonic behavior associated with the chain zigzag mode [613,482]. Recent neutron pair-distribution function studies in Y-124 [518] have found evidence for ferroelectric domains associated with chain-O displacements on a scale of $\approx 10–20$. It was postulated that these domains were associated with polaronic effects of holes in the CuO$_2$ planes.

F. Other Evidence for Strong Electron-Phonon Coupling

In addition to the above experiments, which have a direct bearing on VHS theory, there are a number of other results which testify to the importance of electron-phonon coupling in the cuprates, but either do not single out a particular phonon mode, or are associated with modes which do not split the VHS degeneracy.

Tunneling studies are a traditional means of measuring electron-phonon coupling strength and, in fact, of determining the full spectrum of coupling in terms of Eliashberg’s $\alpha^2 F(\omega)$. While many studies have been carried out, the results of different groups – or even of the same group on different samples – are not always consistent. Rather than attempting to provide a detailed survey, I will here merely list some suggestive results. $\alpha^2 F$ has been measured for the low $T_c$ material, NCCO [521], and shown to predict the correct $T_c$ values. In BKBO, the results are mixed: Dynes, et al. [621] find coupling to a number of low frequency phonons (as small as 8meV), which cannot fully account for the experimental $T_c$. Similarly, in YBCO, Dynes, et al. [21] find coupling to a high-energy optical phonon, and are able to produce the correct $T_c$. Nevertheless, this measured $\alpha^2 F$ yields $\lambda \approx 2$, $T_c \approx 60K$, which means that electron-phonon coupling is by no means negligible! Finally, recent measurements on Bi-2212 have found a phonon coupling spectrum which leads to $T_c=87K$, $\Delta = 22meV$ [523]. Strong coupling is not restricted to any one mode, but is spread out over a large number of phonons, including a number of high frequency phonons – in particular, phonons at 57meV (axial apical O mode) and 72meV (Cu-O stretch mode). On the other hand, the direct contribution to $T_c$ of the
high frequency phonons is small. For example, eliminating the 57 (72) meV peak from the analysis reduces $T_c$ by only 6.6 (3.3) K.

Point-contact spectroscopy of YBCO also finds modulations associated with particular phonon frequencies [623]. The modulations are very selective; only certain phonons show strong coupling, generally those which show large frequency shifts at $T_c$ (i.e., at the pseudogap).

The $a,b$-plane optical conductivity of several of the cuprates shows a series of notches at frequencies corresponding to $c$-axis polarized longitudinal optical phonons [624]. This suggests that the phonons, associated with O stretching and bending, couple strongly to the electrons via some symmetry-breaking mechanism, perhaps associated with incipient CDW/SDW formation.

While the isotope effect on $T_c$ is very small in optimally-doped YBCO, there appears to be a large O isotope effect on the penetration depth, $\lambda$, due to an isotope effect on the effective mass, with $-d \ln(m^*)/d \ln(M_O) \approx -0.6$ [625]. This was interpreted as evidence for strong phonon anharmonicity and/or breakdown of the Migdal approximation (associated with polaron formation).

### X. PHASE SEPARATION

Phase separation is one of the most complicated and controversial issues in the study of the high-$T_c$ cuprates. There is thought to be a phase separation of the holes, which can be limited to very short range by Coulomb forces. Many experiments have now found evidence for phase separation in the cuprates, often on a very fine (nanoscopic) scale. Such a phase separation arises in a number of different theories involving strong correlations, including the VHS theory. Indeed, it has been hypothesized that phase separation and superconductivity are closely related phenomena [624, 1076]. This can be seen quite easily: the smallest scale possible for phase separation occurs when the hole-rich domain contains exactly two holes. But this can be thought of as a state of real-space pairing. If larger-scale phase separation is inhibited, and the pairs become mobile, then one can envision a Bose condensation of these pairs into a superconducting state. (While conceptually appealing, this is not what appears to happen in the cuprates, but nevertheless it motivates the proposed connection between phase separation and superconductivity.) For calculations on finite clusters, it is easier to detect evidence of phase separation, so the recommended procedure is to delineate the domain of phase separation, then look near this region for signatures of superconducting pair correlations [627].

Emery and Kivelson (EK) [628, 629] have shown that low-carrier-density superconductors, such as the cuprates, are generically sensitive to phase fluctuations, both classical and quantum. Classical phase fluctuations are governed by a phase fluctuation temperature $T_\theta^{\text{max}} \propto \hbar^2 n_s \xi/4m^*$, where $n_s$ is the superfluid density and $\xi$ a coherence length. Fluctuations of the phase of a superconductor become important when $T_c \approx T_\theta^{\text{max}}$, and are negligible when $T_c << T_\theta^{\text{max}}$. EK find that the latter condition holds for conventional, A15, and heavy Fermion superconductors, but that $T_c \approx T_\theta^{\text{max}}$ for the cuprates and some organics, with BKBO and the C$_{60}$ superconductors in an intermediate position. Quantum fluctuations [624], on the other hand, become important when the conductivity $\sigma(T_c) \leq \sigma_Q \equiv 4e^2/bc$, where $b$ is a microscopic length. Again, quantum fluctuations are negligible for conventional superconductors, $\sigma(T_c)/\sigma_Q >> 1$, but this ratio falls to \sim 10 in the optimally doped cuprates, and is smaller in the underdoped materials. If the ratio becomes less than one, superconductivity can be destroyed.

Despite the experimental evidence for phase separation, despite the many theoretical investigations, despite two international conferences [630] (with a third imminent), there is still considerable reluctance to seriously consider the role of phase separation in the cuprates. This is presumably because in these complex, multi-component systems, great care is needed to ensure that the materials are in thermodynamic equilibrium (phase separation could arise from incomplete mixing/oxygenation). In optimally-prepared samples, the ‘phase separation’ is usually restricted to such nanoscopic scales that it ceases to resemble the more familiar phase separation in other materials: thus, the superconducting transition temperature can change smoothly with doping, since the domain size is comparable to the coherence length. Further complicating the experimental detection, this nanoscale phase separation can be dynamic, so a particular probe can detect a homogeneous average if it averages over many fluctuation lifetimes. Moreover, particularly in the low doping regime, effects of phase separation can be confused with localization effects, particularly as the nanoscale domains can easily localize on potential fluctuations. In this and the following sections, I will provide a detailed summary of the evidence, both theoretical and experimental, for such a phase separation. In particular, there are circumstances in which more conventional, large-scale phase separation can occur. Table V summarizes the experiments I have found that provide evidence for such phase separation. At this point, one should begin to go beyond gathering such data, and attempt the harder task of showing that all experiments are consistent with this picture. As a first step in this direction, Section XI.J briefly summarizes experiments which are suggested to provide evidence against phase separation.

#### A. Phase Separation in the VHS Model

Hole phase separation arises in a number of theories. As the hole density is varied, the free energy is found to have a region of concave curvature (negative compress-
ibility), for which the state of uniform hole density is unstable. When doped into this region, the holes will tend to spontaneously phase separate into domains of low and high hole density, outside of the unstable range (the exact densities are found by a Maxwell construction). The various theories differ in the forces which act to stabilize the two end-phases, but once phase separation has occurred, all predict similar physics for the resulting domains, dominated by strong charging effects.

In the VHS model, it was found that one end-phase always lies exactly at the VHS, stabilized by strong electron-phonon coupling (see Section VIII.A). Essentially, this is due to the diverging compressibility near a VHS (Appendix A) manifested as a strong electron-phonon coupling. The Van Hove – Jahn-Teller effect, by splitting the DOS peak, lowers the free energy of the combined system of electrons and phonons, but only when the Fermi level coincides with the VHS! The free energy lowering has a $ln$ or $ln^2$ divergence, Eqs. 3 and 3. The associated free energy minimum leads to a remarkable state of affairs: while the hole doping precisely at the VHS is thermodynamically stable, both the underdoped and overdoped regime are unstable, and lead to a phase separation between the VHS phase and a second, stable phase with very different hole doping. On the underdoped side, the second phase is the antiferromagnetic insulator (AFI) with zero hole doping (half filled band); in the overdoped case, this phase appears to be a normal metal, but its exact nature is still unclear. (Bok has suggested that the superconducting condensation energy can stabilize the VHS phase. This may be possible, but would require very strong coupling, since phase separation starts near room temperature, far above $T_c$.)

A similar cusp-like minimum of the free energy can arise from either VHS nesting (Eq C9) or conventional nesting (Eq C3). Grilli and Castellani, et al also find that strong electron-phonon coupling can enhance the instability towards phase separation.

It should be noted that, within the Van Hove scenario, phase separation is an added complication: in the basic scenario, which most VHS theorists have followed, the idea of phase separation is not addressed. Even in the generalized Van Hove scenario, the occurrence or non occurrence of phase separation depends sensitively on material parameters (e.g., the low frequency dielectric constant). It does not seem to play an essential role in enhancing $T_c$, but rather competes with it. In short, if it exists, it can be understood (and was predicted) within the VHS model, but it is not a necessary consequence of the model.

### B. Nanoscale Phase Separation

Mott has pointed out that for a general metal-insulator transition, the number of free carriers should jump discontinuously at the transition. A consequence of this is that there should be a region of phase separation near the transition. Two special cases of this are the Mott-Hubbard transition near an AFI, and the CDW transition in BKBO/BPBO. Phase separation associated with doping away from an AFI phase at half filling was recognized prior to the discovery of high-temperature superconductivity. Nagaev’s book provides a detailed description of the nanoscopic nature of such a phase separation for a 3D AFI. More recently, Nagaev has reviewed phase separation in the cuprates on the basis of this model. Since the holes are trying to phase separate by bunching up, the resulting domains will not be electrically neutral unless the doping ions are sufficiently mobile so as to be able to follow the hole motion. In the extreme limit that these ions are unable to move (the Sr in LSCO seems to be a good approximation), the phase separation is purely associated with hole bunching, and Coulomb effects restrict the domain size to a scale of a few nanometers (the exact size depends sensitively on the value of the low-frequency dielectric constant and the level of doping). While Nagaev speaks of islands of the minority phase in a background of the majority phase, I have found that a lower energy state is associated with a phase in which the minority phase is segregated into grain boundaries between large domains of the majority phase. Such grain boundary phases have also been found in Hartree-Fock calculations of the doped Hubbard model. Fig. shows schematically how complicated the resulting phase diagram can become: Fig. shows the free energy vs doping for the bulk phases, suggesting a macroscopic phase separation. However, Coulomb repulsion arrests this macroscopic phase separation, stabilizing a variety of finite domain structures. 

#### 1. What’s in a Name?

In a sense, the phrase ‘phase separation on a nanoscopic scale’ is a contradiction in terms. These are single-phase materials that have the intrinsic property that the charge (or spin) is inhomogeneously distributed on a nanoscopic scale. Perhaps a more neutral phrase, such as ‘charge bunching phase’, would be preferable. However, at this point, our knowledge of the detailed structure of these phases is too vague, and moreover, there seems to be a continuum of states from the charge bunching limit to true macroscopic phase separation. Hence, I will continue to use the technically incorrect but striking phrase, nanoscopic phase separation.
Recently, it has become popular to designate these as CDW phases. I think this is also potentially misleading. While any charge bunching of the holes will of necessity be accompanied by local lattice distortions, I believe that underlying driving force (two preferred hole densities) is distinct from the driving force for conventional, Peierls-distortion-cum-CDW formation (Fermi surface nesting), and designating both phenomena by the same name will only lead to confusion – especially as both phenomena may be present in the cuprates.

2. Phase Separation vs. Localization

This nanoscale phase separation can easily be confused with localization effects. For instance, in LSCO, even if there were no tendency for either holes or Sr to phase segregate, there would still be a random distribution of Sr ions, with either single ions or small clusters. This random clustering will induce a random potential on the CuO$_2$ planes, which could lead to hole localization. Now if the localization potential is random, some holes will be strongly localized, others more weakly. Thus, while localization leads to an inhomogeneous distribution of holes on the CuO$_2$ planes, it also leads to a broad distribution of hole densities. The characteristic feature of nanoscale phase separation is that there are only two preferred hole densities, one high and one low (zero near the AFI), and all of the holes are distributed between these two types of sites. Of course, this is an idealized situation. If the size of the dense hole domains is truly nanoscopic, i.e., containing only a few holes, then finite size (including charging) and proximity effects will cause the equilibrium hole density to depend somewhat on domain size. Furthermore, such small domains will feel the background potential due to, e.g., Sr inhomogeneity, and can in turn become localized. Fortunately, it is possible to dope LCO by either Sr or Ba substitution or by excess oxygen. Because the interstitial O’s have a high mobility, the phase separation expands to a macroscopic scale. Despite this, many of the resulting phenomena, including superconductivity, depend only on the local hole density, independent of the doping method, providing strong evidence that they are dominated by the physics of hole bunching.

3. Phase Separation Realized as a Form of CDW

Recent cluster calculations, involving a variety of tJ and Hubbard models, but including a long-range Coulomb interaction [638], have found that the phase separation is replaced by a regime of CDW’s. Now, these CDW’s are not a phase separation in the conventional sense; the energy remains concave as a function of hole density, and the hole domains have a finite equilibrium width rather than diverging to infinity. However, these CDW’s are precisely a form of nanoscale phase separation, as illustrated in Fig. [59c]. Instead of the weak charge fluctuation typically associated with CDW’s (Fig. [59a]), these domains show maximal modulation, with all holes confined to one domain of the CDW, and the other domain remaining an AFI. This ‘phase-separating CDW’ bears some resemblance to the discommensurations introduced by McMillan [637]; Fig. [59b]; however, the usual discommensurations are controlled by the Peierls distortion which accompanies the CDW, while in the present case, it is the charge modulations which play the dominant role. For example, a common realization of discommensurations arises with atoms or molecules adsorbed onto or intercalated into graphite. In this case, the graphite planes provide preferred sites for the adsorbed/intercalated atoms to occupy, so there is a set of filling factors for which these atoms are exactly commensurate with the substrate. For other filling fractions, a uniform, periodic array of atoms would be incommensurate. However, the atoms can lower their energy by forming commensurate patches, with incommensurate domain walls in which the atomic density is either higher or lower, to accomodate the atomic excess or deficit. If the adsorbed or intercalated layer is charged, the electronic density will also be modulated, but the modulation is controlled by atomic commensurability effects. In the nickelates, a similar, but electronic mechanism seems to arise, Fig. [59], below: there are charge stripes in which every other or every third atom has an excess hole. In the cuprates, however, the charge bunching is believed to be a hole doping effect, due to the existence of one (or two) preferred hole densities, and not due to commensurability effects (most of the calculations do not consider the ions explicitly).

Variations in doping lead to changes in the periodicity and width of the hole-rich domains, with relatively small changes in the hole density in those domains. The distinction between these CDW’s and the conventional notion of CDW’s as weak modulations can be illustrated by a particular example discussed in Section XVII.B. In UPt$_3$, a CDW phase is found to be associated with two separate superconducting transitions. Based on the present view of CDW’s, we might have assumed that the two T$_c$’s were associated with the high and low density components of the CDW; instead, the CDW has been assumed to involve only a negligibly weak electronic density modulation, with its main role being to lower the lattice symmetry.

Despite this distinction between the electronic striped phases and conventional discommensuration-related CDW phenomena, the former will nonetheless involve a significant contribution from lattice distortions. First, within the VHS model, the phase separation is driven by the strong electron-phonon coupling, via Hume-Rothery effects (Section VIII.A). Secondly, on any model, Coulomb effects oppose the phase separation, and nanoscale phase separation is possible only if the Coulomb effects are sufficiently screened by the back-
ground dielectric constant. In the cuprates, the low frequency dielectric constant is quite large, due to strong phonon polarizibility. Hence, charged stripe formation will be accompanied by significant lattice relaxation.

It should be noted that in this nanoscale, CDW phase, the breakup into hole-rich and hole-poor domains is automatically accounted for, so $E(n)$ remains a concave function, and the compressibility is positive. Equivalently, the chemical potential $\mu$ is not flat (independent of hole density $n$). This is important, because the chemical potential has been measured, and the fact that it usually has no flat regions as a function of $n$ has been taken as evidence against phase separation. These results can readily be understood. The free energy is a local property. If the phase separated domains exist on a sufficiently nanoscopic scale, then a free energy which is an average over a local cell can be defined. If, on the other hand, the domains can grow to macroscopic size, then no local free energy can be defined, and a phase separation occurs to tie together the free energies of the two limiting phases. The calculations in the following subsection provide examples of such stripe or CDW phases; note in particular Castro Neto’s local phase separation regime ‘above the spinodal’.

4. Calculations of Nanoscale Phase Separation

Löw, et al. [637] developed a spin 1 Ising model to study the effect of Coulomb effects on retarding phase separation. They found clear evidence for nanoscale phase separation, into a complicated array of stripe and checkerboard phases. Again, the resulting domain structures have positive compressibility. The size of the individual domains depends on the strength of the Coulomb repulsion, i.e., on the background dielectric constant [638,642]. Chayes, et al. [640] have recently explored the competition between CDW order and superconductivity in such a model. Mehring and coworkers [641] have also applied Ising, as well as Ginsburg-Landau models to study the phase separation. The effect of Coulomb repulsion in arresting a phase separation at nanoscopic scales arises in many situations that have little to do with superconductivity. Some of these are discussed in Section XII. The numerical simulations [642,643] typically lead to stripe (~domain wall) or island phases. Castro Neto and Hone [644] modelled the stripe phase via a real space renormalization approach as an anisotropic nearest neighbor Heisenberg exchange model, and were able to reproduce the magnetic phase diagram of LSCO. Zaanen, et al. [644] studied the dynamics of a domain wall fluid, suggesting that this could describe the low frequency magnetic dynamics of the cuprates, and showing that there could be a crossover from a classical to a quantum fluid.

Castro Neto [644] showed that if the holes form a Fermi liquid, then the phase separation can be described in terms of Landau Fermi liquid theory. He found that even in the absence of long-range Coulomb effects, there is a regime of local-scale phase separation (charged stripes). The condition for long-range phase separation is the vanishing of the compressibility (the spinodal line), when the Landau parameter $F_0 < -1$, and he derived formulas for the rate of domain growth. Coulomb effects limit the domains to a finite size. The compressibility becomes wavenumber dependent,

\[
\kappa(q) = \frac{\kappa_0}{1 + F_0 + \frac{2\pi e^2 N(0)}{eq}},
\]

where $\kappa_0$ is the unrenormalized compressibility and $\epsilon$ is the background dielectric constant. Thus, phase separation is limited to sizes smaller than

\[
R \sim \frac{\epsilon[1 + F_0]}{e^2 m^*}.
\]

Note that near the Mott-Hubbard transition at half filling, $m^* \to \infty$ and $R$ takes its minimum size.

5. Phase Separation Realized via Staging

There is yet another way to introduce a modulated structure which allows the hole gas to separate into hole-rich and hole-poor domains: that is for the doping ions to form a 1D modulated structure in the direction perpendicular to the CuO$_2$ planes. A similar phenomenon has been thoroughly studied in graphite intercalation compounds (GIC’s) [647], where it is known as staging. Staging was initially reported for a related compound, La$_2$NiO$_{4+\delta}$ (LNO), when doped by excess oxygen [648], but has more recently been found in the cuprates [649,650]. Intercalation is a phenomenon in which the dopant atoms or molecules form intercalated layers, with a fairly uniform composition, between the layers of the host molecule (graphite, LNO). Increasing the level of doping corresponds to adding extra layers of intercalant. These layers repel one another, and tend to form with a regular spacing between layers. Staging is the name given to this phenomenon: the stage number is the number of host layers between successive intercalant layers – i.e., a stage 3 K-intercalated GIC has three layers of graphite separating every layer of potassium. Since the composition of the intercalant layer is (fairly) constant, a stage $n$ compound corresponds to a particular doping level. For doping levels intermediate between two stages, the extra intercalant can be incorporated in a number of different ways: by adjusting the intercalant density in a given layer, by inserting extra layers, either at random or in a regular pattern, or by phase separating into two regular staged regions [651].

For stage index $n \geq 3$, the hole doping is nonuniform, with the majority of holes concentrated on the layers adjacent to the intercalant layer [652]. Thus, if the holes have a natural tendency to phase separate, then staging
is another method for accommodating this phase separation on a nanoscopic level. In light of this, it is interesting to note that in both LNO and LCO, the lowest observed stage is 2; for \( n \geq 2 \), the hole density in the boundary layers is nearly independent of stage, whereas for stage 1, the hole density would nearly double.

In LCO, there is a well-defined transition to a phase-separated state, near room temperature. The nature of the high-T phase is not well understood, and it may be pertinent to recall the Daumas-Herold [653] model of staging in GIC's. They suggest that there is actually the same number of intercalant molecules in every layer, but below the phase separation temperature, these molecules phase separate into high and low density regions in each layer. Interlayer coupling then causes the formation of well-staged domains. Thus, the transition from a uniform to a well-staged compound (or an interstage transition, as extra intercalant is added) can take place without any molecules having to hop between layers. Note also that, within an individual layer, the phase separation is identical to the traditional view of phase separation in LCO: the special features associated with staging involve interlayer coupling only.

Since the intercalant tends to nestle into geometric depressions in the adjacent host layer, the host’s stacking sequence can change across an intercalant layer. Thus, for K in GIC, the K fits into the hole in the benzene-like rings of the graphite, so the K-layer changes the graphite stacking sequence from AB, where rings on consecutive layers do not line up, to AA, where they do; the intercalant forms ordered antiphase domain boundaries. The antiphase boundaries lead to additional spots in the diffraction pattern. Such antiphase boundaries are seen in LNO and LCO, and cause what is essentially a one-dimensional phenomenon to appear as a complex 3D ordering. Hence, much of the early work, which did not recognize the staging phenomenon, needs to be reinterpreted. Clearly, staging presents additional complications when the hole doping is achieved by simultaneously varying both \( x \) and \( \delta \); the resulting phases are independent functions of both \( P \) and \( \delta \).

It should be noted that in a layered material subject to nanoscale phase separation, Daumas-Herold domains should form even if the doping molecules are completely immobile. All that is required is that holes which bunch on one layer avoid bunched holes on an adjacent layer. Such interlayer screening will lower the cost in Coulomb energy for growth of the charged domains. It will also tend to confine the charges along the c-axis, since charges on one layer will tend to see an insulating phase on adjacent CuO\(_2\) layers.

C. Macroscopic Phase Separation

Phase separation also exists in an opposite limiting case, in which the doping counterions are mobile. The canonical example is La\(_2\)CuO\(_{4+\delta}\) (LCO), in which holes are introduced by adding excess oxygen. This oxygen occupies an interstitial site, and remains highly mobile at temperatures below room temperature. Hence, when the holes phase separate, the interstitial oxygen can follow. Since the two equilibrium phases are now electrically neutral, the resulting domains can now be macroscopic [654,655]. Experiments on oxygen-doped LCO will be further discussed in Section XI.A.1.

The experimentally observed contrast between Sr-doped and O-doped La\(_2\)CuO\(_4\) is striking. In the former case, the direct evidence for phase separation is weak and controversial; the domains are so small that \( T_c \) varies continuously with doping, due to proximity effects, while the Meissner fraction tracks \( T_c \) (at extremely low magnetic fields, proximity effects can lead to intergranular Josephson coupling, and the Meissner fraction is found to increase). In O-doped samples, however, there is clear two-phase coexistence, with one phase the AFI and the second phase a high-\( T_c \) superconductor; varying the O-doping, \( \delta \), only involves changing the relative fraction of the two phases. Yet despite these striking differences, the optimal superconducting phase is very similar, in both O-doped and Sr-doped material. This would amount to an incredible coincidence, if it had not been predicted by the Van Hove theory [656].

Double doping experiments (both Sr and O) provide further evidence of the essential universality of the superconducting phase [654]. For each \( x \) between 0.01-0.15, there is an oxygen doping \( \delta \) which produces a compound with \( T_c \approx 40K \). Iodometric titration studies find \( P = 0.16 \) at optimum \( T_c \), independent of \( x \) or \( \delta \) individually.

Most of the other cuprates can also be hole doped by insertion of highly mobile oxygen atoms in sites off of the CuO\(_2\) planes. These phenomena are generally considered independently in each material, but it is informative to consider them together; in particular, there is evidence for phase separation, or at least density-wave formation of the excess O’s in almost all the cuprates, and for most there is a connection with optimum \( T_c \). This evidence will be discussed in Section XI.A.1-4.

D. Other Models of Phase Separation

It should be noted that phase separation is also predicted in several different theories, totally unrelated to the Van Hove scenario; indeed there have been a number of international conferences to discuss phase separation in the cuprates [639]. All versions sound superficially similar, since the role of long-range Coulomb repulsion is essential in limiting the phase separation to a nanoscopic scale. The theories vary, however, in the driving force for the phase separation. These alternative theories mainly fall into two groups, depending on whether the driving force is magnetic, associated with doping away from the AFI [658,659,652], or electronic, associated with Cu-O
valence fluctuations [660]. In addition, Phillips [194] has a model in which the physics is dominated by defects off of the CuO₂ planes. This model also involves nanoscale phase separation, with superconducting islands and insulating boundaries, and his papers provide numerous additional examples of experiments which can be interpreted in terms of such a local phase separation.

1. Magnetic Models

One point must be kept clear from the start. Magnetic phase separation — that is, a phase separation which sets in when the material is doped away from a Mott-Hubbard insulating state at half filling — is present in the VHS model, and appears to be a very general feature of the Mott transition. Indeed, it was well-known in the 3D problem, long before cuprate superconductivity was discovered. However, in the VHS model, the underdoped material contains domains of the Mott-Hubbard and VHS phases, and the latter are crucial for superconductivity. By contrast, there are strictly magnetic models, where the nature of the conducting phase is not discussed, and superconductivity arises in the phase separated regime, from the presence of the nanoscale size, fluctuating domains. It is to this class of theory that I now turn.

The magnetic models are basically similar to the ferron phase discussed by Nagaev [634]. Here, a hole can delocalize over a finite domain by flipping the spins of the neighboring Cu’s, forming a small ferromagnetic island. A second hole can lower its energy by localizing on the same island. In principle, this looks like a real space pairing mechanism, but at higher doping levels, additional holes are found to be attracted to the same island, and the phenomenon is seen to be one of nanoscale phase separation. In the 3D materials that Nagaev studied, this phase is not clearly seen, because it competes with trapping on point impurities. In this case, the cuprates offer a better possibility for experimental realization, since the dopant ions are on a separate layer, so the Coulomb interactions are considerably weakened.

Since this magnetic phase separation is expected to be present in the pure tJ model, there has been considerable theoretical study of the conditions for its occurrence, recently reviewed by Dagotto [218]. It is clearly expected if the exchange is large, \( J/t > 1 \) [661], but the physical regime of smaller \( J \) remains controversial [662]. The majority of studies find that the phase separation is arrested at the smallest possible scale — individual pairs. Such single pair states could be interesting, but do not appear to be consistent with experimental findings. Phase separation close to half filling has been found in the large-N [663] and large-S [664] limits of the tJ model, and in Kondo lattice models [665].

Since the ferron islands constitute local regions which violate time reversal symmetry, they should have been found by the various probes for anyons, so it can be taken as experimentally determined that ferrons are not present in the cuprates. Interestingly, however, antiferromagnetic to ferromagnetic transitions are found in some other perovskites, notably \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) (Section XI.H.5), and Nagaev has suggested that the transition is a manifestation of the ferron phase [635]. Emery has stated that the hole-doped domains in his model [602] need not be magnetic, but no details have been published. In the VHS model, the state near half filling differs in that the hole-doped regions are non-magnetic metals at the VHS concentration.

Note that even if the purely magnetic model for phase separation should turn out to be correct, the fact of phase separation probably rules out many magnetic models for superconductivity, which are based on the properties of holes in a magnetic background, and assume a smooth evolution with doping within a homogeneous phase. It remains a possibility that the domain fluctuations themselves could play a role in Cooper pairing, as discussed below.

2. Valence Fluctuation Models

The origin of phase separation in the valence fluctuation model follows from the last term of Eq. 21. This term depends self-consistently on the renormalization, and hence can lead to an instability against phase separation when \( V \) exceeds a critical value \( V_c \approx 0.78eV \approx 1.1eV \) [532]. The phase separation should persist in the presence of long-range Coulomb effects, as long as there is some screening [660]. This value of \( V_c \) is somewhat larger than the value estimated from most LDA-type analyses, Table III. Moreover, Feiner, et al. [665] find that the use of more realistic models (\( U_H < \infty, U_P > 0 \)) further suppresses the tendency towards phase separation. Phase separation has also been found in an extended Hubbard model, in the weak coupling but \( d \to \infty \) limit (with \( d \) the dimensionality) [663]. The condition for the onset of the valence fluctuation instability can be shown [669] to coincide with the onset of the charge transfer instability [670], and hence phase separation precludes this latter possibility.

While these models can produce regions of nanoscale phase separation, I do not see how either theory can explain the phase diagram, with a very narrow region of single phase, and domains of phase separation for either under- or overdoping. In particular, in the valence fluctuation model, there is no reason for the underdoped phase to coincide with the AFI [602]. Caprara, DiCastro and Grilli [671, 662] have recently addressed this issue, and find that they can approximately reproduce the phase diagram by including both mechanisms — magnetic in the underdoped material, Cu-O charge transfer for overdoped, Fig. 41. Their model thus is becoming quite similar to the VHS model, although it still differs, in
that it is a purely electronic model for both phase separation and high $T_c$. While this is quite an interesting possibility, the model does not explain why the optimum superconductivity exists in such a narrow region between two phase separated regimes, and it is not clear how this model would explain such properties as the strong electron-phonon coupling or the presence of pseudogaps.

3. Fluctuation Driven Superconductivity

Within both models, the presence of two degenerate states has led to a proposal of a novel superconducting mechanism, based on the anomalous fixed point of the multi-channel Kondo model [672, 673]. While these models are interesting, they do not seem to be consistent with the experimentally observed phase separation in the cuprates. Thus, the fixed point is the point where the two phases are degenerate in energy, which should approximately correspond to the percolation crossover, where the two phases are in most intimate contact. On the other hand, superconductivity seems to optimize in a single-phase regime, where there are relatively few domains of the second phase. The existence of macroscopic phase separation (e.g., $\text{La}_2\text{CuO}_{4+\delta}$) is particularly hard to explain on these quantum fluctuation models.

XI. PHASE SEPARATION: EXPERIMENTS

There is considerable evidence for phase separation in the cuprates, which has been summarized in several reviews [14, 502, 674, 675], and has been extensively discussed in the proceedings of two international conferences [31]. Recently, Goodenough and Zhou [676] have reanalyzed the experimental situation, and find strong support for a double transition – two regimes of phase separation separated by a narrow pure phase which corresponds to the optimum $T_c$. They find this pure phase to be associated with ‘correlation polarons’, where both strong electron-phonon coupling and correlation effects play a significant role. This would appear to be a fair description of the dynamic JT phase.

In this section, I will attempt to give an overview of the variety of experimental evidence for phase separation in the cuprates. Table V summarizes the experimental observations, while the following subsections give brief descriptions of the individual cases. Figures 61-62, 64, 68-69, and 71 show the experimentally determined phase diagrams for a series of cuprates (LCO, LSCO, YBCO) and related compounds (LNO, LSNO, BKBO).

A. Underdoped Regime: Macroscopic Phase Separation

1. O-doping of $\text{La}_2\text{CuO}_{4+\delta}$

In $\text{La}_2\text{CuO}_{4+\delta}$, the interstitial oxygen phase separates below room temperature into O-rich domains of macroscopic size $\approx 1 \text{~mm}$. Jorgensen, et al. [677] estimated the domain size in a polycrystalline sample from the neutron diffraction linewidths; in all cases, the magnetic phase was found to be correlated over distances $> 5000 \text{Å}$, while in the metallic phase the domain size was $\approx 3000 \text{Å}$ ($> 5000 \text{Å}$) for a sample which was 30% (60%) metallic. For a single crystal, about 35% metallic, both phases had correlation lengths of $\approx 500 \text{Å}$ [678]. Ryder, et al. [679] carried out TEM studies of these materials, and found a striking herringbone pattern of domains; in their sample, the domain width varied from 300 – 1500 Å. A magnetic field dependence of the diamagnetic fraction is taken as evidence for the electronic nature of the phase separation [680].

The phase separation begins at about 300K, and is arrested around 200K, when the oxygen diffusion becomes too slow to stay in equilibrium [654, 655, 681, 680, 581]. As discussed in Section VI.B, there is some uncertainty about relating the O content $\delta$ to the hole doping, $P$, with different groups finding relations from $\delta = 2P$ [50, 157] to $\delta = P$ [157]. Here, we assume the intermediate result, Eq. 29. In addition, there seems to be some sample or preparation dependence of the phase separation: thus, while the present phase diagram suggests that phase separation is absent for a range of $\delta$’s near $\delta = 0$, phase separation was initially discovered through the observation of an infinitesimal superconducting fraction in nearly stoichiometric material, $\delta \approx 0.017$ (see Refs. [683, 680]). [Note: in early work, it was believed that the low-O phase corresponded to $\delta = 0$; by conservation of mass, this moved the O-rich phase boundary to $\delta = 0.08$, with $P = 28$ = 0.16 [677], the hole doping of optimal $T_c$. Newer work, both on the phase diagram and on the relation between $P$ and $\delta$, has led to the revised view discussed in the text.]

Recent neutron diffraction studies of electrochemically oxygenated LCO crystals find that the O-rich phase is organized into well-staged regions [649], similar to graphite intercalation compounds and LNO (discussed below). Stages from 2 (interstitial O’s between every other CuO$_2$ plane) to 6.6 (presumably an average over several layer spacings, 6, 7, etc.) were found. Each pure stage corresponds to a particular doping, $\delta$, and for intermediate doping regions, phase coexistence between several different stages (2, 3, 4) or between a stage $n$ and the undoped AFI phase were found. Wells, et al. [649] have surveyed the earlier literature, and suggest that most of the findings are consistent with staging, in which the weak superlattice spots were not observed. Similar staging has also been found in the two-phase coexistence regime $\delta \approx 0.015$ [50], with an onset near 250K, which displays some ($\approx 10K$) hysteresis. Most interestingly, at $\approx 220K$
the staged region itself undergoes a structural transition to a phase with superlattice order $\approx 70\text{Å}$ along the $a$-axis – perhaps a stripe phase of the Daumas-Herold domains.

By electrochemically oxygenating LCO, it is also possible to produce samples with $O$ doping higher than the miscibility gap ($\delta \approx 0.08 - 0.12$). These samples are found to be approximately single phase, but with large-period superlattices ($157,158,159,160,161,162$). For a given $\delta$, there can be several different superlattices ($160$). While the superlattice structures have not yet been worked out, they appear to involve modulated octahedral tilts ($157$) or regular shear planes ($158,159$). Much clearer superlattice effects are found in the analogous L$_{\delta}$NiO$_{4+\delta}$ compounds, discussed further below.

In electrochemically doped L$_2$CuO$_{4+\delta}$, there is a range of $\delta$ over which two superconducting phases coexist, with $T_c$'s of 32K and $\approx 40 - 45K$ ($157,158,159,160,161,162$). Grenier, et al. ($160$) suggested that these two phases correspond to $\delta = 1/16$ and $1/8$, respectively, while Johnston ($160$) finds the two-T$_c$ coexistence between 0.06 $\leq \delta \leq 0.11$, with a single $T_c \approx$43-45K for 0.11 $\leq \delta \leq 0.12$. There are strong quenching/annealing effects in this second two-phase coexistence regime ($158,160$), but not for $\delta = 0.11$ ($160$). The two superconducting phases have a characteristic difference in pressure dependence: for the 32K phase, $\partial T_c/\partial p$ is large and positive, while for the 43K phase, it is nearly zero ($159$).

The transition temperature of the higher-$T_c$ phase depends somewhat on the nature of the sample: 40K in a single crystal, 43-45K in polycrystalline powders, and 47K in thin films ($158$). Moreover, in the films, there is evidence for yet another, higher $T_c$ phase, this time with $T_c \approx 55-60K$ ($158$).

Recent experiments ($691,692$) have added yet another wrinkle, suggesting that electrochemical oxidation produces metastable phases, and that, for samples annealed at 110°C, the phase diagram looks very different, Fig. ($693$). The phase boundary of the lower two phase region extends to much lower $\delta$, 0.006 $\leq \delta \leq 0.047$ (note that $P = 2\delta$ is assumed). At room temperature, there is a second two-phase regime, for 0.075 $\leq \delta \leq 0.17$, between two orthorhombic phases, with the $\delta = 0.17$ phase having a large orthorhombicity, 0.019. (The phase at $\delta \approx 0.17$ is inferred by extrapolation; it has not proven possible to synthesize bulk LCO for $\delta > 0.12$.) At low temperatures, Meissner effect measurements suggest that this splits into two adjacent two-phase regions, 0.06 $\leq \delta \leq 0.085$ and 0.085 $\leq \delta \leq 0.12^+$. All three end-phases are superconducting, with the $\delta = 0.085$ having a reduced $T_c$, reminiscent of the LTT phase in LBCO, LSCO (in fact, $P$ is reported to be 0.125 for this phase, although how this was estimated is not stated). Since the x-ray analysis found no evidence for this extra phase, it is assumed to be due to an electronic phase separation.

There are two ways to experimentally study the crossover from macro- to nanoscopic phase separation: by quenching L$_2$CuO$_{4+\delta}$ or by double doping, L$_{2-x}$Sr$_x$CuO$_{4+\delta}$. By quenching L$_2$CuO$_{4+\delta}$ through the region of high O mobility ($158,159$), it is possible to reduce the domain size, approaching the domain of nanoscale phase separation. Thus, the superconducting fraction and $T_c$ both decrease with degree of quench, although $T_c$ seems to have a series of plateaus, near 40-45K, 32K, and 28K. These various $T_c$'s seem to be associated with different structural instabilities near the quench temperatures ($694$). In quenched polycrystalline samples, a Cu EPR signal is observed (although none is seen for a single crystal) ($694$). This signal is antiparallel with the superconducting signal, and was interpreted in terms of the formation of spin-polarized clusters. Similar results are reported for underdoped YBCO ($695$). In microwave absorption of L$_2$CuO$_{4+\delta}$, a dip is observed at zero applied field (called the low-field signal, LFS) ($674$). This signal is similar to that seen in granular superconductors, due to weak links between superconducting domains; consistent with this, it is found to vanish at $T_c$. The amplitude of the LFS is sensitive to cooling rates, being largest for a slow cool. Similar LFS are found in LSCO, but only in the metallic island regime ($x \geq 0.05$); the signal height is independent of cooling rate, suggesting that the islands form at temperatures higher than room temperature.

In double doping experiments, Sr doping is found to inhibit the O-related phase separation, with evidence for phase separation disappearing at $x = 0.03$ (interestingly, in the phase separated regime, $T_c$ is a strongly decreasing function of $x$) ($157$). For finite $x$, the low-$\delta$ phase is forced away from the AF1 phase at $P = 0$, and this is believed to destabilize the phase separated state.

In studying these phase separations, it will be important to develop new probes which are sensitive to the fine spatial scales and slow fluctuations. Thus, Mehring, et al. ($641$) studied the La nuclear spin-lattice relaxation rate in L$_2$CuO$_{4+\delta}$; they found that the ordinary longitudinal ($T_1^{-1}$) and transverse ($T_2^{-1}$) relaxation rates were insensitive to the phase separation onset, whereas a stimulated echo relaxation rate ($T_1^{*-1}$), specially chosen for sensitivity to slow fluctuations, had a strong peak at 230K, the onset of phase separation. (On the other hand, Hammel, et al. ($190$) found a large peak in ($T_1T$)$^{-1}$.)
between two types of domain \[298\], by assuming that \(T_c\) is 58K in the ideal Ortho II phase, and 93K in ideal Ortho I, and that charge transfer takes place only from domains which exceed a minimal size. The same model \[89\] can also explain the room-temperature annealing studies \[700\] as due to a gradual growth of the ordered domains. At exactly \(\delta = 0.5\), the Ortho II phase transition occurs at 398K, Fig. 62; however, domain growth is logarithmically slow, due to random field effects \[701\].

A number of experiments now find that, as the O-doping is varied, YBCO is composed of microscopic islands of three compositions, corresponding to the under-doped (\(\delta = 1\)) AFI phase, the Ortho II phase, at \(\delta = 0.5\), and the Ortho I, at \(\delta = 0\). This is seen in the splitting of crystalline-electric-field (CEF) transitions, when a few percent of a rare earth is substituted for the Y \[702, 703\], or from Tm NMR in TmBCO \[704\], and in the resonance Raman spectrum of a YBCO\(_{6.4}\) crystal \[705\]. Two anharmonic relaxation peaks (labelled PH1, PH2) have been hypothesized to be associated with Ortho II or Ortho I domains \[603\], and a plot of their intensity vs \(\delta\) yields a similar distribution plot.

However, electron microscopic studies have also reported a number of other intermediate phases. One of these, the Ortho III phase, has now been confirmed by neutron diffraction to exist at \(\delta \approx 0.23\), for \(T \leq 375K\) \[700\]. Figure 26 shows a theoretical \[707\] phase diagram of YBCO, along with phase boundaries determined by electron diffraction \[708\].

Inelastic neutron scattering studies \[55\] find, in addition to the pseudogap onset at high temperatures, a true gap in the spin response spectrum: the imaginary part of the susceptibility, \(\chi(q, \omega)\), vanishes for \(\omega \leq E_g\). This gap seems to be related to superconductivity, in that \(E_g\) is found to be proportional to \(T_c\) (see Ref. \[709\]). However, the constant of proportionality changes with doping, being 3.5 in the mixed Ortho I – Ortho II regime, and only 1 in the Tetragon – Ortho II regime (\(T_c \leq 60K\)). This suggests that the antiferromagnetic domain walls in the latter case act as pairbreakers.

While this O phase separation is usually analyzed completely in terms of ionic (O-O repulsion) effects, hole bunching could also provide the driving force, and it may be that the two effects are complementary. Thus, at YBCO\(_{6.5}\), with every other chain fully occupied, adding more O (here, reducing \(\delta\)) leads to exactly the same phase separation as in La\(_2\)CuO\(_{4+\delta}\), except that the excess O’s are restricted to sites on the non-fully occupied chains. The annealing studies suggest that the O loses mobility in about the same temperature range in YBCO \[700\] as in La\(_2\)CuO\(_{4+\delta}\). Bekker, et al \[702\] concluded that in the Ortho II phase there are hole chains in the CuO\(_2\) planes running parallel to the occupied chains, as in a CDW, and this is consistent with the fact that the Meissner fraction is substantially lower in the Ortho II phase than in the Ortho I \[707, 711\].

Recent experiments in Ca or La substituted \(Y_{1-x}A_xBa_2Cu_3O_{7-\delta}\) (\(A = Ca, La\)) have found a very striking confirmation of this idea, Fig. 26 \[206\]. It is found that the 70K plateau is present for each value of \(x\) (as \(\delta\) is varied), but the plateau falls at a fixed hole doping \(P \approx 0.12\), and not at a fixed value of \(\delta\)!. It should be noted that this doping is approximately the same as the \(\approx 1/8\) doping where \(T_c\) is suppressed in LSCO and LBCO (Section XIII); indeed, in the plot of \(T_c\) vs \(x\) for LSCO, the dip at 1/8 makes the curve (Fig 24) look very similar to those in Fig. 63.

Further evidence that hole phase separation is important is the finding that YBCO\(_7\) is overdoped \[712\], and shows evidence for phase separation (Section XI.F). Such behavior would be unthinkable if the phase separation is due to O-ordering, but is expected in a VHS model, since there is no reason for the VHS to fall exactly at \(\delta = 0\).

Hence, it is plausible to assume that the Ortho II phase is also driven by hole phase separation, perhaps a stripe CDW phase similar to those found in La\(_2-x\)Sr\(_x\)NiO\(_4\) (discussed below). The chain ordering would then be the associated Peierls distortion stabilized at \(\delta \approx 0.5\) by commensurability effects. Franck \[255\] has suggested an alternative possibility, that the Ortho II phase is associated with a second VHS. He finds that the Cu isotope effect becomes vanishingly small twice: both at optimal doping \(\delta \approx 0\) and on the plateau \(\delta \approx 0.3\). As discussed above (Section VI.D.4), a VHS is known to produce a minimum in the isotope effect.

3. A Test Case: 1-eV Feature in YBCO

The present model of nanoscale phase separation should have predictive or at least explanatory power. Here, it will be used to propose an explanation for the sharp peak found at \(\approx 1eV\) below the Fermi level by photoemission experiments in YBCO, Fig. 38. This feature is found to shift significantly with doping, Fig. 38, but to be nearly independent of doping in the range 6.7-6.5. Comparison with the phase diagram of YBCO strongly suggests that this feature is associated with the Ortho II phase: it is independent of doping when the Ortho II is the majority phase, and shifts, due to proximity effects, when the Ortho II is a minority phase.

Moreover, the present model suggests the origin of the feature. The Ortho II phase is considered to involve hole segregation on the planes in parallel with chain ordering: alternating stripes of hole-doped and undoped unit cells. The doped stripes are superconducting, but with reduced \(T_c\) and Meissner fraction. Similarly, the undoped stripes are insulating, but with a reduced charge-transfer gap. The photoemission spectrum has the expected form, Fig. 38b. Thus, the 1eV feature may be the signature of the reduced charge-transfer gap. In underdoped material, it smoothly evolves into the larger gap of YBCO\(_6\) \[92\].

One complication in interpreting this feature is that it may also be related to a surface feature. Thus, if the surface cleaves preferentially on the chain layer, it is possible
that half of the chains go with each surface, to maintain approximate charge neutrality. In this case, each surface would be left with approximately an Ortho II surface layer, which would display the 1eV feature.

4. O-doping in Bi- and Tl-Cuprates

Extra, interstitial oxygen is also found in the Bi-cuprates. This does not lead to phase separation, but to an incommensurate CDW, which Bianconi and Misori [459] interpret in terms of a nanoscale (polaronic) phase separation. Doping on the Ca site seems to lead to a phase separation into two phases with different (commensurate) superlattice periods [713].

Finally, while the hole-doping process in the Tl-cuprates is not completely understood, it is known that Tl$_2$Ba$_2$CuO$_{6+\delta}$ (Tl-2201) is overdoped when fully oxygenated, and must be reduced in argon to become superconducting (T$_c$ ≥ 85K). The fully oxygenated samples are again found to contain interstitial oxygen [714,715], which may lead to a phase segregation [713]. In orthorhombic Tl-2201, incommensurate modulations are observed in electron [716] and x-ray [714] diffraction, accompanied by a splitting of the Cu-NQR peaks [717].

5. Photodoping

A macroscopic phase separation, similar to O-doped La$_2$CuO$_4$, also arises from photodoping of YBCO and LSCO. This is discussed in detail by Emery and Kivelson (their Section 4.1) and by Yu and Heeger [718]. Photoexcitation produces a population of holes, which migrate to the CuO$_2$ planes, and electrons, which localize on a different layer, assumed to be at O vacancies on the chain layer in YBCO. These electrons are much more mobile than any chemical species, so if the holes tend to bunch up, the electrons follow, leaving charge-neutral domains. In La$_2$CuO$_4$, there is a striking change in the spectrum of Raman active phonons: the Raman peaks associated with the undoped material are bleached, while those peaks associated with the optimally doped material appear [426]. This is just what would be expected in a phase separation scenario: the photodoping produces islands of optimally doped material, thereby reducing the volume of undoped material. Also, the electronic part of the photoabsorption spectrum matches that of optimally doped LSCO, independent of the laser intensity [713] – that is, the holes preferentially bunch up to the doping of optimum T$_c$. Just as in La$_2$CuO$_{4+\delta}$, this is very strong evidence for the VHS model, as opposed to a model in which the upper limit of phase separation is random, or one in which the superconductivity arises in the two phase regime. In a sense, this experiment provides the stronger evidence, since the electrons can follow the hole motion to lower temperatures than the interstitial O’s, which freeze out near 200K.

Similar effects are found in YBCO [720,721] and Tl compounds [722]. Strikingly, there is a dip in the resistivity suggestive of a superconducting transition on the metallic islands. While the transition is not evident at the lowest photon intensities (perhaps due to proximity or charging effects in the smallest drops), once the transition appears, the onset temperature is ≥ 100K, independent of light intensity [723]. This is actually higher than in optimally doped YBCO – particularly when it is realized that the chains remain badly broken, due to the large oxygen deficiency (δ = 0.7). Could the photoexcited electrons be superconducting? A similar T$_c$ enhancement (to ≃ 40K) is found in photodoped La$_2$CuO$_4$ [716].

The appearance of the Raman phonons associated with the optimally doped material provides additional information on the role of electron-phonon coupling. Chemical doping changes the phonon spectra in two ways: first, due to metallic screening, and secondly, due to tetragonal-orthorhombic transitions in both LSCO and YBCO. Photodoping also produces both of these changes [424,724]. This is strong evidence against the purely ionic model of the HTT-LTO transition in LSCO.

The above experiments have all dealt with transient photoconductivity after a short laser pulse is absorbed by the sample. The sample’s response to a long-time continuous irradiation reveals an additional feature: a persistent photocurrent, which can last indefinitely if the sample is kept well below room temperature, but which anneals away near room temperature [725]. Some echo of this phenomenon is found in the pulsed experiments, in that at high pulse intensities the photocurrent decay becomes very slow [726]. This is the opposite of what is usually seen in semiconductors, where photoirradiation enhances disorder. It is believed to be associated with better oxygen ordering in the chain layer – larger domains of the Ortho I and II phases. This can also be driven by the electronic phase separation: if the oxygen follows the holes, then the photoinduced phase separation leads to the growth of larger Ortho I domains. When the light is turned off, part of the hole excess decays, but the oxygen does not have enough energy to diffuse and disorder the domains. The better domain order leads to larger hole transfer to the planes, and hence improved superconductivity [729]. This residual hole transfer is small compared to that induced by the direct photoexcitation: T$_c$ is much less than the ≈ 100K inferred from the pulsed experiments. On warming to room temperature, entropic effects become important, the oxygen disorders, and the excess photocurrent decays.
A similar macroscopic phase separation may be found in H-doped YBCO, although the experimental situation is confused at present. In bulk powder samples, H NMR shows evidence for a number of inequivalent H environments \[32\], one associated with antiferromagnetism with a high transition temperature, \(T_N \approx 420K\), another with superconductivity \[28\]. The superconducting onset temperature remains constant at 92K throughout the doping regime, until superconductivity is completely destroyed \[28\]. However, in epitaxial films, a sharp transition is found at all H dopings, and \(T_c\) falls smoothly to zero as the H concentration increases \[28\]. Moreover, it is believed that the phase separation has more to do with the H than with the holes \[27\]. On the other hand, in Tl-2201, there is a correlation between the H-induced phase separation and the degree of hole-doping \[32\]; there is clear phase separation in underdoped materials, while there appears to be a continuous H-doping in the (hole) overdoped regime.

### B. Underdoped Regime: Single Hole

Nanoscale phase separation is much more difficult to prove, since the scale is comparable to that of fluctuation effects. Thus, in LSCO, \(T_c\) varies continuously with doping in the underdoped regime, so any superconducting domains must be comparable in size to the superconducting coherence length, \(\approx 16\AA\). Indeed, at this point, it is more correct to think of this as a unique phase characterized by charge bunching, rather than in terms of a phase separation. Nevertheless, there is considerable evidence for this unique phase.

Indeed, when even a single hole is doped into the half filled AFI state, there is evidence for localization effects. Since a Mott insulator requires exactly one electron per atom, adding even a single electron or hole to a half filled band should result in an insulator-to-metal transition. This is confirmed by detailed calculation in both 1D and 2D systems, but is not observed experimentally in the cuprates. Instead, it is found that the insulating phase exists over an extended doping regime, indicating that the first doped holes are localized \[30\]. Localization can arise from a number of causes, including disorder or (charge or spin) polaronic effects. Such effects arise naturally in a model of nanoscale phase separation: the added hole would tend to form a compact region of well-defined hole density, rather than spreading out to change the average density by a small amount over a large spatial area. This compact charged region would then be sensitive to localizing on a charge fluctuation. This would be particularly true in LSCO, where the dopant Sr forms an immobile charged impurity.

In a study of lightly doped \(La_2CuO_{4+\delta}\) (\(\delta = 0.014\)), Falck and coworkers \[31\] found two peaks in the reflectivity, at 0.13eV and at 0.5eV. These features correspond to the two components generally found in the mid-infrared absorption of the cuprates, at 0.13-0.16eV and 0.5-0.75eV. Now since these mid-infrared features are found at essentially all dopings in all the cuprates, they must be intrinsic features of the CuO2 planes, insensitive to the structure and doping of the other layers. In the lightly doped sample, Falck, et al. \[31\] suggest that the 0.5eV feature may be an exciton associated with Cu \(d_{x^2-y^2} \rightarrow d_{z^2-r^2}\) transitions. Why these are not seen in the undoped material is unclear; however, if their interpretation is correct, this transition is not of immediate interest. The other transition, at 0.13eV, is potentially very interesting. Falck, et al. interpret this as due to the ionization of a \textit{localized polaron}, in agreement with Bi and Eklund \[32\].

The strong T-dependence of this peak is due to thermal ionization, with activation energy 0.035eV; the large difference between this thermal ionization energy and the photoionization energy, 0.13eV, is ascribed to a Frank-Condon effect: it is the energy of the local lattice distortion associated with strong coupling to \(\approx 43\)meV optical phonons. For a simple \textit{molecular JT} effect, the net energy is a combination of elastic and electron-phonon terms, of the form

\[
E = \frac{K}{2} x^2 - Gx, \tag{70}
\]

where \(x\) is the JT distortion. Minimizing \(E\) with respect to \(x\) gives the thermal excitation energy, \(E_{IT} = G^2/2K\) at distortion \(x_0 = G/K\). If this is \(\approx 35\)meV, then the optical excitation energy is the energy for a vertical transition between the two JT-split states, \(E_{opt} = 4E_{IT} \approx 140\)meV, in good agreement with observation. Thus, the initially doped holes are readily localized because of strong polaronic effects. This is precisely what is predicted by the VHS phase separation scenario. Note that, in the magnetic phase separation model, the first holes would form \textit{magnetic} polarons – small ferromagnetic patches – and not the \textit{dielectric} polarons observed experimentally.

There are also experiments which have been interpreted as evidence for magnetic polarons. For instance, in a magnetic neutron scattering study of YBCO, Burlet, et al. \[34\] found a coexistence of magnetic Bragg peaks with rods of magnetic scattering, for \(y = 1 - \delta = 0.37\), a doping too low for any superconductivity to exist. Further, for \(y = 0.3, 0.33\), the magnetic Bragg peaks have a reentrant feature: below a temperature \(T' \approx 50 - 100K << T_N\), the intensity of the Bragg peak starts to decrease with decreasing temperature. They attribute both of these features to AF-polarons \[34\].

However, these magnetic polarons should be local domains of ferromagnetic order – i.e., regions in which time-reversal symmetry is violated. Now there was an extensive search for just such domains, in the context of anyon theory, and the demise of that theory is directly correlated with the inability of experiments to detect the rele-
vant domains. Hence, I think that it is unlikely that ferromagnetic domains exist in equilibrium in the cuprates. On the other hand, the quenching experiments discussed in Section XI.A.1 showed that a metastable phase with non-vanishing EPR signal, suggestive of spin-polarized clusters, can be quenched in (see also Section XI.F.3).

C. Underdoped Regime: AFM Islands

Nanoscale phase separation presents a rich phase diagram as a function of doping, Fig. 58. For $x < x_{VHS}$, there is a two-phase regime involving a magnetic insulator and an ‘anomalous metal’ (VHS) phase, while for $x > x_{VHS}$, the two phases are the VHS phase and a normal metal. Near the midpoint of each of these regimes, there will be a percolation crossover. Thus, the underdoped material should evolve from an antiferromagnetic metal to a phase with antiferromagnetic islands separated by grain boundaries of VHS-like phase, to a metallic phase with ‘intrinsic’ weak links (VHS phase islands with magnetic grain boundaries) to a pure VHS phase. The AFM-island phase should display superparamagnetic behavior, and can presumably be identified with the ‘spin glass’ phase in lightly doped LSCO; indeed, recent experimental evidence has been presented for just such a phase [557]. Of course, the physical properties of the grain boundary material will be strongly modified by proximity effects. This is presumably why the threshold for superconductivity is at $x \approx 0.05$, close to the upper limit of the spin glass phase.

1. Finite-size-corrected Néel Transition

The magnetic properties of single-layer cuprates have recently been reviewed in detail by Johnston [734], including evidence for phase separation. From the peak in the (neutron scattering) dynamic spin structure factor, $S(q, \omega)$ at $q = (\pi/a, \pi/a)$, Keimer, et al. [730] deduced the magnetic correlation length $\xi(x, T)$, and showed that it could be fit to the form

$$\xi^{-1}(x, T) = \xi_0^{-1}(x) + \xi^{-1}(0, T),$$

(71)

where $\xi_0^{-1}(x) = \xi^{-1}(x, 0)$. Emery and Kivelson [502] pointed out that this is just the form expected for phase separation, if the magnetic domains have size $\xi_0(x)$. This allows an estimate of the magnetic domain size, $\xi_0(0.02) = 200 \text{Å}, \xi_0(0.04) = 40 \text{Å}$. Cho, et al. [657] showed that the doping dependence of the Néel temperature in LSCO, Fig. 54, could be understood as due to finite size effects in the AFM-island phase:

$$T_N(x) = T_N(0)[1 - (\frac{x}{x_c})^n],$$

(72)

with $T_N(0) = 301 K, x_c = 0.0212, n = 1.9$. From mean-field theory, this suggests that the AFM domain size $L$ scales like $L(x) \propto x^{-n/2} \propto 1/x$, which implies 1D domains (stripes). Consistent with this model, they showed that the Néel peak in the susceptibility could be scaled onto a single curve for all samples with $x \leq 0.02$, and that $L(x)$ could be quantitatively equated to Keimer, et al.’s $\xi_0(x)$.

2. Roughening Transition

The above analysis holds for $T \geq 50 K$, when the holes are mobile. Below this temperature, the holes become localized [737], presumably on the potential disorder associated with the random Sr distribution. At $T_f \approx (815 K)x$ (about 8-16K), there is a large peak in the $^{139}$La nuclear spin relaxation rate [735], similar to one seen in LBCO [728] and La$_2$CuO$_{4+\delta}$ [734], and $L(x) \propto x^{-1/2}$ for $T < 50 K$. This has been interpreted as follows [740]: the random potential is assumed to completely break up the domain walls into isolated holes, and $T_f$ represents a freezing of the transverse components of spins of Cu’s adjacent to these O holes. The resulting transition appears to be totally unconnected with the spin glass phase found at slightly higher dopings (see the next paragraph), and I would like to suggest an alternative picture. As the holes localize, the domain walls start to meander and collide, the stripes break up into more equiaxed domains, leading to $L(x) \propto x^{-1/2}$. Thus, $T_f$ would represent a disorder-induced roughening transition [741], with the resulting domains identical to those found in the spin glass phase, Fig. 55.

3. Spin-Glass Phase

For higher doping, $0.02 \leq x \leq 0.08$, there is no long-range Néel order, and the spin freezing transition is replaced by a spin-glass-like transition, $T_{gl}$, Fig. 54. However, the presence of a specific heat peak at the transition suggests that it is not a conventional spin glass [742]. This transition is also interpreted in terms of the AFM-island phase, with domain size $L(x) \propto x^{-1/2}$ [743], again in agreement with the AF correlation length, $\xi_0$. The molecular field transition predicts $T_{gl} \propto J'(\xi_0/a)^2 \propto L^2 \propto 1/x$, in good agreement with experiment, Fig. 54.

D. Underdoped Regime: Metallic Islands

From Mössbauer measurements on $^{57}$Fe$^{3+}$ in LSCO (0.5% Fe) and $^{176}$Yb$^{3+}$ in YBCO, Imbert, et al. [744] found that the spectra at arbitrary hole doping could be decomposed into a superposition of a magnetic part, similar to the undoped state, and a metallic part, similar to optimum doping. Figure 56A shows the magnetic
fraction found in the two materials. The magnetic domains are quasistatic, but the local probe cannot determine their size. In LSCO, the low $x$ ($0.06 \leq x \leq 0.16$) appears to be a glass phase, while higher-$x$ samples ($0.16 - 0.25$) display no spontaneous spin freezing. For $0.14 \leq x \leq 0.16$, the two components overlap. Similar results are found by Kobayashi, et al. [743], from La $T_1$ measurements, in which a rapidly decaying component is associated with magnetic domains, and from $\mu$SR measurements by Weidinger, et al. [740], which also measure the magnetic fraction and local magnetic field. Both results from local probes are seen to be in good semiquantitative agreement. More recent measurements find that the magnetic fraction vanishes at the optimum $T_c$ in LSCO [747]. Niedermayer, et al. [267] reported similar $\mu$SR results, finding a common scaling for both LSCO and YBCO, when the doping is expressed as $T_c/T^\dagger$, where $T^\dagger$ is the optimum $T_c$ for LSCO, and is approximately equal to $T_c$ for the Ortho II phase of YBCO ($T^\dagger = 60K$, $T_{c,II} = 58K$). However, their more recent work has failed to confirm the presence of a separate magnetized fraction [748]. They suggest that the result is not incompatible with the presence of a striped phase, since fluctuations could average out the magnetization on the slow time scale of the $\mu$SR measurement.

In a more recent study, Imbert, et al. [749] have gone to ultralow Fe concentrations, by doping LSCO with radioactive $^{57}Co$, which decays to form $^{57}Fe$. They found characteristic differences from their earlier study, which suggest that the Fe is not simply a passive probe. I would interpret the changes (in a slight modification of their interpretation) as showing that the Fe locally pins the insulating regions. Thus, for the ultra-low-Fe-doped samples, the Mössbauer found only Fe associated with the insulating domains, up to $x = x_1 = 0.19$ (in these samples, the measured $x$ may be too large by $\delta x \equiv 0.02 - 0.04$ [449]), and there was no doping range in which both spin glass and metallic domains coexisted. I would suggest that the latter behavior is more representative: in the lightly doped samples, the isolated Fe always pinned the insulating domain wall locally, whereas in the higher-doped samples, most walls were pinned, so some Fe remained in a metallic domain. The concentration $x_1$ would then represent the highest doping at which any insulating domain walls were present. These results further suggest that, at least near an Fe impurity, there is not much difference in the insulating phase, whether it is in a large AFM island, or the domain wall on a metallic island.

**E. Crossover at Optimum $T_c$**

**I. Meissner Effect**

Some properties show a striking crossover as the doping is varied from the underdoped to the overdoped regimes. Thus, early evidence for nanoscale phase separation came from measurements comparing the doping dependence of $T_c$ and the Meissner fraction of LSCO. Both were found to depend strongly on $x$, maximizing at the optimum doping and falling off for either underdoped or overdoped materials [750, 751, 89]. Fig. 7a. Allgeier and Schilling [711] find that the proportionality between the Meissner fraction and $T_c/T_{c,max}$ holds in LSCO, YBCO, and several Tl and Bi cuprates as well, Fig. 7b. More recent measurements in LSCO find that the Meissner fraction is strongly field dependent, and can reach large values even in underdoped samples, if the field is low enough ($\approx 0.1G$). In fact, this is what would be expected for nanoscale phase separation: the superconducting regions are close enough to be Josephson or proximity effect coupled, but this coupling can be destroyed by a very weak field. Yoshimura, et al. [751] also found that, in all compositions studied, a small fraction of the sample went superconducting near the optimum $T_c$, and concluded that only the sample with $x = 0.16$, $\delta = 0$ is single phase. The field dependence shows a characteristic difference between the underdoped and overdoped regimes [752]: the underdoped sample ($x = 0.11$) consists of superconducting grains separated by weak links, while the overdoped sample is mostly nonsuperconducting, but the superconducting regions can still couple at low fields (suggestive of proximity-effect coupling over long distances via normal metal regions).

The discussion by Kitazawa, et al. [753] shows how careful one must be in estimating the Meissner fraction, in the presence of pinning and weak links. However, they are trying to prove that their samples are homogeneous, and I believe that their measurement cannot rule out the nanoscale phase separation we are discussing. In terms of the present model, I would interpret their results as follows. (1) It is extremely difficult to produce a uniform nanoscale phase separation; most preparation techniques lead to some larger scale phase separation, with evidence for domains with distinct $T_c$'s. (2) In sufficiently low magnetic fields a 100% Meissner effect is found, but this is broken down by quite low fields, due to the domain walls acting as weak links. For example, a magnetic field of only 0.061Oe was needed to reduce the Meissner fraction of a single crystal by nearly 50% [442,752]. In stoichiometric YBCO, a similar effect is found, but for a much higher field, $\approx 300$Oe. [754] This suggests that, in the uniform nanoscale domain regime, the domain walls are less than $\xi_0 \approx 16A$ thick. Other experiments suggest that the domain walls are only about one unit cell in thickness. (3) The range of doping over which a 100% Meissner fraction can be found should be an estimate of the percolation crossover between the VHS phase and the second phase. These limits are $x = 0.085$ on the underdoped side and $x = 0.25$ for overdoped material, both reasonable values. (4) One should keep in mind that for YBCO, a large Meissner fraction is found over a broad doping range even though it is clear that there is nanoscale phase separation between the Ortho I and Ortho II phases [753].
2. Susceptibility

A similar crossover behavior is found for the susceptibility [712,711]. In underdoped cuprates, the susceptibility above $T_N$ can be scaled into a universal form [179]. For overdoped cuprates, this same form holds, if a Curie-Weiss term is first subtracted off [756]. In LSCO and LBCO, the Curie constant grows linearly in $x - x_{VHS}$, where $x_{VHS}$ is the doping of optimal $T_c$, up to $x \approx 0.26$. The origin of these paramagnetic centers is not clear, but for all dopings, they correspond to less than 1% of the Cu spins. Tallon and Flower [712] point out that these spins can act as pairbreakers, thereby reducing $T_c$ in the overdoped cuprates, but caution that they could be extrinsic, due to impurity phases.

Neutron scattering experiments find a large falloff in magnetic scattering on going from optimum doping, $O_{6.92}$ to a small overdoping, $O_{6.97}$ [757].

3. Spin-Lattice Relaxation

Whereas the nuclear spin-lattice relaxation rate, $T_1^{-1}$ shows a $T^3$ falloff below $T_c$ in YBCO, suggestive of a d-wave energy gap, $T_1^{-1}$ shows a ‘saturation’ effect at low temperatures in LSCO, which changes its form between the underdoped and overdoped regimes [758]. In underdoped samples ($0.1 \leq x \leq 0.15$) $T_1^{-1}$ saturates to a $T$-independent value, which is interpreted as evidence for the presence of localized magnetic islands. The saturation can be suppressed by an applied magnetic field. Unfortunately, the interpretation is complicated, since the saturation is not observed in a sample with $x = 0.085$, and the observed effects may be associated with local regions of LTT phase, centered near $x = 0.115$, similar to the LTT phase of LBCO. For overdoped samples ($0.2 \leq x \leq 0.24$), a very different behavior is observed: after a dip at $T_c$, the Korringa law, $T_1^{-1} = const.$ is obeyed, suggesting the presence of normal carriers in the superconducting state. While this was interpreted as due to pairbreaking effects in a d-wave superconductor [758], it could also be a result of nanoscale phase separation in the overdoped regime, where the second phase is an ordinary metal.

4. Transport Effects

The insulating grain boundaries between metallic grains should behave as ‘intrinsic weak links’, greatly reducing the ability of these materials to carry critical currents. Evidence for such weak links had been found in many early experimental studies, and some more recent studies have placed this picture on a firmer basis. Most of these studies, however, involve either YBCO in the mixed Ortho I – Ortho II regime or overdoped LSCO; in other words, the two domains consist of ‘VHS’ and metallic islands. Thus, Jones, et al. [759] studied the critical current on the 90K plateau of YBCO. They found that $J_c \rightarrow 0$ as $\delta \rightarrow \delta_c$, with $\delta_c \approx 0.2$ marking the edge of the 90K plateau. This was taken as evidence that the current flows by a percolation path of Ortho I material.

In measuring magnetization hysteresis, a characteristic ‘fishtail’ or ‘peak effect’ is often observed. While a number of models have been proposed, one possibility is that it is associated with domains of a second, metallic phase. In LSCO, this effect is found only in overdoped samples, $x \geq 0.14$ [760]. However, in overdoped YBCO, it can be eliminated by proper O annealing [761].

Finally, it should be expected that these domains would play a role in the weak link problem associated with grain boundaries [757], particularly since the grain boundaries could act as nucleation sites for domains. Hence, it is most interesting that evidence has been found for regions of hole depletion near the weak link boundaries [763]. The width of the depletion region, $\sim 80 - 600\AA$, while highly sample dependent, is much larger than the scale of the structurally disordered region $\approx 10\AA$ or of metallic cation disorder, $\approx 50\AA$, but is comparable to the typical sizes of Ortho I, II domains.

F. Overdoped Regime

1. Miscibility Gap

Overdoped LSCO was one of the original three cuprate materials in which Jorgensen, et al. [654] reported a miscibility gap. The second (higher hole density) phase is found to be $x \approx 0.5$ [654] (for samples annealed below $\approx 1100\,K$, a different phase, La$_3$SrCu$_2$O$_6$, is formed [761]). Radaelli, et al. [689] find single-phase behavior only in samples which are annealed at $T \geq 1170^\circ C$ and then quenched to room temperature. The samples need to be fired at $1170^\circ C$ for only 24 hours or less to produce homogeneous samples. However, if these samples are subsequently annealed in 20% oxygen at temperatures between 950-1050$^\circ C$ for 24 hours and then quenched, evidence for two-phase behavior appears. This is strong evidence that at $T=1170^\circ C$, entropy wins out and produces a homogeneous phase, but that phase separation spontaneously develops at lower temperatures, proving that the phase separation is an equilibrium phenomenon. Note that this is a macroscopic phase separation; the samples quenched from $T=1170^\circ C$ would be ideal candidates for studying a purely electronic (nanoscale) phase separation at low temperatures.

Studies on LCO doped with both Sr and Nd [765] find similar results. Even in samples carefully preannealed and then quenched from 1150$^\circ C$, there is evidence for Sr inhomogeneity. Strikingly, high-resolution (200A$\times$200A) EDX analysis found that the Nd is uniformly distributed, whereas there are significant variations in the Sr content.
(and hence in hole doping). This suggests a stringent test of the phase separation models. The Sr distribution should be highly non-random. Ideally, there should be a bimodal distribution, but the possible existence of striped phases would allow the presence of intermediate Sr dopings. Additional EDX studies have been promised, and it is hoped that these distributions will be measured.

A similar study by Takagi, et al. [604, 603] reported quite different results, finding evidence for ‘compositional fluctuations’ in their as-prepared overdoped samples. While they ascribed their results to random fluctuations, the Meissner signal clearly showed two well-defined plateaus, with one corresponding to the optimum $T_c$. However, long term annealing (one month at 1000°C) reduced the amount of this optimally doped fraction, and added curvature to the Meissner signal, as if there were now a broad distribution of $T_c$'s. If the equilibrium state of the overdoped system involved macroscopic phase separation, then very different behavior would be expected, with the two plateaus sharpening with increased annealing. What can one say in the light of such incompatible results? Clearly, more experiments are needed to sort out the situation. A number of groups have disputed a main conclusion of Takagi, et al., that the HTT phase is nonsuperconducting, noting that this is inconsistent with pressure [277, 278] and Bi substitution [76] studies, in which the LTO phase disappears long before superconductivity does. Contrariwise, by substituting Pr for La, the HTT-LTO transition can be shifted to much higher Sr doping, but the superconductivity still disappears at $x \approx 0.24$, well within the LTO phase [603].

Moreover, to explain the residual $T_c$'s found in the HTT phase, Takagi, et al. suggested that there are residual regions of LTO phase present, which again would be consistent with a nanoscale phase separation. I propose therefore that the best interpretation of their data is in terms of nanoscale phase separation, involving a VHS phase of LTO symmetry and a metallic phase of HTT symmetry. Since the phase separation is nanoscopic, a macroscopic probe will resolve only a single lattice structure, which will cross over from LTO to HTT very close to the point at which the holes have a percolation crossover, from LTO domains with HTT walls to HTT domains with LTO walls. Hence, in Takagi’s macroscopic HTT phase, the superconductivity would arise from the LTO domain walls, with $T_c$ reduced by proximity effects (the second plateau would be associated with larger grains of LTO phase). Annealing would cause the HTT islands to grow, stretching out the LTO domain walls between adjacent islands. The larger domains of metallic phase would lead to a stronger proximity-effect reduction of $T_c$, in accord with the data. Note that the fact that the pre-annealed samples already show a proximity effect means that the average scale of the LTO domains is only $\xi \approx 16\AA$, the superconducting correlation length. The fact that a month-long anneal does not homogenize the material on this length scale strongly suggests that the phase separation is an equilibrium phenomenon. Moreover, neutron derived radial distribution functions find that the local symmetry in the HTT phase for $x > 0.2$ is orthorhombic [55] (similar results were found earlier for lower $x$ [54]).

A further hint of phase separation in overdoped LSCO comes from positron-annihilation spectroscopy [100]. In overdoped samples, a smearing of the data is found, which obscures the shape of the Fermi surface, leading to poor agreement with band structure calculations. After ruling out a number of possible origins for the smearing, one remaining candidate would be a distribution of segregated phases.

A significant difference should be noted between these results and the O-doping discussed earlier: the temperature range. Whereas in O-doped material, macroscopic phase separation begins near room temperature, for Sr the separation is found near 1000°C. This difference may be due to the zero-point motion of the oxygen. The characteristic energy scale of hole phase separation should be $\sim J \approx 1300K$, the exchange constant.

2. Cu NQR

Cu NQR, a very local probe, sees evidence for two distinct Cu sites in the metallic phase of LSCO [608, 604, 656]! (The signal from the AFI phase is shifted to much higher frequencies by the large hyperfine field of the ordered Cu moments.) The relative intensities are T-independent, but vary in an inverse sense with doping: the metallic phase is approximately $x = 0.4$, close to the value $x \approx 0.5$ found by Jorgensen, et al. [654]. The splitting cannot be caused by proximity to a Sr impurity, since the same two NQR frequencies are found in La$_2$CuO$_{4+x}$ as in LSCO [608]. However, there are some features which make it difficult to interpret these two sites as regions of superconducting and normal metal phase. Thus, while the two sites coexist primarily in the overdoped regime, site $B$ persists down to $x = 0.12$ while it seems to be absent at $x = 0.10$ [758], the A peak also disappears at slightly lower doping, due to a very short spin-spin relaxation time. Moreover, the relaxation rate of both peaks is modified almost identically by the onset of superconductivity, with the same $T_c$ at each site. This is not what I would have expected for a nanoscale phase separation, where the normal islands may have a lower or zero $T_c$. Hence, the origin of these two peaks remains puzzling. It should also be noted that LDA calculations have been unable to reproduce either of the EFG values for the planar Cu’s, whereas the same calculations work well for the other constituents, including the chain Cu’s in YBCO [771]. Martin [772] analyzed this problem via quantum chemical calculations on clusters, and
concluded that the second peak could be due to Cu neighbors of a *localized* hole, and that $\approx 25\%$ of all the holes are localized. If this is the case, there may be a relation between these holes and the anomalous paramagnetic sites discussed in the following subsection. However, their connection with the nanoscale phase separation remains unclear. In a recent experiment, when Goto, et al. made a special effort to homogenize their samples (to see the suppression of $T_c$ at $x \approx 0.115$), they found only a single Cu NQR site in LSCO at $x \approx 0.15$, although two sites were still found in similarly prepared LBCO.

$^{89}$Y-NMR finds evidence for broadened peaks in overdoped YBCO; at lower temperatures ($\approx 100K$) two well resolved features are seen. The second peak is, however, ascribed to O deficiency.

3. EPR

For completeness, I should briefly comment on reports of EPR signals in the cuprates, which have often been taken as evidence for phase separation in these materials. First, it is important to note that EPR is usually *not* seen in either the optimally doped or the antiferromagnetic insulating cuprates, the signals which are occasionally reported being due to impurity phases. As discussed by Mehran and Anderson, this is a very surprising result, and has led to a number of careful searches, up to 1150K in La$_2$CuO$_{4+\delta}$, and for low concentrations of Cu in La$_2$NiO$_4$, which failed to find any signals. It is tempting to think that this might be a signal of dynamic tilt modes, similar to what is found in BaTiO$_3$, discussed above; however, while this would work for the optimally doped cuprates, it is not clear whether there is dynamic tilting in the AFI.

In the intermediate doping regime, there have been persistent reports of EPR signals, which might be associated with phase separation. EPR in quenched samples was discussed above. EPR has also been seen in underdoped YBCO, where it has been assumed to be associated with paramagnetic centers on CuO chain fragments. In a detailed analysis of the specific heat of YBCO, Phillips and coworkers have attributed the linear term in the specific heat to a sample dependent density $n_2$ of Cu$^{2+}$ moments, which also produce a Schottky anomaly in $C_v$ in a magnetic field. The superconducting fraction $f_s$ is found to be suppressed by $n_2$, as $f_s \approx 1 - n_2/0.012$. If $n_2$ is associated with chain fragments, the correlation with $f_s$ is consistent with the Poulsen model of $T_c(\delta)$, which assumes that the plane is locally nonsuperconducting if the adjacent chain is too short. This would also explain why there is no simple correlation between $n_2$ and $\delta$.

4. Superconductivity

While the overdoped phase has been characterized above as an essentially normal metal, there is some evidence that it can also be a superconductor, usually with a reduced $T_c$ value. Thus, as mentioned above, in electrochemically oxygenated La$_2$CuO$_{4+\delta}$, there is a series of superconducting phases, with increasing $T_c$'s. The 40-47K phase seems to correspond to $P = 0.16$, as in optimally doped LSCO. At even higher doping levels (so far, only found in thin films) an even higher, 55-60K superconductor is found. In overdoped LSCO, Zhou, et al. find several doping ranges in which there are two coexisting superconducting phases, even though x-ray analysis finds only one phase present.

Finally, in YBCO, the optimum doping (maximum $T_c$) occurs at $\delta \approx 0.1$. In the overdoped regime, $\delta \leq 0.09$, there is evidence for the simultaneous presence of two superconducting phases. From combined specific heat and susceptibility measurements, Janod, et al. show that the two $T_c$'s are split by $\approx 4K$ at YBCO, and smoothly merge near the optimum $T_c$ in underdoped samples! (The conversion between annealing temperature, used in [788], and $\delta$ is discussed in [789].)

Janod, et al. interpret the split transition in terms of limited oxygen diffusion: a thick shell near the grain surface is fully oxygenated, impeding diffusion into the grain interior. Conder, et al. have shown that this interpretation is unlikely, and that nanoscale phase separation is a more probable interpretation. However, recent experiments on high quality YBCO crystals find only a single peak in the heat capacity in the overdoped regime.

While considerably more experimental work is necessary to sort out the details of this new superconducting phase, a few speculations about possible origins can be made. One possibility is that the other phases are associated with subsidiary VHS peaks, such as might be generated by interlayer coupling or spin-orbit coupling effects, discussed above. Since split $T_c$'s are not observed in overdoped Bi-2212 or TI-2201, it might be thought that the second peak is somehow associated with CuO chains. However, Ca substitution shows that the appearance of the second peak correlates with hole overdoping in the planes, and not with $\delta$. 

[73]

[773]

[774]

[778]

[781]

[789]

[791]
A different possibility is that these phases are due to proximity effects between superconducting and normal domains. This is similar to the Allender-Bray-Bardeen (ABB) model of excitonic superconductivity \[92\], arising from proximity effects associated with intimate contact between a metal, with large carrier concentration, and a semiconductor/semimetal with strong electron-phonon coupling but low carrier density. In the present case, superconductivity could arise in the overdoped normal metal due to intimate proximity with the VHS phase. Interestingly, the dominant thermodynamic weight is associated with the lower \( T_c \) phase (this phase correlates with the transport \( T_c \)). This would suggest that the lower \( T_c \) phase is the VHS phase, and the metallic phase has a higher \( T_c \). If true, this could confirm ABB’s prediction that such excitonic coupling could enhance \( T_c \).

However, it must be cautioned that several recent studies of the heat capacity of YBCO have failed to observe a split peak in the overdoped regime \[76\] [99].

G. Why are there Several Discrete \( T_c \)’s?

In \( \text{La}_2\text{CuO}_4+\delta \), there seem to be discrete superconducting phases with \( T_c \simeq 32\text{K}, 43\text{K}, 55\text{K} \), and possibly 28K, while the Ortho II phase in YBCO has \( T_c\approx 59\text{K} \). Such a series of \( T_c \)’s arises naturally in a model of nanoscale phase separation, either as a result of staging \[64\] or due to CDW formation. In the case of staging, the different stages resemble the layering seen in, e.g., Bi-22(n-1)n, and the different stages would be expected to have different characteristic temperatures. In analogy with intercalated graphite, most of the holes would be attracted to the layers bounding the intercalated O’s. Hence, a single stage could display two \( T_c \)’s, one associated with the bounding layers, one with the interior layers.

Alternatively, a similar effect could arise from commensurability effects in a CDW phase: as the doping is varied, the CDW periodicity changes, and certain periodicities are associated with the bounding layers, one with the interior

H. \( \text{La}_{2−x}\text{Sr}_x\text{NiO}_4 \): An Analogy with Well-defined CDW’s

\( \text{La}_2\text{NiO}_4 \) is isostructural to \( \text{La}_2\text{CuO}_4 \), and can similarly be doped either by Sr substitution or by excess O, which occupies the same interstitial site. The phase diagram is also very similar, with an AFI at half filling, crossing over to a spin glass phase, and finally a conducting phase. However, the conducting phase arises only for much higher doping \( (x \approx 1) \), and no superconducting phases are found. The intermediate doping regime is most relevant to the present discussion, since nanoscale phase separation seems to be manifest in a complicated series of CDW’s, associated with rational filling fractions. Most interestingly, these phases show evidence for strong polaronic effects.

However, much work still needs to be done to answer some very basic questions concerning the nickelates. For instance, when holes are added, which states are occupied? Isolated Ni\(^{2+}\) is a spin 1 system, with two holes, one \( d_{x^2−y^2} \), one \( d_{z^2−r^2} \), with spins parallel to satisfy Hund’s rule. In the nickelate, the \( d_{x^2−y^2} \) hole will tend to hybridize with O \( p_x \) and \( p_y \) orbitals from the planar O’s, while the \( d_{z^2−r^2} \) hole will hybridize with the apical O’s \( p_z \) orbital, forming two bands which cross the Fermi level. At half filling, this hybridization is quenched by the large Hubbard \( U \), leading to a charge transfer gap of \( \Delta \approx 4\text{eV} \) \[74\], about twice as large as in the cuprates. The first holes doped in are about 30-40% Ni, 60-70% O \[79\], comparable to NiO \[79\] (in the cuprates, the holes for \( x > 1 \) have a metal-like character, whereas the fraction of La nuclei experiencing this field falls linearly to zero at \( x = 1 \). The large magnitude of the field can be explained by a transferred hyperfine field on some of the La nuclei \[79\], which remains nearly constant in magnitude up to \( x = 1 \), whereas the fraction of La nuclei experiencing this field falls linearly to zero at \( x = 1 \). The large magnitude of the field can be explained by a transferred hyperfine field between the La and the Ni \( d_{x^2−y^2} \), coupled via the apical O \[79\].

In this picture, doping \( 0 \leq x \leq 1 \) predominantly eliminates the \( d_{x^2−y^2}−p_z \)-band, so that doping \( x > 1 \) would be similar to the cuprates. This could explain why the holes for \( x \leq 1 \) are so much more strongly localized – the material remains insulating at all dopings, and antiferromagnetic interactions persist out to much larger dopings. Also, the material with \( x > 1 \) has a metallic conductivity down to low temperatures, \( T \geq 100\text{K} \), while for \( 1.2 \leq x \leq 1.5 \), it remains metallic to the lowest temperatures \[80\].

However, there is a number of objections to this picture. Thus, the Cu-apical O distance decreases with \( x \), so that the NiO\(_x\) octahedron is almost undistorted at \( x = 1.4 \), suggesting that the \( d_{x^2−y^2} \) and \( d_{z^2−r^2} \) orbitals are nearly degenerate \[80\]. Moreover, band structure calculations find the first holes to be of \( t_2g \) symmetry \[80\]. Also, the ‘mid-infrared band’ of the optical conductivity has an identical \( x \) dependence in both LSNO and LSCO \[32\], suggesting that the doped holes are very similar (i.e., of \( x^2−y^2 \) symmetry). The fact that the \( p \) component of the holes is an equal mix of
$x$, $y$, and $z$ states suggests that a similar mix holds for the $d$ states. Indeed, much more complicated behavior is possible; certainly, there appears to be an anomaly near $x = 0.5$ \cite{800,797} (the resistivity has a maximum), which could signal a charge transfer to the $d_{x^2-y^2} - p_{x,y}$ band \cite{797}. Also, it has been suggested that, since the NiO$_2$ planes become more compressed as $T$ decreases, there could be a high-spin ($S = 1$) to low-spin ($S = 1/2$) transition at low $T$, even near $x = 0$ \cite{800}.

1. \textit{La}_2\textit{NiO}_{4+\delta} (LNO)

In \textit{La}_2\textit{NiO}_{4+\delta} (LNO), the oxygen doping leads to a series of phases, closely related to the LTO, LTT, HTT, and Pccn phases of LSCO; however, in LNO, these phases are separated by at least four regimes of phase separation in the doping range $0 \leq \delta \leq 0.18$ \cite{803,804}, and there are a number of additional phase transitions below room temperature. Several of the phases are antiferromagnetic, often with a weak ferromagnetic component due to spin canting \cite{803,804}.

An added complication, which has only recently been recognized \cite{648}, is that the oxygen interstitials form well-defined staged compounds, analogous to graphite intercalation compounds (GIC’s) \cite{647}. Staging as a means of achieving nanoscale phase separation is discussed in Section X.B.5. The phase diagram of LNO shows evidence for several distinct stages, Fig. 68 \cite{648}. Moreover, when the doping densities are intermediate between the dopings associated with pure phases, there is a well-defined regime of phase separation (e.g., between stage 2 and stage 3). This regime of phase separation was predicted for GIC’s \cite{651} and has been taken as evidence that the interstitial O’s have a preferred density, which may be controlled by a hole phase separation \cite{648}. A similar staging has recently been reported for La$_2$CuO$_{4+\delta}$ \cite{633}.

Whereas neutron and X-ray diffraction studies typically find evidence for phase separation, electron microscope investigations generally find a complicated series of CDW’s, which appear to be associated with commensurate ordering of the O interstitials, and are associated with rational doping fractions, $\delta = 1/2n$, $n = 1, 2, 3, ...$ \cite{807} Incommensurate CDW’s are also observed, which appear to gradually evolve between two neighboring commensurate CDW’s. More recent neutron and X-ray studies do find evidence for superlattices, but only below room temperature \cite{803}, while the electron diffraction studies find these superlattices at room temperature. A number of possibilities exist for explaining this difference \cite{648} – the thinner samples may stabilize superlattices, or the locality of the probe may better reveal local structure, or the vacuum or electron-beam heating may effect subtle adjustments to the oxygen concentration or mobility. In any case, the electron diffraction studies reveal a tendency which is now clearly revealed in low-T diffraction studies.

While the phase diagram of these materials is still being worked out, Fig. 68 provides a clear impression of its complexity. Note that the staging is found for $0.03 \leq \delta \leq 0.11$; for higher doping, the commensurate magnetic order disappears, and is replaced by an \textit{incommensurate} magnetic order \cite{805,806}, similar to LCO for $\delta > 0.06$. Whereas for lower doping, the Néel temperature is decreasing with $\delta$, for $\delta \geq 0.11$, $T_N$ increases with increasing $\delta$. There is long-range incommensurate order below the Néel temperature and short-range incommensurate order above, extending beyond $2T_N$.

This incommensurate phase is most clearly defined at $\delta = 0.125$, and has much in common with a phase found in LSNO at a similar doping, $x \approx 0.2$ (discussed below). Both have peaks in the susceptibility when the magnetic field is parallel to the $a,b$ planes (for lower doping, the susceptibility peaks in a perpendicular field). Moreover, the incommensurability has the same symmetry, and is interpreted in terms of hole-rich domain walls \cite{808}. The incommensurate magnetic ordering is accompanied by incommensurate \textit{charge} ordering, at half the periodicity \cite{809}. This provides strong evidence for the charge domain wall model: the magnetic domains have a period twice as long, because the holes invert the phase of the antiferromagnetic spin order, thereby acting as antiphase domain boundaries. This is expected if the holes are predominantly on oxygens, as originally pointed out by Aharony, et al. \cite{810}: the hole, located on a planar O, causes both adjacent Cu spins to line up antiparallel with the hole spin and hence parallel with each other. Moreover, the incommensurability is found to be strongly temperature dependent, with a tendency to lock in at rational filling fractions. This is interpreted as due to a competition between hole and O ordering, and may lead to a devil’s staircase of ordered phases \cite{809}. A similar combined spin and charge ordering is found in antiferromagnetic Cr \cite{811}, and more recently, in LSNO, with $x = 0.2$ \cite{812}. It should be noted that in LNO, unlike the cuprates, the hole doping is assumed to follow $P = 2\delta$; the close similarity found between LNO, with $\delta \approx 0.125$ and LSNO with $x = 0.2$ would tend to confirm this assignment.

At higher doping, a compound LNO$_{4,25}$, prepared by electrochemical oxidation, is found to have long-range order of the interstitial O’s \cite{813}, accompanied by CDW’s in the NiO$_2$ planes.

2. \textit{La}_{2-x}\textit{Sr}_x\textit{NiO}_4 (LSNO)

If the situation is confused for LNO, it is even more confused for La$_2$-Sr$_x$NiO$_4$ (LSNO). This is in part because LSNO readily takes up extra oxygen, particularly for $x \leq 0.2$, and many studies do not measure the value of $\delta$. Not only does this mean that the hole content is not known, since $P = x + 2\delta$, but it may strongly influence the properties of superlattices. One electron microscopic
examination found that, when \( x \) and \( \delta \) were both non-zero, superlattices were observed only when \( \delta \geq 0.06 \), independently of \( x \).

Surprisingly, the magnetic properties and the HTT-LTO transition temperature \( T_{\text{LTO}} \) of LSNO are very similar to those of LSCO: long-range antiferromagnetism is eliminated at a quite low doping, \( x \approx 0.04 \), being replaced by a low-temperature spin-glass transition. Fig. 68. More recent \( \mu \)SR experiments have found onsets of magnetic ordered states at considerably higher temperatures, throughout the doping range \( 0.4 \leq x \leq 1.2 \), with a local maximum at \( x = 0.5 \) (open squares in Fig. 69). The spin glass phase has been interpreted in terms of a hole-rich domain wall model, very similar to that subsequently applied to LSCO. In LSNO (specifically studied at \( x = 0.2 \)), this phase is associated with incommensurate modulations of the antiferromagnetic scattering peak – thereby making a connection between domain walls and incommensurability which has only been theoretically assumed in LSCO. The modulations differ, in that the incommensurate peaks in LSNO are at \( (\pi \pm \delta \pi, \pi \pm \delta \pi) \) and \((\pi \pm \delta \pi, \pi \mp \delta \pi)\), while in LSCO they are at \( (\pi \pm \delta \pi, \pi) \) and \((\pi, \pi \pm \delta \pi)\), but the values of \( \delta \) are quite comparable. The domain size is also similar, \( \approx 9 \times 17 \) \( \AA \). The incommensurability also appears to be dynamic: at \( 2K \), the fluctuations are slow compared to the characteristic neutron-diffraction time scale, 10\(^{-11}\) s, but by \( 80K \), the fluctuation time has fallen to \( \approx 10^{-12}\) s. One curious feature is that the susceptibility has a peak at the transition for the B-field oriented within the a-b plane.

The incommensurate phase near \( x = 0.2 \) bears a strong resemblance to the phase in LNO at a comparable doping, \( \delta = 0.125 \). As might be expected (since the Sr is much less mobile than the O), the incommensurate phase in LNO displays true long-range order below 110K, whereas in LSNO there is only a short-range spin freezing in the same temperature range 812. The fact that this phase is so similar for both Sr and O doping shows that it is driven predominantly by hole ordering, as opposed to ordering of the interstitial O’s. As further evidence, the correlation length actually increases with increased Sr doping and hence is unrelated to the spacing between Sr impurities. Finally, since there is nothing comparable to staging for Sr doped samples, this incommensurate phase persists to lower doping, \( x \approx 0.135 \), with the degree of incommensurability scaling with \( x \).

The electron-phonon interaction seems to be about three times stronger in LSN0 than in LSCO. Thus, Bi and Eklund have identified polaronic peaks in the optical conductivity, at \( \approx 18\text{meV} \) in LSCO and 50meV in LNCO. This interpretation for LSCO has been challenged, but is supported by studies in much more lightly doped Cu materials. Similarly, in neutron scattering (Fig. 50) the softening of the O-O stretch mode in the undoped materials is considerably larger for the nickelates than for the cuprates (although some caution must be exercised, since the LNO sample seems to be slightly O-doped). A strong coupling of the \( x = 0.5 \) phase with an O-stretch mode was noted above. A related compound, \( \text{Nd}_2\text{NiO}_4 \) has been studied, be-
cause it has a similar sequence of phase transitions to LBCO, HTT→LTO→LTT; its orthorhombicity is about 5 times larger than the cuprate, consistent with stronger electron-phonon coupling. This may explain the characteristic differences found in its microscopic properties.

Correspondingly, polaronic effects in LSNO should be stronger, and the mixed charge and spin domain states discussed above have been interpreted in terms of polaronic phases [813,821]. These phases are very similar to those postulated above for the cuprates. Thus, whereas phase separation in the cuprates is mostly short-range and dynamic, LSNO has a well-developed series of striped phases [819], with varying spacing of the (second-phase) domain walls. These phases can display simultaneous polaronic and magnetic order, as has been found in the LTT phase in LBCO. Moreover, the polaronic effects keep LSNO in the small polaron limit: the materials remain insulating to much higher doping levels, and there have been no unambiguous demonstrations of superconductivity in these materials.

The polaronic behavior has been theoretically analyzed in terms of a three-band Hubbard-Peierls model [823], assuming coupling to O-O breathing modes, similar to the above discussion for the cuprates, Section VIII.D. However, these modes do not show strong signs of softening for both cuprates and nickelates, it is important to try to understand the role of the quadrupolar and 1D stretch modes, which do display strong softening.

4. A VHS Theory for LSNO?

Qualitatively, the compounds based on LNO share many features in common with the cuprates, and it will be important to try to understand their similarities and differences. Given the uncertainty in the symmetry of the Ni component of the doped holes, it would be difficult to develop a very quantitative theory at this point. Nevertheless, one can always speculate on how a VHS model might look.

Can a VHS theory be applied to these materials? Since there are two Fermi surfaces, there will be two sets of VHS’s, with a potential for very interesting interplay – although it should be noted that the \( d_{x^2−y^2} \) band may be considerably more three dimensional. In principle, a five-band Hubbard model should describe the bands, with correlations accounted for by the slave boson model. A preliminary set of band parameters is available [802]. From the doping dependence of various properties, I would guess that the Ni contribution has approximately equal admixtures of \( d_{x^2−y^2} \) and \( d_{z^2−r^2} \) symmetry, and that doping from \( x = 0 \) to \( x = 1 \) involves mainly a transition from high-spin to low-spin.

The staging phenomenon in O-doped LNO provides a clue to a preferred hole doping, close to \( x = 0.2 \), since all stages \( n \geq 2 \) have approximately the same hole density. Moreover, the material at \( x = 0.2 \) is very similar, for both O and Sr doping, and there seems to be a clear crossover in behavior from underdoping to overdoping about this point. (Also, samples with \( x < 0.2 \) tend to easily take up extra O, while for \( x > 0.2 \), a slight oxygen deficiency is often found.) For all these reasons, I would suggest that \( x = 0.2 \) corresponds to a VHS in this material; the value is slightly larger than found in LSCO, but comparable to YBCO. The fact that LSNO is non-superconducting could then be explained as due to too strong polaronic coupling, possibly complicated by the smaller bandwidth associated with a \( d_{x^2−y^2} \) component. In the underdoped material, the staging would be a manifestation of nanoscale phase separation. The persistence of magnetism would follow from the fact that, for \( n \geq 3 \), some layers are weakly doped – the reduction in \( T_N \) following from reduced interlayer coupling.

The enhanced electron-phonon coupling in the nickelates favors the VHS model for phase separation, as opposed to a magnetic model. Unfortunately, whereas the VHS model was cited in a number of early experimental studies of phase separation [657,796,785,853], it fell into disfavor, so that recent nickelate studies cite only the magnetic models for phase separation.

At higher doping, there is clear evidence for charged stripe phases at rational fillings, \( x \approx 1/2, 1/3 \). These would follow from the same phase separation model, Fig. 58h, provided that the free energy has a minimum associated with \( x = 1 \). This is very plausible chemically; indeed many materials cannot be continuously doped, but instead form a macroscopic phase separation, with a miscibility gap between the two end members. Note, however, that the observation of rational fractions \( x \approx 1/2, 1/3 \), shows that the two lowest free energy minima are at \( x = 0, 1 \). In this case, doping should just mix these two phases, and other phases with shallower minima (e.g., the VHS) should not be stable – unless the phase separation is sufficiently nanoscale that properties evolve fairly smoothly with doping.

5. Another Anomalous Perovskite: \( \text{La}_{1−x}\text{Sr}_x\text{MnO}_3 \)

The colossal magnetoresistance compounds \( \text{La}_{1−x}\text{Sr}_x\text{MnO}_3 \) came to my attention too late to be adequately described in this survey, but their properties are so similar to the nickelates that just a brief mention should be made. While these nearly cubic compounds are the best studied, there are also layered structures with similar properties [826,827], including in particular \( \text{La}_{1−x}\text{Sr}_{1+x}\text{MnO}_4 \). Just as in the nickelates, there are charge ordered phases at a commensurate doping, \( x \approx 1/2 \) [828,829,826] (see also [830]). The most interesting physics is the colossal magnetoresistance, associated with a crossover from an AFM insulating phase to a conducting ferromagnetic phase, near \( x \approx 0.2 – 0.45 \), with the transition temperature tunable by a magnetic field.
This conducting phase bears a close resemblance to the ferron phase discussed above [633].

The physics has traditionally been analyzed in terms of the double exchange model: three electrons are strongly coupled in $t_{2g}$ states to form a localized $S = 3/2$ state on each Mn ion. The remaining $1 - x$ electron is in a potentially mobile $e_g$ state, also with a strong Hund’s rule coupling to $S$. This coupling means that the hopping rate depends strongly on $S \cdot S'$, where $S$ and $S'$ are the spins of the two atoms involved in the hop. At half filling, LaMnO$_3$ is an AFI: hopping is greatly reduced, since $S$ and $S'$ point in opposite directions, so the hopping electron loses its Hund’s rule stabilization. By creating a local FM domain the electron can delocalize, thereby lowering its energy. At a critical doping, the system goes ferromagnetic, possibly by a percolation crossover.

Millis, et al. [467] have shown that the double exchange model cannot be the entire picture – the localization effects are too weak – and that a ferron (or magnetic polaron [831]) model is unlikely to improve the situation. They propose a dynamic JT model [832], involving predominantly a quadrupole O-O stretch mode (Appendix C) (see also Ref. [833]).

Recently, much evidence has accumulated that there is strong coupling between the magnetism and lattice distortions [334-338]. Thus, within an LDA model, JT distortions of the planar quadrupole form are essential to produce an AFI groundstate [839] (see also Ref. [840]). Particularly striking is a giant negative oxygen isotope effect on the magnetic transition temperature [841], which has been interpreted in terms of a JT polaron [842]. Photoemission studies [843] find that the insulating behavior is due to strong small polaron effects, which contribute to a charge fluctuation energy of $\approx 1.5$eV, and which are reduced below the ferromagnetic transition, which restores a finite dos at the Fermi level. Interestingly, the JT polarons can contribute only a small fraction of the charge fluctuation energy, and the main small polaron effect is due to the large difference in ionic size ($\approx 20\%$) between Mn$^{3+}$ and Mn$^{4+}$. Neutron pair-distribution function studies [844] find a local lattice formation occurring very close to the metal-insulator transition. Some of the largest polaronic anomalies are associated with a doping $x \approx 1/8$ [338], and a charge ordered phase at that doping has now been found [845]. There is also evidence for $T, x$ regimes of multiple phase coexistence [836,846]. In La$_{0.5}$Ca$_{0.5}$MnO$_3$, electron diffraction studies find evidence for charge ordering [847] with a commensurate-to-incommensurate(!) transition coinciding with the AFM to FM transition.

I. Relation to Dynamic JT Effect

The previous sections have summarized evidence for two different classes of anomalies in the cuprates: nanoscale phase separation and local (dynamic) structural disorder. Aesthetically, it would be preferable if these two anomalies were aspects of a single underlying phenomenon. The prospects of such a unification are clearly present: the domain walls of the local LTT phase are exactly the LTO structure which is stable in the undoped regime. However, this identification will require some modifications of the previously developed picture. This section will describe these modifications, and the experimental support for them.

Such a connection arises naturally in the VHS model of phase separation: the VHS phase is stabilized by a strong electron-phonon interaction, so it would be expected that the VHS phase is associated with a particular lattice structure, and for this structure to persist in the hole-rich domains. Looking back at the picture of a dynamic JT soliton, Fig. 49, it is striking how much it resembles a nanoscale phase separation, with the LTO soliton walls as AFI phase, and the LTT domains, with tilt less than the critical value, as the superconducting phase. This impression is further enhanced by comparing to the experimentally derived models of the LTT phase, Fig. 14, and the Bi-2212 domains, Fig. 19. Thus, it is an interesting possibility that the dynamic JT phase is itself a form of nanoscopic two-phase mixture. This is consistent with the picture of LSNO presented above.

The full implications of this possibility have not yet been worked out, but it would lead to some modifications of the interpretations given earlier. One striking modification has to do with the fact that LSCO at optimum doping is in the LTO phase. If this is a dynamic JT phase, then even at optimum doping there is a two-phase mixture, with the residual (LTO) domain walls constituting a remnant of the AFI phase. This would, however, explain the observation of incommensurate peaks in the neutron diffraction of a sample with $x \approx 0.14$, i.e., close to optimum doping [340], or even $x = 0.2$ in Nd substituted material [514], which is otherwise very puzzling.

Further evidence can be seen in the La NMR experiments, Fig. 54 [547]: while the superconducting phase has a broad distribution of tilt angles, the AFI phase has a well-defined LTO tilt (the splitting of the AFI peaks is due to the magnetic field). Hence the AFI appears to be correlated with a static LTO phase, like the solitons in Fig. 19. Neutron scattering studies of the HTT-LTO transition [48] confirm this picture. The transitions in the doped and undoped materials are strikingly different. While the undoped material has critical fluctuations near the transition, in the doped material ($x = 0.13$), fluctuations and anharmonic effects are present over an extremely broad range of temperatures. The two samples have different values of the critical parameter $\beta$ (orthorhombic diffraction peak intensity $\propto (T_{C=0} - T)^{\beta}$), and the doped material shows evidence for a central peak, similar to SrTiO$_3$ and suggestive of the proximity of a tricritical point. (However, even in the undoped samples, diffuse scattering suggests that the local symmetry is lower than the long-range symmetry [123].)

Another clue is provided by the LTT phase (Section
doping dependence, with T \( \neq 0 \) and the pseudogap temperature is less than the charge ordering temperature, and both are much less that the pseudogap temperature. Nevertheless both the magnetic stripe order temperature \( T_{ms} \) and the pseudogap temperature \( T^* \) have a similar doping dependence, with \( T_{ms} \) vanishing near \( x = 0.2 \) \( [543,544] \) and \( T^* \) near \( x = 0.27 \) \( [99] \). Also, the stripes are more stable in the Nd substituted material than in pure LSCO, just like the LTT phase. This is suggestive that both pseudogap and stripe phases are related phenomena, with the pseudogap being the dominant factor.

Finally, it should be noted that the charge stripe phase in \( \text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3 \) is accompanied by a combined tilt mode and JT structural distortion \( [463] \).

**J. Arguments Against Phase Separation**

The previous experiments have provided considerable evidence in favor of a (nanoscale) phase separation. My own feeling is that the evidence for some kind of phase separation is quite strong. The early experimental results were by and large arrived at independently, without much guidance from theory or even awareness of others’ findings. Indeed, one purpose of the present survey is to gather all these results into one place. The neutron diffraction evidence for striped phases seems decisive \( [543,544] \).

Nevertheless, at this point the harder question must be asked: can such a phase separation account for all experimental observations, or are there some experiments which argue against this picture. Many experiments have simply been interpreted in terms of a uniform system; they should now be reanalyzed to see whether they could also be interpreted in terms of phase separation – particularly in the nanoscale limit, when it is more appropriate to speak of a novel charge bunching phase. Here, I will concentrate instead on those experiments which have been taken as evidence against such phase separation.

Evidence in favor of a uniform phase for the doped cuprates falls into three categories: (a) smooth variation of properties with doping; (b) too much structure as a function of doping; and (c) absence of evidence for phase separation from microscopic probes. In the following paragraphs, I will expand on these arguments, and show how they might be understood within a nanoscale phase separation model (better: in a charge-bunched phase).

Many properties of the cuprates are observed to change smoothly with doping, whereas in a macroscopic phase separation model, they would be expected to take on the two discrete values of the end phases. The most obvious examples are the superconducting transition temperature \( T_c \) and the pseudogap transition \( T^* \). While these quantities are somewhat sensitive to quenching vs. slow cooling, the overall reproducibility of these quantities within many different experiments on many different samples suggests that there is a well-defined, thermodynamic state that the system evolves into as phase separation is confined to ever finer scales. The hypothesis of this review is that charge bunching remains an essential feature of this state.

Once the phase separation is arrested on a sufficiently nanoscopic scale, then the physics is dominated by pattern formation: how to arrange the domains to minimize surface tension – in this case, the excess Coulomb energy. Hence, a certain regularity is expected in different experiments. Moreover, properties should not be expected to change linearly with doping; in particular, many properties will change suddenly at a percolation crossover, Fig. 58.

In the absence of a detailed model of such a state, perhaps an analogy would be useful (the following section will discuss a variety of analogies.) In analyzing Type I and Type II superconductors in a magnetic field, one treats the system as two phase only initially, to justify the separation into Type I or Type II behavior in terms of whether the interfacial surface tension is positive or negative. After that, one treats vortices in Type II superconductors as a form of elementary excitation, and largely ignores ideas of phase separation. For Type I superconductors in the intermediate state, the field domains are much larger, so ideas of phase separation remain important. It is important to note that a given superconductor can be interconverted between Types I and II by appropriate materials processing: introducing disorder or thinning down a sample in the direction parallel to the applied field pushes the material toward Type II behavior.

In the cuprates, there also appears to be a distinction between Type I (more macroscopic) and Type II (nanoscale) phase separation, with Type I behavior promoted by slow cooling from high temperatures and by thinning down samples for electron microscope examination. I think that the great confusion displayed by the data in this section stems largely from incomplete control of these processing steps, and that real progress in this area will come with systematic studies of the effects of processing on the degree of phase separation.

The nanoscale limit of a ‘charge-bunching phase’ is the most interesting, but unfortunately the hardest to understand. A possible model is the charged soliton domain wall model of Section XI. If or (?)equivalently) the ‘Berry-
onic phase’ of doped C_{60}, Section XVII.C. At present, its properties can only be suggested by analogy with Type II superconductors. In these materials, there are not discrete T_c’s for the superconducting and normal (T_\text{c}=0) phases, but a single T_c, which evolves smoothly with magnetic field (i.e., with fraction of the normal phase). Something similar would be expected in the cuprates. In the same way, long mean free paths are quite compatible with Type II superconductivity.

The third type of evidence is the most difficult to handle: there are essentially local probes, which would be expected to show the presence of two different populations of, say, Cu atoms. Indeed, some probes do show such multiple environments, as the NQR and Mössbauer data described above. Yet what is one to make of it if these domains are not seen? (For example, the NMR Knight shifts in LSCO and YBCO are not split at intermediate dopings.) Again, the analogy of the Type II superconductor is useful. Muon spin resonance is a useful probe of the local magnetic field, but in a flux lattice a single sharp response is seen. Detailed analysis shows that the line-shape function is given by the dos of the 2D flux lattice, and the sharp peak is the associated VHS (\textit{!?} \[849\]). Similarly, NMR linewidths are not split, but can be significantly broadened \[\text{[774]}\]. Thus, in the presence of a charge-bunching phase, one needs a full microscopic theory to understand just what a local probe should see. At present, we are far from having such a theory.

In conclusion, these experimental observations constrain the possible form of a charge-bunching phase, and detailed calculations will be required to see if such a phase can be made consistent with all experiments. I strongly urge additional experiments, to further test the ideas of charge bunching. Meanwhile, evidence in favor of such a phase – often in the form of striped phases – continues to mount. Clearly, a better theoretical understanding of these phases is needed – in particular, the compatibility between these phases and the pseudogaps in underdoped cuprates.

### XII. ANALOGS FOR ARRESTED PHASE SEPARATION

Arrested phase separation in the presence of Coulomb effects is not a very well understood phenomenon, and in order to develop model calculations for the cuprates, it is useful to have some analogous systems which have been better studied. Indeed, there is considerable literature on \textit{modulated phases}, which has recently been reviewed \[\text{[550]}\]. A common formalism can be applied to a number of disparate systems. One should also recall the comparison with CDW’s, in Section X.B.3. Indeed, the charge ordered phases seen in the nickelates and manganates (Section XI.H) are very good analogues for the cuprates, and hence eminently suitable for further study.

### A. Dipolar Systems

One class of analogs includes a group of dipolar fluid or polymeric systems characterized by short-range attractive and long-range repulsive interactions. These systems include Langmuir monolayers \[\text{[551]}\], charged colloidal suspensions \[\text{[552]}\], block copolymers \[\text{[553]}\], and ferrofluids \[\text{[554]}\]. In all cases, the phase separation is arrested on a finite scale, but the scale is sufficiently macroscopic that the resulting domain pattern can be visually inspected (the repulsive force typically falls off faster than the bare Coulomb force). Both island and grain boundary (or stripe) phases are common. In a 2D dipolar model, Ng and Vanderbilt \[\text{[555]}\] find stripe phases near half filling and a hexagonal lattice of circular drops at other dopings. A theory of the dynamics of the phase separation has been presented \[\text{[556]}\]. Chemical reactions can also inhibit phase separation at finite length scales \[\text{[557]}\]. The resulting domains (Figs. 2 and 3 of Ref. \[\text{[557]}\]) resemble the mixed phase in a Type I superconductor \[\text{[558]}\], discussed below.

### B. Superconductors

The crossover between the mixed and intermediate states of a superconductor in a magnetic field provides an interesting example of the unusual physics that can arise when domains are restricted to a sufficiently nanoscopic scale. In a finite sample of a Type I superconductor, demagnetization effects at the sample surface lead to a mixed state, with superconducting domains in the Meissner state and normal domains in which the field penetrates. These can form stripe or domain wall phases, but indeed there is a rich variety of possible structures, strongly dependent on the history of how the field was applied, beautifully illustrated in the classical book by Huebener \[\text{[558]}\]. These domains are typically of macroscopic size (there are no charging effects), but are closely related to the intermediate, or vortex phase of a Type II superconductor.

The vortex phase can again be looked upon as a two phase system, but one phase, the normal magnetic phase, is reduced in size to the smallest possible value, a single flux quantum per vortex. Whether the mixed or the vortex phase is found in a given superconductor depends on the sign of the surface tension between superconducting and normal domains: for a positive surface tension, the system tries to minimize the size of the superconducting-normal interface, leading to a perfect Meissner state for an infinite sample, or to the mixed phase in a finite sample. If the surface tension is negative, the system maximizes the amount of interface, by making the size of the normal domains as small as possible. Generally, the sign of the surface tension is taken as the defining characteristic as to whether a superconductor is Type I or Type II. However, in an intrinsically Type I superconducting
film in a perpendicular field, there is a crossover from Type I to Type II behavior as the thickness of the film is decreased \( \kappa \). This behavior follows from Maxwell's equation, \( \nabla \cdot B = 0 \): for a thin film in the Meissner state, the magnetic field would also be excluded from a significant volume of space outside the superconductor, above and below the film. As the superconductor is made thinner, there is not enough condensation energy to compensate for the magnetic energy, so the film enters the mixed state. As the film gets even thinner, the magnetic field must become more and more uniform, so the normal domains shrink until they contain only a single vortex, and the film is effectively Type II.

**C. QHE**

For either the integer or fractional quantum Hall effect (QHE), there is a series of incompressible phases at increasing magnetic fields, associated with fixed (integral or fractional) values of flux to charge density ratio. The intermediate regime, when the field moves between two of these fixed values, has often been described as some sort of two-phase regime, where either the magnetic field or charge bunches up to keep the ratio of charge to flux fixed at the incompressible values. Thus, the free energy of a 2D electron in a magnetic field has a series of downward-pointing cusps corresponding to integral filling of Landau levels, reminiscent of the cusp in Fig. 58a; similar cusps are found for the fractional QHE, due to electron-electron interaction. In 3D electron gases, the integral cusps have long been known to be responsible for a phase separation of magnetic domains (magnetic interaction) \( \kappa \). A variety of percolation or dHvA magnetic interaction models have been proposed. Again, a crossover is found, from uncharged magnetic domains in thick samples, to charged domains with uniform field in thin samples. In the fractional QHE regime, Laughlin's quasielectrons and quasiholes \( \kappa \) play the role of charged vortices: topological excitations corresponding to the smallest unit of a second phase. Chalker and Coddington \( \kappa \) developed a model of this percolation which has been utilized by a number of other researchers \( \kappa \), including for the fractional QHE.

Recently, there has been some experimental evidence of the instability of the uniform phase. Eisenstein, et al. \( \kappa \) have measured the compressibility \( \kappa \) of the 2D electron gas, and find that it is negative over broad ranges of magnetic field. At the fractional steps (filling factor of 1/3, 2/3) they find a peak in \( \kappa^{-1} \), consistent with the broadening of an incompressible state. On either side of the peak are prominent negative minima, interpreted as a broadened negative divergence in \( \kappa^{-1} \) associated with a low density of quasiparticles or quasiholes.

Apparently, the compressibility \( \kappa \) is negative due to the large negative contributions to the free energy from the exchange and correlation energy of a 2D electron gas \( \kappa \), and a similar effect is predicted to occur in zero field, if the density is low enough \( \kappa \). These contributions to the Coulomb energy are both negative, and become more negative as the density increases. Hence, the Coulomb energy would spontaneously lower if the electron gas compressed – the origin of a negative compressibility. So why doesn’t the gas collapse? The reason is that there is a hidden, positive contribution which is actually infinite. That is, the system is overall charge neutral, and the infinite repulsion of the electron gas is exactly compensated by an infinite attraction to a background positive charge.

There are two possible situations. If the positive background is effectively fixed (e.g., due to impurity atom doping), then a spontaneous compression of the electron gas would lead to a net charge imbalance, and an infinite increase in direct Coulomb energy. However, if the electron gas breaks up into neutral cells, and the charge redistributes within each cell in such a way that there is no net dipole moment, then there will be a net energy increase, but diverging only weakly, at the quadrupolar order. The balance of the exchange and quadrupole energy could then lead to a net inhomogeneous electron gas, which would be a form of Wigner crystal.

On the other hand, if the compensating charge can move, then both electron gas and compensating charge can collapse in parallel, until they reach the density corresponding to the minimum of the combined exchange plus correlation energy. Such a state can be realized in a photoexcited semiconductor, in the form of an electron-hole liquid. In this case, the phase separated droplets can attain macroscopic dimensions. Which case applies to the QHE? In GaAs, the compensating positive charge is usually fixed, due to a doping layer, and hence the nanoscale phase separation model is more appropriate.

On the other hand, in a Si inversion layer, the compensation is due to highly mobile charges on the metallic gate. In this case, macroscopic charge islands might form \( \kappa \).

In the integer QHE, something similar has been observed. When a sandwich structure of 2D electron gas above 2D hole gas is formed, macroscopic strips of compressible material form and spread away from the edge states, as the doping is varied \( \kappa \). An interesting possibility is that this phase separation into compressible and incompressible domains is reflected in the energy dispersion in the form of flat bands \( \kappa \).

While the above picture seems to clarify Eisenstein’s data, puzzles remain. The most curious feature is that these are experimental results, even though a negative compressibility would be a violation of the second law of thermodynamics. Presumably, the domains are somehow stabilized by Coulomb effects associated with screening charges in the metallic gates. Thus, while the QHE provides a very interesting analogy to the cuprates, its own physics still needs to be better understood.

In a spin-polarized QHE step, similar textures can arise...
as islands of reversed spins, or ‘skyrmiions’ 876, when the 2D electron gas is doped away from exact rational filling. In this case, the Zeeman effect from the applied magnetic field plays a role analogous to Coulomb forces, making the spin-reversed domains more costly in energy, and leading to a finite domain radius.

D. ‘Relaxor’ Ferroelectrics

Another possible analog is provided by ‘relaxor’ ferroelectrics 877, which display diffuse phase transitions extending over a range of temperatures. There is evidence for nanoscale domains, 30-100Å in diameter, some of which are charged. The suggestion that these nanodomains are stabilized by long-range Coulomb repulsion 878 has led to numerical simulations of this nanoscale phase separation 843.

XIII. THE LTT PHASE IN LBCO, LSCO

While the experimental discovery of the LTT phase helped rekindle interest in the VHS model, there was always something ‘not quite right’ about this phase. In particular, it falls at the wrong hole doping: the VHS seems to be clearly associated with the doping of optimum $T_c$ $x \simeq 0.15 - 0.17$ in LSCO or LBCO, but the LTT phase arises at a much lower density, $\approx 0.125$ in LBCO and $\approx 0.115$ in LSCO. The range over which the LTT phase is stable can be greatly extended by cosubstituting a rare earth (R) ion on the La site, as in La$_{2-x-y}$R$_y$Sr$_x$CuO$_4$ (LSCO:R). While many properties of the LTT phase are independent of cosubstitution, there are some differences. Thus, the LTT phase is present over a broad doping range in the cosubstituted materials, mainly on the overdoped side of optimum $T_c$. In the non-cosubstituted LSCO, LBCO, the LTT phase exists only in a very narrow doping range in underdoped material; it is essentially a line compound, now believed to be a striped phase pinned by commensurability effects, with separate magnetic and charge superlattice 843. Hence, it will be convenient to discuss these two situations separately.

This section will attempt to summarize what is known about this unusual phase and show how it fits into the VHS model. There has been much experimental study of this phase, because superconductivity is found to be suppressed in its vicinity 879,880. In fact, there are four anomalies which are found in the same general doping range: the LTT transition, superconductivity suppression, normal state transport anomalies, and antiferromagnetism. Detailed multiple doping studies on the system La$_{2-w-x-y}$-R$_w$Ba$_x$Sr$_y$Ca$_z$CuO$_4$ have been carried out, with $R = $ Nd, Sm, Gd, or Tm, to determine whether all these anomalies are aspects of a common phenomenon or are independent of one another. While magnetism and $T_c$ suppression seem to be most closely related, the relation of the other two phenomena is less clear, and remains somewhat controversial.

A recent series of experiments on LSCO:Nd has provided a fundamental insight into this problem: superconductivity is suppressed (and a magnetic phase appears) only when the octahedral tilt is sufficiently large, $\Phi \simeq \Phi_c \simeq 3.6^\circ$ 839,881. For smaller tilt angle $\Phi$, superconductivity can persist in the LTT phase with essentially no change in $T_c$. As Nd content $y$ is reduced, the line $\Phi = \Phi_c$ extrapolates to $y = 0$ at $x \simeq 1/8$, thus explaining the anomalous behavior of the LTT phase in LBCO. This behavior follows naturally within the VHS model: the splitting of the density of states peak, due to the lifting of the VHS degeneracy, is proportional to the square of the LTT tilt angle. Only when the angle is large enough would a significant drop in the dos be expected. (Note however that this can only work if the VHS is pinned to the Fermi level in the LTT phase. In the following sections, evidence will be presented for the nanoscale phase separation which produces this pinning.) In light of these experiments, the cosubstituted material with $R = $ Nd is better understood than the $x = 1/8$ phase, and will be discussed first.

A. LTT in LSCO:Nd

Rare earth (R) cosubstitution in LSCO (La$_{2-x-y}$R$_y$Sr$_x$CuO$_4$) greatly extends the doping range over which the LTT phase is present, and allows some separation of hole doping vs structural effects. Starting from the doping of optimum $T_c$, the LTT phase is favored by enhancing the interlayer mismatch, either by decreasing the doping (less Ba,Sr) or by decreasing the average ionic radius at the La site (by substituting Nd, Eu, Gd, Dy, Tb) 823. Many experiments have used $R = $ Nd, since this can be doped up to $y = 0.75$ before converting to the $T'$ structure (the structure of Nd$_2$CuO$_4$, the parent compound for the electron-doped superconducting cuprates, with no apical O’s). In this compound, while many anomalous properties are found at arbitrary doping, two particular hole compositions, $x = 1/8$ and 0.15, appear to be special.

Thus, in LSCO:Nd the doping $x \simeq 1/8$ displays much stronger $T_c$ suppression, onset of localization, and Hall and thermopower anomalies 882,883. At $x \simeq 0.15$, which has the highest $T_c$ when $y = 0$, there is a sharp, first-order transition when $y \geq 0.18$ 884, which is both an LTO-LTT transition and a superconductor-insulator transition. For $0 < y < 0.18$, the LTT transition, which would occur at a lower $T$ than the superconducting transition, is arrested at $T_c$, and there appears to be a phase separation, with the Meissner fraction being approximately 1 - (fraction of LTT phase) 825, while there is a small residual fraction of superconducting material at larger $y$.

For $x < (>)0.15$, there is a wide range of Nd doping for
which a Pccn (LTT) phase is stable. The most interesting results have to do with overdoped samples, $x > 0.15$. In these samples, there is a wide range of Nd doping for which $T_c$ is also suppressed, but only if the octahedral tilt exceeds a critical value, $\Phi \geq \Phi_c \approx 3.6^\circ$[13]. For smaller tilts, the LTT phase is stable, but superconductivity is not reduced, and there are no resistive anomalies. At the same value of critical tilt that suppresses $T_c$, the resistivity has a sharp jump at the LTT transition, and increases with decreasing $T$ in the LTT phase. Moreover, at approximately the same Sr doping, magnetic anomalies suggestive of local antiferromagnetic order (but with much larger transferred hyperfine fields than in antiferromagnetic LCO) appear below $\approx 32K$ [885]. The magnetic transition may be driven by a critical tilting, due to spin-orbit coupling [866]. There also seems to be a change in the nature of the LTO-LTT transition, at a critical tilt similar to $\Phi_c$[125]: for larger $\Phi$ values, the transition is sharp and first-order: the orthorhombic splitting of LTO X-ray peaks remains unchanged, while an unsplit LTT peak appears between them, and grows in intensity as the transition proceeds. For smaller $\Phi$, the transition is smeared or continuous, with the orthorhombic splitting continuously decreasing as the transition is approached. From the available data, it is not possible to tell if this change occurs precisely at $\Phi_c$ or not.

The two special dopings, $\approx 1/8$ and $0.15$, also seem related to the critical value of $\Phi_c$. The first doping is at the intersection of the lines $\Phi = \Phi_c$ and the line $y = 0$. At $x = 0.15$, the sharp superconductor-insulator transition is due to the coincidence that at this doping the LTO-LTT transition intersects the $\Phi_c$-line. By using a different RE from Nd, this intersection is shifted to a lower doping, and it is possible to have bulk superconductivity in the LTT phase, even at $x = 0.15$, when $\Phi < \Phi_c$.

Thus, in LSCO:Nd, the superconducting, resistive, and magnetic anomalies all appear to be correlated, and all occur in the LTT phase when the octahedral tilt exceeds a critical value. While it is possible that the large tilt drives the magnetic transition, which in turn quenches superconductivity, this picture does not explain the resistive anomaly at the LTT transition, which rather suggests a large modification of the Fermi surface. Indeed, the entire sequence of anomalies is just what would be predicted by the VHS-JT effect, in which the structural distortion splits the VHS degeneracy. However, this explanation can work only if the VHS remains pinned at the Fermi level over this extended doping range. In fact, overdoped LSCO is believed to phase separate, with one phase remaining pinned at the VHS (Section XII.F). Can such a model also apply to LSCO:Nd? The materials preparation technique used in these studies is known to produce significant local variability of Sr content (i.e., of hole content) [865], while there is clear evidence of phase separation in the regime $\Phi > \Phi_c$[13]. Even in this regime, there is evidence for a superconducting transition, with zero resistivity; however, the Meissner fraction is very small and the resistivity is restored by a small magnetic field. These superconducting domains appear to be fairly large: the onset of the resistive transition falls at nearly the same temperature over an extended range of Sr doping (see Fig. 3 of Ref. [13]), as expected for macroscopic phase separation.

Given the picture of nanoscale phase separation discussed in Section XI.F, the results on LSCO:Nd can be readily understood in terms of the splitting of the VHS degeneracy in the end phase at $x \approx 0.15$. What is learned in these experiments is that (a) the same VHS splitting (same critical tilt angle) holds throughout the overdoped regime; and (b) even at the VHS, $x = 0.15$, as Nd is added there is a phase separation. This is associated with the LTT-LTO transition, but is highlighted by the fact that superconductivity is destroyed only in the LTT phase (even though both phases have the same magnitude of $\Phi$).

One note of caution should be sounded: while there is a clear correlation between the LTT transition and the metal-insulator transition in Nd-doped material, the correlation is less clear when other ions are substituted. In mixed La$_{1.775}$Ba$_{0.125}$Sr$_x$CuO$_4$, a resistivity minimum is found at higher $T$ than the LTT transition[884]. In another study, the LTT phase was probed by studying La$_{1.775}$R$_{0.10}$Sr$_{0.125}$CuO$_4$, with $R = $ La, Nd, Sm, Gd, or Tb [887]. The results fall into two groups, with Nd very similar to La, and the other R’s showing very different behavior: for these, there is a well-defined LTT transition, with the transition temperature varying strongly with $R$ (up to $\approx 150K$ for R=Tb), but the anomalies in $\rho$ and $S$ fall at $\approx 80–100K$, independent of $R$. Thus the electronic and structural anomalies are not completely correlated. Again, there may be a problem of critical tilting for the VHS splitting to affect the electronic properties. This would go in the right direction: the smaller the ionic radius of $R$, the worse is the interlayer mismatch, so the LTT transition occurs at a smaller VHS splitting.

### B. LTT Phase as a Striped Phase

What is special about $x \approx 1/8$? In the VHS model, I believe there are two competing effects. First, an LTT-type structural instability is favored by the VHS-JT effect when the Fermi level is at the VHS, $x \approx 0.15 – 0.17$. However, at this high doping the interlayer mismatch is small, so the octahedral tilts are small, $\Phi < \Phi_c$, with small barriers between adjacent potential minima. This leads to a dynamic LTO phase near the VHS, with local LTT symmetry and dynamic domain walls; experimental verification of this prediction was discussed in Section IX.B. When the interlayer mismatch increases, by, e.g., reducing the hole doping, $\Phi$ gets larger and the potential barriers increase, leading to a more static LTT phase. Extrapolating the LSCO:Nd data, $\Phi = \Phi_c$ at $x \approx 0.125$, and the LTT phase appears near this doping, with reduced $T_c$. However, for smaller $x$, the AFI phase (with
LTO-type tilting stabilized by AFM umklapp scattering) tends to dominate. Thus, there is only a narrow window where a static LTT phase is stable. Within this window, commensurability effects act to pin the phase at a fixed doping.

The $T_c$ suppression is closely correlated with an antiferromagnetic phase, and both are pinned at a commensurate doping value, $x = 1/8$, in LBCO \cite{897,773}, but at $x \approx 0.115$ in LSCO \cite{888,773}. Double doping experiments \cite{889} have demonstrated that the $T_c$ suppression occurs at a fixed hole content $x$, and does not depend on, e.g., Ba concentration. Similar results but at a, b-plane, as in La$_2$CuO$_4$, by introducing oxygen defects (i.e., δ < 0, which occur predominantly in the CuO$_2$ planes) \cite{890,891}. Again, the largest $T_c$ suppression occurs when $P \approx x + 2\delta = 0.125$, but as $|\delta|$ increases, so does the value of this minimum $T_c$. At the same time, the LTO-LTT transition temperature is enhanced. Finally, hydrostatic pressure suppresses the LTT transition and enhances $T_c$ and the Meissner fraction, but these still remain small compared to other doping values \cite{892}. Near the critical filling, the Meissner fraction is reduced \cite{773}, but there is not a perfect correlation between Meissner fraction and reduced $T_c$. It appears that the Meissner fraction is reduced over about the same doping range in which the antiferromagnetic phase exists. This range is considerably less than the range over which the LTT phase appears (in LBCO), but on the other hand, the $T_c$ reduction is confined to an even narrower range, particularly in LSCO.

The magnetic ordering was detected by $\mu$SR \cite{893,888} and by Cu and La NMR \cite{773}. The transition appears to be antiferromagnetic, with Cu moments pointing in the a,b-plane, as in La$_2$CuO$_4$, with a Néel temperature ≈30K. The internal field is smaller than in La$_2$CuO$_4$, but different groups find different values, in the range of $\sim 0.1 - 0.26 \mu_B$ per Cu \cite{773,894,892}. The small size of the moment is not uncommon for an antiferromagnet with a low $T_N$. Magnetic order at such a high doping is quite surprising for the cuprates, and may be a sign of a commensurate phase separation, such as the stripe phase found in LSNO, Section XI.H – perhaps similar to the soliton model discussed in Section VIII.C.6, which involves domains of LTT phase, with domain walls of LTO phase, Fig. 49. Indeed, recently, Tranquada, et al. \cite{543} found neutron diffraction evidence for a coexisting magnetic and charge domain striped phase in Nd-substituted LSCO; this will be discussed in the following subsection.

The LTT phase in LBCO resembles the Ortho II phase of YBCO, in that it seems to be associated with a fixed filling fraction $\approx 1/8$ (see the discussion of Fig. 43). Near this filling, earlier studies found that the holes form two types of domains, one of LTO phase with optimal $T_c$ and the other of LTT phase with reduced $T_c$ \cite{890}, with domain size $\approx 300\AA$ \cite{153}. (The orthorhombic domains have greatly reduced orthonormicity, and may be of Pcn rather than LTO symmetry \cite{457}.) In the mixed LTT-LTO regime, $T_c$ of the LTT phase depends on doping, possibly due to elastic strain effects between the two types of domain \cite{896}. There are contradictory results on the doping range for coexisting LTT and LTO order, with some studies finding a large LTT fraction only at the doping of maximum $T_c$, reduction \cite{789,499}, while others find that the LTT transition is nearly complete ($< 5\%$ LTO phase) over a wider range, at both $x = 0.125, 0.15$, while only at the former value ($x = 1/8$) is superconductivity suppressed \cite{897}. This is consistent with the LSCO:Nd results, since $\Phi < \Phi_c$ at $x = 0.15$.

The situation in LSCO is even less clear. The $T_c$ suppression is confined to an extremely narrow range of $x$. Acoustic measurements suggest the onset of LTT-type order in this vicinity \cite{568}, but long range order has not been found by x-ray or neutron diffraction. In a study where Sr or Ca was substituted into LBCO in such a way as to keep the hole doping fixed at $x = 0.125$, the onset of $T_c$ depression was found to coincide with the onset of the LTT phase \cite{898}. At $x = 0.115$, an electron diffraction study \cite{899,561} finds evidence for the LTT transition in LSCO, with onset at 110K – that is, at a higher $T$ than in LBCO, $x = 0.125$, for which the onset is at 70K. The electron diffraction study also finds superlattice spots; when the structure is modified by Sm addition, as La$_2-x-y$Sm$_x$Sr$_y$CuO$_4$ \cite{61}, the superlattice spots seem to occur only at $x \approx 0.115$. Such a combination of magnetic and structural anomaly resembles those seen in La$_{2-x}$Sr$_x$NiO$_4$ (Section XI.H) and in LBCO at $x = 0.125$ \cite{543}. However, some caution is advisable. It is possible that the superlattice spots are an artifact, due to double diffraction \cite{458}. In addition to the electron microscopy, there is an anomaly in the specific heat of LSCO, $x = 0.09$, at $T=70K$, which resembles the LTT transition in LBCO \cite{500}. Also, at $x = 0.12$, Raman scattering \cite{563} finds evidence for Raman forbidden phonons, as if very close to this composition, the inversion symmetry of the crystal is lost, due to local distortions. There are also anomalies of the low-T Raman shift for several Cu-O related phonons \cite{501}. Thus, more work is required to determine if this interesting superstructure is really present in LSCO, $x = 0.115$.

The VHS model also provides an explanation of why this anomalous phase occurs at different dopings in LBCO and LSCO. In a VHS model, commensurability can refer to a rational fraction of the VHS density, $xVHS$, rather than a rational hole per atom value. Thus, in LSCO, the VHS falls at a doping $x = xVHS \approx 0.14 - 0.17$. If $xVHS = 1/6$, then a commensurate superlattice with three cells doped to $x = xVHS$ and the fourth undoped would fall exactly at $x = 1/8$. On the other hand, if $xVHS < 1/6$, the supercell would have to have commensurations to exactly match the VHS doping, and would have $x < 1/8$. 

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C. Combined Magnetic and Charged Stripes

In Nd-substituted LSCO, \( \text{La}_{1.48}\text{Nd}_{0.4}\text{Sr}_{0.12}\text{CuO}_4 \), Tranquada, et al. [543] have found neutron diffraction evidence for a phase consisting of alternating magnetic and charge stripes. The charge periodicity is four cells, and the magnetic periodicity is twice as large. In the presence of Nd, the distortion is static, but it is hypothesized that the same striped phase is present dynamically in the Nd-free material, since the degree of incommensurability \( \epsilon \) is the same in both materials. The results have now been extended to higher doping, \( x = 0.15, 0.2 \) [544]. The charge ordering cannot be studied in much detail, given the weakness of the diffraction peaks, but the magnetic phase transition decreases with increasing doping, falling below \( \approx 15K \) at \( x = 0.2 \). The doping dependence of \( \epsilon \) matches that of LSCO. In the VHS model, it is surprising to find stripes persisting to \( x = 0.2 \), above optimum doping. However, it should be recalled that the pseudogap in LSCO only closes around \( x \approx 0.27 \), Fig. 21 [99]. Moreover, the slope of \( \epsilon(x) \) has a sharp break near \( x = 0.12 \), suggesting a change in the nature of the stripes. In general, the stripe ordering temperature has a doping dependence parallel to that of the pseudogap, but is much smaller in magnitude.

A simple model of the stripes is as follows: there are alternating charge stripes of width \( M_0 \) (in units of the lattice constant \( a \)) and magnetic stripes of width \( M - M_0 \), so the total charge stripe repeat distance is \( M \). The magnetic stripes are assumed to be undoped, while the hole doping in the charge stripes is \( x_0 \). Thus, at a doping \( x \), we must have \( xM = x_0M_0 \). The degree of incommensurability is then \( \epsilon = 1/M \). For \( x \leq 0.125 \), the experiments find \( \epsilon = 1/2x \) implying that \( x_0M_0 = 1/2 \). This is compatible with the assumption that both the charge stripe doping \( x_0 \) and the width of the charged stripes \( M_0 \) are independent of doping.

This model can explain why the magnetic periodicity is twice the charge periodicity. If the exchange coupling across the charge stripes is antiferromagnetic, then the rows of spins separated by the charge layer are out of phase. If the magnetic stripe contains an odd number of (AFM coupled) rows, the first and last row will be identical. Hence, the first rows of adjacent cells will have opposite spin order, so the magnetic periodicity is doubled. Note, however, that if the magnetic cell had an even number of rows, there would be no period doubling. Hence, to explain the experimental observation that the magnetic periodicity evolves smoothly with doping, it must be assumed that the magnetic stripes can only have an odd number of layers. Alternatively, the magnetic stripes would all have to be even if the intercell exchange were ferromagnetic.

On analogy with the nitrates, Tranquada, et al. [543] propose that the stripes consist of three cells of undoped, antiferromagnetic phase, and one cell of hole-doped boundary phase, \( M_0 = 1 \), with \( x_0 = 0.5 \), leading to an average doping of \( 0.5/4 = 1/8 \). However, the analogy with LSNO is far from exact. Thus, in LSNO, the stripe phases extend throughout the full doping range, with strong commensurability effects found at all commensurate filling factors, with the largest effects at the lowest factors, 1/2 and 1/3. In comparison, if \( x_0 = 0.5 \) in LSCO, then the strongest anomalies would be expected at \( x \approx 0.166, 0.25 \), instead of the near complete destruction of superconductivity at 0.125, with nothing comparable at the higher filling fractions.

Moreover, in the Nd-substituted LSCO, the stripe phase periodicity deviates strongly from that expected for constant-density charge stripes above a doping \( x \approx 0.12 \). Whereas for \( x \leq 0.12 \), \( \epsilon \approx x \), for higher doping, \( \epsilon \) saturates near a value \( \epsilon_m \approx 1/6 \). I suggest that this saturation can be best understood if \( M_0 > 1 \). Thus, assuming that the stripe width is \( M_0 = 3 \), the corresponding hole density in the stripe domains becomes \( x_0 = (4/3) \times (1/8) = (1/6) \), close to the doping of optimum \( T_c \) for LSCO. Or, if \( M_0 = 2, x_0 = 1/4 \), somewhat large for the optimum doping, but close to the doping at which the pseudogap is found to close, Fig. 21 [44]. A case could be made for either value, and since the interpretation of the data is different in the two cases, I will briefly discuss both.

First, assume \( M_0 = 2 \). The saturation of \( \epsilon \) can be understood as follows: if \( M_0 = 2 \), then the at \( x = 0.12 \), the magnetic stripe is two cells wide. From our earlier discussion, the magnetic cell width must always try to be even, so \( x = 0.125 \) is the highest doping at which this phase is stable. For higher doping, the magnetic stripes become only one cell wide, yielding \( M = M_0 + 1 = 3 \), or \( \epsilon = 1/6 \). Because of the reduced stability of the magnetic cell, the magnetic transition temperature drops rapidly. For higher doping, the magnetic cells would be eliminated, leaving a pure charge phase, which does not contribute to the magnetic diffraction peak.

For \( M_0 = 3 \), the saturation of \( \epsilon \) is easily understood: the magnetic stripes are eliminated, leaving a uniform charge-ordered phase. But then, why is there an incommensurate diffraction peak at all? This seems to require two effects. First, the charges themselves must be ordered. Something like this happens in \( \text{La}_{2-x}\text{Sr}_x\text{MnO}_3 \), where a \( x=1/8 \) phase has now been found [545], Section XL.H.5. The phase consists of alternating layers of undoped material and a uniform charge-ordered phase of one hole per 4 sites. For Nd-substituted LSCO, there would have to be an ordered array of one hole per six lattice sites. Moreover, this hole phase would have to be magnetic. This would be consistent with the findings of Büchner, et al. [439], that a new, insulating magnetic phase appears in this doping regime when the tilt angle is larger than a critical value.

From either of the above models, the expected doping of the critical phase \( \epsilon_m = 1/6 \) is \( x = 1/2M = 1/6 \). However, \( \epsilon \) only asymptotically approaches this value for \( x \geq 0.2 \). This suggests that at high Sr doping, some holes dope sites which are off of the CuO\(_2\) planes. This could
help explain a number of anomalous features of overdoped LSCO: for instance, susceptibility and heat capacity studies find that the VHS gap only closes at \( x \approx 0.27 \) [19]; the phase diagram in Fig. 3a also suggests that the gap does not quite close at \( x = 0.17 \), but remains fairly constant for an extended doping range. Furthermore, the thermopower [205, 206, 514] and the pressure dependence of \( T_c \) [273, 270] both deviate from the ‘universal’ curves in overdoped LSCO.

One residual problem is to reconcile the magnetic phases found by Tranquada, et al. [543, 544] with those found by other groups. The transition temperatures found by Tranquada, et al. [544] \((T_m \approx 50, 43, \text{ and } 14K\) for \( x = 0.12, 0.15, \text{ and } 0.2, \) respectively) are close to the temperature found by Breuer, et al. [885] \((T_m \approx 32K \text{ at } x = 0.12)\) in Nd-substituted LSCO, and to the magnetic ordering temperature found in LBCO, Fig. 64. \( T_m \approx 30K \text{ at } x \approx 0.12. \) However, the magnetic transitions in LBCO do not evolve smoothly to the Néel temperature as the doping is reduced, but fall off below \( x = 0.12, \) while the magnetic phase seen by Breuer, et al. is associated with a critical tilting angle, \( \Phi > \Phi_c, \) which again only holds for \( x \geq 0.125 \) [43]. Hence, the magnetism seems more probably associated with the hole-doped stripes, and not with the ‘magnetic’ stripes.

**XIV. THE RENORMALIZATION GROUP THEORY: RELATION TO 1D METALS**

As seen above, the VHS plays an important role in both superconductivity and structural instability. This same competition is found in the old high-\( T_c \) superconductors, the A15’s, and in the g-ology theory of 1D metals [8]. In 1D perturbation theory, it is found that if both superconducting and charge-density instabilities are treated on an equal footing, they exactly cancel each other out. The renormalization group (RG) proved to be a powerful technique for studying a system with such competing instabilities. It was found that, in exploring the full parameter space of the electron-electron interaction parameters, \( g_i, i=1,4, \) the leading divergence can be either CDW or spin density wave (SDW) or singlet or triplet superconductivity.

Dzyaloshinskii [1] and Schulz [2] pointed out that the VHS theory also contains competing divergences – this time \( \ln^2 \) divergences – and suggested that a similar renormalization group (RG) calculation could be applied to the VHS. The idea is that, since the singularities all arise in the immediate vicinity of the VHS’s, the dominant singularities are properly described if the entire Fermi surface is replaced by a set of points associated with each VHS. Now, in the usual Brillouin zone scheme there are four VHS’s, at the \( \pm X \)-points and the \( \pm Y \)-points of the zone. However, the points \( +X \) and \( -X \) are separated by a reciprocal lattice vector, so are really the same point. Hence, the reduced Fermi surface consists of two points, at \( X \) and \( Y \). Near the \( X \) (\( Y \)) point, the Cu-O hybridization is essentially 1D, with hopping only in the \( x \) (\( y \)) direction along Cu-O-Cu-O bonds (in the CuO$_2$ planes). In the 1D metal, the Fermi surface also consists of two points, but at \( \pm X/2 \), for the case of half filling. This picture of a two-point Fermi surface bears a close relation to the band Jahn-Teller (JT) effect, discussed in Section VIII.C.3.4, where the two VHS’s provide the electronic degeneracy.

**A. Renormalization Group Calculations**

The early work of Dzyaloshinskii and Schulz considered only the most singular case, corresponding to a square Fermi surface at half filling \((t_{OO} = 0 \text{ or } t' = 0)\) In this case, there are \( \ln^2 \) singularities both in the Cooper channel, supporting superconductivity, and in the zero-sound channel, favoring CDW or SDW instability [2]. Dzyaloshinskii and Yakovenko [502] showed that there could be a very rich phase diagram, depending on the values of the electron-electron coupling constants, \( G_i \).

In the Hubbard model, all \( G_i \)'s are equal, \( G_i = U/4\pi t \), and the density wave instability will dominate – SDW or CDW depending on the sign of \( U \). If, following Schulz [2] we assume that the on-site Coulomb repulsion \( U > 0 \) dominates the electron-electron interaction, the singularity at half filling will be SDW. A large \( U \) suppresses both CDW and sSC (s-wave superconducting) responses, while enhancing dSC (d-wave superconducting) response, although the SDW response still dominates.

Schulz [2] showed that, if the material is doped away from half filling, the SDW response is suppressed, while the dSC response is unaffected, so that at critical doping the material will cross over to a d-wave superconducting state. I would suggest a slight variant on this calculation. The VHS actually falls away from half filling, at a finite hole doping, due to \( t_{OO} \neq 0 \), although correlation effects can keep the VHS pinned near the Fermi level over an extended doping range (Section VII.B). The resulting competition between CDW and sSC was analyzed in mean-field theory [105], by assuming that the pinning is perfect, so that for all dopings, the curvature of the Fermi surface changes in such a way that the VHS is always at the Fermi level (Section VII.B). For a square Fermi surface, at half filling, the nesting dominates, leading to a CDW instability. Once \( t_{OO} \neq 0 \), for intermediate dopings, nesting becomes weaker, and the \( \ln^2 \) divergence of the CDW susceptibility is cut off to \( \ln \). In this regime, the CDW and superconducting instability can coexist, with the superconducting \( T_c \) increasing with doping, Fig. 52.

This VHS pinning model can readily be applied to the RG calculation. When the VHS Fermi surface is not square \((t_{OO} = 0 \text{ or } t' = 0)\), the Cooper pair diagram still diverges as \( \ln^2 T \), while the zero sound diagram is cut off at low temperatures, leaving only a \( \ln T \) divergence. Figure 70 shows a numerical integration of the RG equations.
(details of the calculation are in Appendix D), both for $t_{O0} = 0$ and for a finite $t_{O0}$. In both cases, all $G_i's$ are assumed to be equal initially. In the former case (corresponding to half filling), $G_{SDW}$ is the first coupling to diverge, suggesting that SDW order is dominant. This is consistent with experiment on LSCO, where a weak interlayer coupling stabilizes the strong antiferromagnetic (AFM) fluctuations of the cuprate planes. In the latter case (corresponding to doped LSCO), as soon as the zero sound diagrams are cut off the SDW divergence is weakened, and $G_{dSC}$ is the first term to diverge, suggesting a transition to (d-wave) superconductivity with doping.

A number of remarks are in order. (1) A strong electron-phonon coupling would expand the range of CDW and sSC fluctuations, acting in many ways like a negative-$U$ contribution. If a negative $U$ is assumed, the same calculation would lead to a transition from CDW to sSC as a function of doping. (2) This latter RG calculation is in good agreement with the mean-field calculation of the same model. The latter calculation provides some additional insight. In particular, for a 2D model the dominant singularity does not necessarily eliminate a second phase transition involving a subdominant singularity, since the first transition need not wipe out the entire Fermi surface. Hence, one might expect to find a doping regime in which both density wave (at higher T) and superconducting transition (at lower T) both occur.

So which situation corresponds better with experiment? While LSCO has both an SDW (AFM) instability at half filling and a superconducting transition at finite doping, the two transitions do not overlap, but are separated by a doping regime which is 'spin-glass-like'. On the other hand, if I am correct in identifying the pseudogap as a short-range CDW, then the overall CDW-SC phase diagram is in good agreement with the predictions of the mean field model. Furthermore, the fact that the pseudogap onset temperature in LSCO is always higher than the AFM temperature suggests that CDW effects are stronger. Once the carriers are localized in the CDW state, there could still be a transition to an AFM ordered state at lower temperatures near half filling.

B. Bosonization and the RG Theory of the Fermi Surface

Stimulated by the suggestion that strong correlation effects could lead to a breakdown of Fermi liquid theory in the cuprates, a number of researchers have been exploring the microscopic derivation of Landau Fermi liquid theory, or of some generalized form, such as Luttinger liquids. The main approach has been to seek a generalization of the 1D bosonization technique into higher dimensions, based on the early work of Luther and Haldane. These bosons (electron-hole pairs) behave as sound waves which propagate on the Fermi surface. In this case, the vanishing of the quasiparticle residue ($Z = 0$) is equivalent to the vanishing of the surface tension on the Fermi surface, and signals a phase transition at the Fermi surface. This suggests that the dynamic JT state could be interpreted as a quasi-Bose condensation, since the Fermi surface becomes a slowly varying function of real-space position and time.

A perturbative RG theory of Fermi liquids has been developed. Unfortunately, most of the calculations to date have avoided the highly singular behavior in the immediate vicinity of the VHS’s, but many findings are still relevant. For instance, the Fermi liquid picture is very stable, and it has proven difficult to make a Luttinger liquid in any dimension greater than one. The 1D Luttinger fixed point is a result of the lack of phase space, i.e., the fact that the Fermi surface consists of just two points! Hence, the Dzyaloshinskii-Schulz models of the VHS suggest a new possibility: to the extent that the VHS Fermi surface almost consists of just two points, does this mean that, at that particular doping, the holes almost form a Luttinger liquid? A start of a RG theory of the VHS has now been undertaken by Gonzalez and coworkers. They find that the self energy contains nonlocal divergences, creating a situation reminiscent of string theory. They are able to show the existence of a nontrivial, unstable fixed point, and that above a critical coupling, $U/t$, the renormalization scales to strong coupling.

XV. A PUZZLE: THE ELECTRON-DOPED CUPRATES

From the Fermi surface shown in Fig. 1, one might think that the electron-doped cuprate superconductors were completely understood: the VHS is far away from the Fermi level, so $T_c$ is low: case closed. But this is far from the complete story. In the first place, 22K is a low $T_c$ only in the context of the cuprates. More importantly, the Fermi surface of Fig. is hole-like, whereas most transport measurements reveal the electron-doped cuprates to be electron-like. The possible presence of surface states in the vicinity of the Fermi energy would complicate the interpretation of photoemission spectra in terms of bulk bands.

There is considerable evidence in these materials for multiple phases, with the superconductivity associated with a phase which is stable only in a narrow composition range near optimum $T_c$. For example, in Nd$_{2−x}$Ce$_x$CuO$_4$, Billinge and Egami find evidence for two domains of local structural distortions (domain size $≈$ 6Å). In one domain, the CuO$_2$ planes appear to be flat, as expected from the macroscopic symmetry. In the other domain, the planes are buckled, having a symmetry similar to the LTO phase of LSCO! This happens even though the CuO$_2$ plane appears to be under tension, and such buckling would be expected to be energetically
unfavorable. Moreover, the superconductivity seems to be associated with these tilted domains.

Near the optimal Ce doping of NCCO, the properties of the material are sensitive to excess oxygen [12, 14]. This oxygen tends to localize carriers, favoring magnetic over superconducting order. Even in deoxygenated samples, superconductivity coexists with a large volume fraction (≈ 50%) of magnetic clusters, ≈ 25 – 250Å in diameter [913, 915]. With decreasing oxygen, the Hall coefficient changes from electron-like to hole-like, with optimum Tc falling near the crossover point [916, 917]. Jiang, et al. [917] speculate that the sign change is associated with an electronic heterogeneity, with the hole-like regions associated with the tilted domains found by Billinge and Egami. Mössbauer studies, on a sample with ≈ 20 – 30ppm $^{57}$Co substituted for Cu, found that the superconducting fraction is correlated with a particular five-fold coordinated site – i.e., having one excess oxygen present at an apical site [918]. If the holes superconduct (see also Ref. [118]), then these compounds are more similar to the conventional cuprates. However, the LDA band structure cannot be trusted in detail, since the hole content at optimum doping is not known, and the local structure differs from the macroscopic symmetry, due to oxygen tilts and a possible apical oxygen.

In the related Gd$_2$CuO$_4$ compound, there is a structural distortion of the planar O’s, which can be responsible for the non-observation of superconductivity in this compound, and the simultaneous appearance of weak ferromagnetic order [119]. While the distortion was reported to involve motion of the O’s along the c-axis [120], a detailed analysis finds long range order involving rotations of the O squares about the c-axis [50]. The same structure is found in Nd$_{2-2x}$Y$_x$Ce$_2$CuO$_4$, when $x = 0$, $y = 1.62$ (chosen to have the same average ionic radius as Gd). Hence, the competition of superconductivity with structural instability could be probed by fixing $x = 0.15$ and varying $y$. Increasing $y$ from zero clearly suppresses the superconducting instability, and there is a range of $y$ for which neither superconductivity nor long range structural order is present.

The recent series of experiments on the pseudogap in underdoped cuprates [115, 83, 88, 99] raise an interesting possibility: that the shift of the VHS from the Fermi level is actually the manifestation of the opening of the pseudogap. If one extends this result to NCCO, then there may be a gap near the Fermi level, leaving residual ungapped electron-like pockets. It would be very interesting to search for such effects.

XVI. THE 3D VERSION: BKBO/BPBO

Within the Van Hove scenario, the bismuthates resemble 3D analogs of the cuprates. In BaBiO$_3$, the Fermi level is predicted to fall very near the VHS’s of the cubic phase (Figs. 15 and 16), but a CDW leads to a monoclinic distortion, producing a 1.9eV gap at the Fermi level. In a tight-binding model of the Fermi surfaces, keeping only nearest neighbor Bi-O hopping, the Fermi surface at half filling is perfectly nesting, leading to a strong CDW instability.

This CDW was initially discussed in terms of breathing mode distortions, accompanied by 2Bi$^{4+}$ → Bi$^{3+}$+Bi$^{5+}$ disproportionation – a 3D version of striped phases. However, there is also an octahedral tilting mode distortion in BaBiO$_3$, and recent evidence suggests that this distortion is even more important for the structural instabilities. Thus, LDA calculations find that it is necessary to include both distortions to reproduce the experimental gap [21]. A pure tilt distortion accounts for ≈ 76% of the energy gap. The charge disproportionation amounts to less than 0.1e per Bi; this is consistent with the non-observation of a split Bi peak in photoemission (see Ref. [22] and references therein). The small degree of charge disproportionation suggests that the CDW electrons are localized on the short Bi-O bonds (a bond-order CDW) rather than on the Bi (a site-diagonal CDW) [23]. The role of the tilting is clear: the LDA finds significant distortions from a perfectly nested Fermi surface at half filling, due to more distant neighbor hopping. The tilting reduces this hopping, bringing the Fermi surface closer to nesting. The breathing mode may still play an important role in producing the strong electron-phonon coupling required for superconductivity [21] – again, in close analogy to the situation in LSCO (Section VIII.D).

Once Pb is substituted for the Bi, or K for Ba, in Ba$_{1-x}$K$_x$Bi$_1$-$y$Pb$_y$O$_3$, the breathing distortion is rapidly eliminated, near $x = 0.1$ or $y = 0.23$ [24], leaving an orthorhombic structure ($Ibmm$) with a pure tilt mode distortion. In both BKBO and BPBO, superconductivity seems to be associated with a metastable phase. In BPBO, superconductivity is found for $0.70 \leq y \leq 0.80$, in a tetragonal phase ($I4/mcm$) which is metastable with respect to the orthorhombic phase below $\approx 450K$ [24,25]. Both the tetragonal and orthorhombic phases have nearly the same magnitude of tilt distortion, but the direction of distortion is different, and yet only one phase is superconducting! In the two-phase regime at lower temperatures, the phase separation cannot be macroscopic, since the lattice parameters of both tetragonal and orthorhombic phases vary smoothly with doping.

In BKBO, superconductivity occurs in a cubic phase, but at K concentrations above the room temperature solubility limit, so a two step process (high temperature anneal to incorporate K, lower T anneal to fill O vacancies) is required to prepare the superconducting phases [26]. Within the cubic phase, Tc increases with decreasing $y$, having its maximum value at the cubic-orthorhombic phase boundary, which is also a metal-insulator transition. In mixed compounds (both $x$ and $y$ nonzero), Tc appears to be a smooth function of $x + y$ only, with Tc increasing monotonically as the doping is reduced towards half filling, where the CDW instability is largest [24,27].
A major puzzle in these materials is to understand why they are insulating over such a broad doping range; a nesting transition should only occur in the immediate vicinity of half filling. One suggestion is a phase separation between insulating and metallic domains \[923,924\], Fig. 71. However, a *macroscopic* phase separation can be ruled out by, e.g., the continuous variation of the plasma frequency \[925\] with doping. A number of early theories (based, however, on the breathing mode CDW) postulated a local, or incommensurate CDW order \[921\]. (For a 2eV gap, the coherence length would only be a few A’s.) \[932\] did numerical calculations on a finite lattice, and found that doping preceded by the formation of a local polaron, then bipolaron, with a tendency for cluster formation: i.e., a local phase separation of the added holes. Experimentally, electron diffraction has found evidence for an incommensurate modulation throughout the full doping range of BKBO, but this is not found in neutron diffraction studies, and seems to be enhanced by electron beam heating. A full discussion, with additional references, is found in Ref. \[933\].

A small fraction of superconducting phase is found in insulating BPBO materials \[934\]. Optical studies find clear evidence for a *pseudogap*: a gap is found, peaked at 1.9eV, in pure BaBiO\(_3\). As the material is doped, with either Pb \[935\] or K \[936\], the peak broadens and shifts to lower energy, but remains present for virtually all dopings. Just as with the mid-infrared peak in the cuprates, there is some controversy on this issue, at least in BKBO.

Sato, et al. \[936\] were able to fit the optical conductivity in the metallic regime by a single Drude peak. However, they found a scattering rate of \(\approx 1eV\), considerably larger than the expected pseudogap energy at this doping. In BPBO, a Raman active phonon at \(570\text{cm}^{-1}\), identified with the breathing mode, is strongly resonant with the gap electrons \[937\].

A pseudogap is also seen in the photoemission of BKBO \[938\], and it is proposed that this is due to a *dynamical lattice distortion*, as observed in neutron diffraction pair-distribution-function analysis \[939\]. Evidence for (possibly dynamic) short-range order also comes from EXAFS studies \[940\]. The two different Bi-O bond lengths found in BaBiO\(_3\) are found to persist over the full doping range in BPBO and through the semiconductor range for BKBO, whereas metallic BKBO has a single, but anomalously broadened Bi-O length. On the other hand, neutron diffraction studies find that the oxygen disorder is largest perpendicular to the Bi-O bond axis, suggestive of tilt disorder \[941\].

In heavily doped BKBO, inelastic neutron scattering studies find soft modes associated with BiO\(_6\) octahedral tilts, similar to those in LSCO \[942\]. Moreover, the one-dimensional \(Bi – O\) bond stretching mode softens, but no anomalous softening of the three-dimensional breathing modes is found. Taken together, these results suggest that in BKBO the structural and superconducting anomalies may be associated with a 3D vHs, as in the Bilbro-McMillan model \[942\], which has been applied to the A15’s and BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) \[943\]. Dzyaloshinskii \[944\] has shown that for a 3D (BCC) cubic metal, in the perfect nesting limit, the VHS’s still lead to a weak divergence in the Cooper and zero charge channel susceptibilities, \(\propto ln^3\), and to similar RG equations. A \(ln\) divergence has been found for a tight-binding BiO lattice \[923,944\]. Note that the divergence is in the (density-density) correlation functions, while the dos is flat near half filling.

**XVII. EXTENSION TO OTHER SUPERCONDUCTORS**

**A. A15’s and Martensitic Transformations**

We have already discussed, in Section III, that high temperature superconductivity has regularly been associated with peaks in the density of states and strong electron-phonon coupling, and that the best place to look for new high \(T_c\) materials has been believed to be just on the edge of a structural instability. Daalderop, et al. \[945\] showed that both superconducting and magnetic instabilities were often associated with a narrow peak in the dos, caused by the proximity of an \(M_1\) and an \(M_2\) VHS – which resembles a 2D saddle point with a weak coupling in the third dimension, Fig. 3a (inset)! Hence, a VHS model may play a role in other, more 3D superconducting materials as well. We have seen that, in the A15 compounds, Weger found clear evidence for the important role of (3D) VHS’s \[946\], and the Bilbro and MacMillan \[942\] model for A15 superconductivity involves the 3D VHS. This model was applied to BaPb\(_{1-x}\)Bi\(_x\)O\(_3\) (BPBO) \[945\] prior to the discovery of the cuprates. Sleight showed that in BPBO, there is a miscibility gap, and the optimum superconducting \(T_c\) is associated with the composition of greatest instability, Fig. 71 \[923\]. He points out that many of the cuprates are also *thermo-dynamically unstable* near room temperature, due to the mismatch in interlayer lattice constants.

Many of the A15 compounds have a martensitic JT phase transition just above \(T_c\), which competes with the superconductivity \[947\]. Krumhansl \[948\] points out that the HTT-LTO transition in the cuprates is also a martensitic transition, which is *common to virtually all known high-\(T_c\) superconductors*, as well as to a variety of other perovskite, shape-memory, and related alloys. A common feature of these transitions is a precursor tweed phase, which is a nanoscale segregation of the low-temperature phase domains persisting into the high-temperature phase well above the martensitic transition temperature. Motion of the domain walls is extremely soft, and typically leads to anomalous softening of a shear modulus and enhanced attenuation, even in the absence of a soft mode phonon! The tweed structure can persist into the low-\(T\) phase, or can appear even in the absence of a long-range structural phase transition. In YBCO,
the ‘tetragonal’ phase produced by substituting Co or Fe for chain Cu’s is now understood to be a nanoscale orthorhombic phase, associated with tweed structure [947].

B. Heavy Fermions

The heavy Fermion compounds also provide interesting food for thought. These compounds are associated with extreme flat bands, with an f-level having a resonance near the Fermi level, which may be related to a correlation enhanced VHS. In fact, the Fermi surfaces have been calculated for CeRu$_2$Si$_2$, and found to be in good agreement with dHvA measurements [948]. The heaviest carriers are associated with a ‘pillow-shaped’ hole Fermi surface, whose cross section bears a striking resemblance to the cuprate Fermi surface (except for interchanging electrons and holes). The heavy Fermion superconductors are widely believed to have non-s-wave pairing, which may be due to coupling between the order parameters of superconductivity and a competing order, either magnetic or structural. The compound UPt$_3$ has evidence for structural inhomogeneity on a scale of ≈ 100Å; on prolonged annealing at high temperatures (1200°C), this can be converted into a well-developed incommensurate modulation, which appears to be a CDW plus Peierls distortion [249]. Analysis of the specific heat shows two sharp superconducting transitions in the annealed sample, while the as-grown sample had a single, broadened peak in $C_v$, with reduced $T_c$. Coming to this problem from the high-$T_c$ cuprates, I am struck by the similarity to the split-T$_c$ phase, while the as-grown sample had a single, broadened modulation, which appears to be a CDW plus Peierls prolonged annealing at high temperatures (1200°C). From the relative heights of the $A$ simple model, consistent with observation, might be that there is a coexistent (weak) antiferromagnetic phase. There are differences, however, in overdoped cuprates. There are differences, however, in that there is a coexistent (weak) antiferromagnetic phase. A simple model, consistent with observation, might be: that there is a coexistent (weak) antiferromagnetic phase. The compound UPt$_3$ has evidence for structural inhomogeneity on a scale of ≈ 100Å; on prolonged annealing at high temperatures (1200°C), this can be converted into a well-developed incommensurate modulation, which appears to be a CDW plus Peierls distortion [249]. Analysis of the specific heat shows two sharp superconducting transitions in the annealed sample, while the as-grown sample had a single, broadened peak in $C_v$, with reduced $T_c$. Coming to this problem from the high-$T_c$ cuprates, I am struck by the similarity to the split-T$_c$ phase, while the as-grown sample had a single, broadened modulation, which appears to be a CDW plus Peierls prolonged annealing at high temperatures (1200°C), this can be converted into a well-developed incommensurate modulation, which appears to be a CDW plus Peierls distortion [249]. Analysis of the specific heat shows two sharp superconducting transitions in the annealed sample, while the as-grown sample had a single, broadened peak in $C_v$, with reduced $T_c$.

Comming to this problem from the high-$T_c$ cuprates, I am struck by the similarity to the split-T$_c$ peak in the overdoped cuprates. There are differences, however, in that there is a coexistent (weak) antiferromagnetic phase. A simple model, consistent with observation, might be the following: From the relative heights of the $C_v$ discontinuities, the two superconducting phases are in a volume ratio of about 4:1, with the larger volume fraction associated with the higher $T_c$. Thus, the higher $T_c$ phase might be associated with the domains, the lower with domain walls, where it might coexist with the weak antiferromagnetism. (Fisk and Aeppli [49] suggested that the magnetic phase might be associated with domain walls.)

Whatever such a model can explain the complete phase diagram of U_p-t_3 is unclear at this point. However, it is interesting to note how differently the CDW has been treated by heavy Fermion theorists who are unfamiliar with the cuprate analogy [950]. They interpret the modulation as a conventional CDW, ignore the (presumed weak) modulation of the electronic density, and assume that the dominant effect is the change in the local lattice symmetry associated with the Peierls distortion.

C. Buckyballs

There are also interesting similarities with the buckyball superconductors. In this brief space, I can only touch upon one or two salient features. A VHS model would seem improbable if superconductivity occurs exactly at stoichiometry (e.g., K$_3$C$_60$), since the VHS will probably fall off of half filling, as in the cuprates. It has been suggested [951] that, just as in the cuprates, the half-filled band is a Mott insulator, and superconductivity is associated with metal vacancies. However, recent experiments on cubic families of fullerides, in which the doping can be continuously varied, finds the $T_c$ peak very close to half filling [952]. The situation may be similar to that found in the electron-doped cuprates and Y-124: only a relatively narrow doping range is stable, and this range does not include the optimum stoichiometry for superconductivity. Consistent with this, evidence has been found for a pseudogap in K$_3$C$_60$ [540] (high resolution studies find an extra, sharp feature near $E_F$ [953]).

In electron-phonon coupling models, a remarkable separation is achieved: the electron-phonon coupling constant $\lambda = N(0)V_{intra}$, where $N(0)$ is the dos, determined by inter-ball coupling, while $V_{intra}$ is an effective electron-electron attraction mediated by intra-ball vibrations. The strong electron-phonon coupling is found to be predominantly of a dynamic JT nature [541, 542]. These calculations were classical, but since the JT energy $E_{JT} \approx 40meV < \hbar \omega_{ph}$, quantum corrections, associated with tunneling between equivalent JT minima, should be important. Auerbach [464] solved a semiclassical model of the dynamic JT effect for an isolated molecule of C$_{60}^-$, finding a unimodal distortion for $n=1,2,4, 5$, but a bimodal distortion for $n=3$, the case of most interest for M$_2$C$_60$. Particularly near the strong coupling limit, $E_{JT}/\hbar \omega_{ph} >> 1$, this problem is best understood in terms of the Berry phase which develops from the combined electronic-molecular vibration. Auerbach, et al. [557] generalized these calculations for more realistic, weaker couplings, by a combination of exact diagonalization and perturbation theory calculations. They found that the JT effect greatly enhanced the pair binding energies over those calculated by standard Migdal-Eliashberg theory.

However, interball hopping can interfere with this dynamic JT effect in a manner which is not clearly understood. Manini, Tosatti, and Doniach [465] have created a model system, a lattice of Berry phase molecules, in order to explore this competition. Here, an odd number of electrons on a molecule introduces a Berry phase, changing the orbital angular momentum from integer-valued to half-integer-valued (the dynamic JT effect). Intermolecular hopping of an electron thus carries an extra penalty, in that the orbital angular momenta of two molecules must adjust. This favors a correlated hopping of two electrons, leading to a net pairing interaction. The model seems to strongly favor a superconducting insta-
bility, with no tendency towards phase separation. This is a very exciting development in the study of strong electron-phonon coupling.

The inter-ball part of the problem, the dos, is also interesting. Band structure calculations find that the Fermi level in the superconducting $M_3C_{60}$ (M=K,Rb,Cs) compounds is very close to a peak in the dos. Indeed, Mele and Erwin find that it falls at what appears to be a diabolical point of the band structure, which allows the possibility of a highly anomalous, nodeless anisotropic superconducting gap. Experimentally, the dos is found to have a ‘Stoner’ enhancement of a factor of $\approx 2$. The dos (and hence $T_c$) also depends sensitively on the lattice constant $a$; since $a$ is a strong function of temperature, this gives an apparent $T$-dependence to many properties of the material. Thus, the $T$-dependence of the Hall coefficient can be understood as a universal scaling, $RH(a)$. Interestingly, $RH$ is found to change sign in the Rb doped material; such a sign change is expected near a VHS.

In the polymeric compounds, $MC_{60}$ (M=K,Rb), the Fermi level is again found to be near a dos peak, and it is suggested that an antiferromagnetic phase can be stabilized by splitting this dos peak. In $M_4C_{60}$, the suggestion has been made that the insulating phase is associated with a nesting-driven density wave instability or a JT effect. It should be cautioned that these fullerenes have considerable orientational disorder, which can smear the Fermi surface and broaden dos features. Even in the presence of this disorder, a ‘relatively well-defined “Fermi surface” persist’, Fig. 17, and the role of the dos could be more important if there is significant short-range order – perhaps akin to nanoscale phase separation in the cuprates. On the other hand, much of the disorder can be eliminated under modest hydrostatic pressures, which should allow the observation of sharp Fermi surfaces.

D. Other Superconductors

In the Chevrel phases, $MMo_6S_8$, the superconductivity is associated with a rhombohedral phase which is metastable to an insulating triclinic phase at low temperatures. For $M = Sn,Pb$, the transition to triclinic begins at 100K, but is not complete at low temperatures, and superconductivity is found in the residual rhombohedral phase. If $M = Ba$, the transition begins at 350K, and is complete by 100K, leading to a non-superconducting material.

In the new borocarbides, band structure calculations find that the Fermi energy is close to a peak in the dos, and this has been confirmed by heat capacity measurements. Recent studies suggest two phase behavior and pseudogaps. The Uemura plot shows a universal relation between $T_c$ and $n/m$ for the cuprates; it is found that the bis-

Mathematically, this question was answered by Van Hove, who showed that a certain minimum number of VHS’s must be present in any band structure. And yet it is tempting to speculate on why the VHS is so closely associated with instabilities. One point to note is that the VHS only diverges in lower-dimensional materials. This seems to be associated with the general instability of ordered structures in dimensions less than three. For instance, the 2D VHS is formally unstable against arbitrarily small interlayer coupling, which cuts off the $ln$ divergence of the dos. (I hasten to add that the observed broadening of the VHS is small, and has little practical effect; for instance, the superconducting transition temperature depends only on the dos integrated over an interval $\sim 47$, larger than the expected broadening.)

Beyond this, it is important to recall that the 2D saddle point VHS’s are associated with a crossover from electron-like to hole-like conduction. While this seems fairly trivial, physically, it can be extremely important chemically. Thus, the crossover is associated with the saturation of one valence state, and the opening of another – which, for example, determines whether Fe is magnetic or not. In the cuprates, it involves half filling of the Cu $d_{x^2-y^2}$ band, and the doping of an oxygen $p$ band. It is precisely at such points that chemistry happens: where chemical valency plays a large role, and simple band filling ideas run afoul of ‘correlation effects’. In this light, it is interesting to note that recent studies of surface chemistry have concluded that strong surface reactivity is associated with a peak in the local surface dos.

Indeed, there seems to be a general connection between the VHS and the crossover between covalency and ionicity. This has to do with a breakdown of the Born-Oppenheimer approximation, that the electronic motion can instantaneously follow the nuclear motion. Near a VHS, the opposite limit may be more appropriate, since $v_F \rightarrow 0$. Thus, a material may appear covalent away from the VHS, in that holes can hop rapidly enough that the ions have an average, non-integer valence, whereas near the VHS, hopping can be so slow that a well-defined valence can develop. For the O’s, the large difference in ionic radius between $O^{2-}$ and $O^-$ means that in the ionic limit, there will be significant relaxation of the positions of neighboring ions, leading to the local structural disorder (and enhanced electron-phonon coupling).
XIX. SUMMARY

The original draft of this survey was submitted for publication prior to the Houston 10th Anniversary Meeting and the 1996 March Meeting. Yet some of the results presented at these meetings were so exciting and relevant that I felt compelled to incorporate them into the final paper. Recapitulating these results provides a rather fitting summary of this paper as a whole.

One group of papers [113, 118, 159] has to do with the opening of a pseudogap in the underdoped cuprates. This evidence clearly shows that the gap couples to both spin and charge excitations; it is not a spin gap. Furthermore, the data would seem to rule out the basic VHS scenario. One cannot describe the physics of doping the cuprates in terms of shifting a VHS into coincidence with the Fermi level, with or without correlation-induced VHS pinning. On the other hand, the data are in excellent agreement with (and indeed were largely anticipated by) the generalized Van Hove scenario. The opening of the pseudogap is manifested by a splitting of the VHS degeneracy, and the separation of the VHS from the Fermi level is a measure of the pseudogap. As doping is increased, the pseudogap reduces to zero, and, in LSCO, is replaced by an unsplit VHS peak, Fig. 21, still pinned at the Fermi level. (The situation in YBCO is somewhat less clear, due presumably to the presence of additional bands.) To complete the picture, it would be very important to directly observe the second VHS peak, above the Fermi level, and thereby determine how closely the Fermi level is locked to the average VHS position (the heat capacity data [99, 182] rules out the possibility that the peaks are asymmetrically split by a large amount, since that would be seen as a double peak).

At the same time, the Buckley Prize Symposium at the 1996 March Meeting, honoring C.P. Slichter, was devoted to the observation of phase separation and striped phases in the cuprates [173]. Just how the striped phases can be reconciled with the pseudogap remains a most difficult problem in the physics of the cuprates. (A start at this is presented in Sections XI.I, XIII.B,C.) Here, the Van Hove scenario has an advantage, in that both phenomena naturally follow from the proximity of a VHS to the Fermi level. Nevertheless, it remains very difficult to generate a coherent picture of the simultaneous occurrence of both effects. Perhaps the best model is a solitonic model, in which the domain walls of local structural disorder are charged, and hence provide the two nanoscale phases.

XX. CONCLUSIONS

This has been such a long and involved review because the VHS plays an important role in most aspects of the physics of the cuprate superconductors: both normal and superconducting states, both magnetic, structural, including phase separation, and superconducting properties. A major conclusion is that the simple VHS model seems to work well near optimum doping: it can explain why there is an optimum Tc, with linear-in-T electron-electron scattering rate and minimum isotope effect, etc. However, the doping dependence must be handled more carefully. Thus, the VHS model should not be well approximated by a rigid-band theory: correlation effects enhance the VHS (Section VII), electron-phonon coupling enhances the VHS, possibly leading to extended VHS's (Section VIII.D), and defects may further enhance the VHS [199]. At least in the case of electron-phonon coupling, this is due to the slowness of carriers near the VHS: vF ≃ 0. This leads to a breakdown of the Born-Oppenheimer approximation, and indeed to possible antiadiabatic behavior as the electrons may actually move more slowly than the phonons. (See the discussion in Ref. 154.) The same conclusions follow from the (nanoscale) phase separation: the VHS is pinned to the Fermi level over an extended doping range, so any theory which assumes a simple rigid band filling must fail. It is an open theoretical problem to properly incorporate this nanoscale phase separation in analyzing the doping dependence of the cuprates.

This same problem arises in attempting to interpret experiments in terms of a VHS theory: while Tc is optimized at a particular doping, the superconducting properties appear to persist over too broad a doping range, if a rigid band model of the VHS is assumed. It is instructive to look at two classes of phenomenological theories from the point of view of a VHS model. Of these theories, P.W. Anderson [174] has stated “I have serious problems with the two ‘hyphenated’ Fermi liquid theories – the marginal and the antiferromagnetic – because I think they both have inconsistencies. But they have the great advantage that they are experiment based, even though they are a bit ‘myopic’ in that each looks at only a fraction of the experimental data.”

In the marginal Fermi liquid theories, the property of a resistivity linear in T and ω is abstracted into a guiding principle. Varma, et al. [162] postulated a phenomenological form of the hole self-energy, \( Im\Sigma \approx -\omega \), Eq. 14, which leads to a scattering rate linear in \( T, \omega \), and describes a number of other anomalous normal state properties. This form of \( \Sigma \) follows from the VHS model, but only at particular \( \tilde{q} \)-values [29], while the original MFL self-energy is \( \tilde{q} \)-independent. Recently, a number of models have provided an ‘improved’ MFL theory, by putting in a strong \( \tilde{q} \)-dependence, to be able to explain the magnetic anomalies near \( \tilde{Q}_0 = (\pi/a, \pi/a) \) \[133, 220\]. Hence, the \( \tilde{q} \)-dependent MFL model could follow from a VHS theory, but only if the Fermi level coincides with the VHS. Clearly, pinning the VHS near the Fermi level would greatly extend the domain over which a VH-MFL model is valid.

The antiferromagnetic Fermi liquid (AFFL) theory introduces an empirical susceptibility peaked at \( \tilde{Q}_0 \), and shows that many of the magnetic properties follow
from this model. However, the only successful attempts to generate this susceptibility peak from first principles require the VHS to fall near the Fermi level [82]. For a rigid band model, this would lead to too great sensitivity of the peak to doping. However, it is now known that correlation effects pin the Fermi level near the VHS, so the required peak will persist over an extended doping range. Previously, any structure at $Q_0$ was automatically assumed to be due to AFM fluctuations. But if the Fermi level is pinned near a VHS, a peak at $Q_0$ could equally well be due to inter-VHS fluctuations; indeed, in the spin channel, the two will be largely equivalent. On the other hand, the VHS can also couple to the spin channel, the two will be largely equivalent. Hence, more care must be taken to determine whether a particular structure is (e.g.) magnetic or phonon related. Thus, in fully oxidized YBCO, a $Q_0$ neutron scattering peak at 40meV, was found to not be due to magnetic scattering, as previously assumed, but to phonon effects [210]. Magnetic structure is also present, slightly shifted in frequency, which peaks sharply below the superconducting $T_c$ [346,329].

If the nanoscale phase separation is adopted as a fundamental principle, another corollary almost immediately follows: theories of lightly-doped antiferromagnets cannot provide a correct picture for the superconducting state, since the superconductivity first appears well into the phase separated regime, and hence is more likely to be associated with the hole-doped uniform phase (if not driven by the two-phase fluctuations). Thus, theories of a gradual doping of holes into an AFM background are important, to provide the metastable energy vs doping curve upon which the phase separation is superposed. However, superconductivity is best understood by studying the unique composition of optimum $T_c$, and only then extrapolating to the very complex mixed-phase regime of intermediate doping.

One important role envisaged for this review is to establish a data base for those special anomalies in the cuprates which can be associated either with phase separation (Section XI) or strong electron-phonon coupling (Section IX). There is considerable evidence for both classes of effect, but it has been scattered throughout the literature. An advantage of the Van Hove Scenario is that both features follow rather directly from the model, and the model makes detailed predictions which seem to be largely verified. I would like to apologize in advance for any structure at $Q_0$ was automatically assumed to be due to AFM fluctuations. But if the Fermi level is pinned near a VHS, a peak at $Q_0$ could equally well be due to inter-VHS fluctuations; indeed, in the spin channel, the two will be largely equivalent. On the other hand, the VHS can also couple to charge degrees of freedom. Hence, more care must be taken to determine whether a particular structure is (e.g.) magnetic or phonon related. Thus, in fully oxidized YBCO, a $Q_0$ neutron scattering peak at 40meV, was found to not be due to magnetic scattering, as previously assumed, but to phonon effects [210]. Magnetic structure is also present, slightly shifted in frequency, which peaks sharply below the superconducting $T_c$ [346,329].

If the nanoscale phase separation is adopted as a fundamental principle, another corollary almost immediately follows: theories of lightly-doped antiferromagnets cannot provide a correct picture for the superconducting state, since the superconductivity first appears well into the phase separated regime, and hence is more likely to be associated with the hole-doped uniform phase (if not driven by the two-phase fluctuations). Thus, theories of a gradual doping of holes into an AFM background are important, to provide the metastable energy vs doping curve upon which the phase separation is superposed. However, superconductivity is best understood by studying the unique composition of optimum $T_c$, and only then extrapolating to the very complex mixed-phase regime of intermediate doping.

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**APPENDIX A: THERMODYNAMICS NEAR A SADDLE POINT**

Near a 2D VHS, anomalous thermodynamic properties follow from the logarithmic divergence of the dos [15]. These properties can be calculated for a noninteracting Fermi liquid in the grand canonical ensemble, as integrations over the carrier distribution. Thus, the average number of electrons is

$$N = 2 \sum_i f(E_i),$$  \hspace{1cm} (A1)

the internal energy is

$$U = 2 \sum_i f(E_i) E_i,$$  \hspace{1cm} (A2)

and the grand canonical potential is

$$\Omega = 2k_B T \sum_i \ln(1 - f(E_i)),$$  \hspace{1cm} (A3)

with the factor 2 coming from a sum over spins, the Fermi function

$$f(E_i) = \frac{1}{1 + e^{-|E_i - \mu|/k_B T}},$$  \hspace{1cm} (A4)

and $\mu$ the chemical potential. The sum over states can be replaced by an energy integral

$$2 \sum_i \to \int_{-\infty}^{\infty} N(E) dE.$$  \hspace{1cm} (A5)

For the 2D saddle point, we can take

$$N(E) = N_1 \ln\left(\frac{B}{2|E|}\right),$$  \hspace{1cm} (A6)

where the energy of the VHS is fixed at $E_v = 0$, and the limits on the integral of Eq. (A3) are $-B/2$ to $B/2$. This is not the most general form for the dos. The VHS need not be at the band center, and the dos need not vanish at the band edges. However, it is a convenient form for evaluating the integrals, and the thermodynamic functions will display a generic form near the VHS. In this case, $N_1 = 2V/B$, where $V$ is the sample volume.

The low temperature values of the thermodynamic functions can be calculated, following standard techniques [177]. Care must be taken, due to the nonanalytic behavior near the VHS. The number of electrons is $N = n V$, where $n$ is the electron density

$$n = 1 + \frac{2}{B} \left[ \mu ln\left(\frac{eB}{2|\mu|}\right) + k_B T F\left(\frac{\mu}{k_B T}\right) \right],$$  \hspace{1cm} (A7)

where
\[ F(y) = \int_0^\infty \ln \left( \frac{y-x}{y+x} \right) \frac{dx}{e^x + 1}. \]  

(A8)

The function \( F(y) \) must be evaluated numerically. Figure 72a shows both \( F(y) \) (solid line) and two approximations to it: for \( y \to 0, F(y) \to y(\ln y - 1) \) (dotted line), and for \( y \to \infty, F(y) \to -\pi^2/6y \) (dashed line). The temperature dependence of the chemical potential follows from keeping \( N \) fixed, independent of \( T \):

\[ \mu \ln \left( \frac{eB}{2|\mu|} \right) + k_BT F\left( \frac{\mu}{k_BT} \right) = \mu_0 \ln \left( \frac{eB}{2|\mu_0|} \right), \]  

(A9)

where \( \mu_0 \) is the chemical potential at \( T = 0 \). Figure 72b shows the calculated \( \mu \) vs \( \mu_0 \), for \( T = 10meV, B = 1eV \), using either the exact or approximate \( F(y) \) functions.

From Eq. A7, a \( T \)-dependent dos can be defined,

\[ \tilde{N}(\mu) = V \frac{\partial n}{\partial \mu} = N_1 \ln \left( \frac{B}{2|\mu|} \right) + F\left( \frac{\mu}{k_BT} \right) \]  

(A10)

Fig. 72c. As \( T \to 0 \), \( \tilde{N}(\mu) \to N(\mu_0), \) Eq. A8, while for \( \mu \to 0 \), the small-y limit of the function \( F(y) \) can be used in Eq. A3. Then

\[ \tilde{N}(\mu) = N(\mu_0) \frac{\partial \mu_0}{\partial \mu} \to N_1 \ln \frac{B}{2k_BT}. \]  

(A11)

This function directly enters the expression for the compressibility \( \kappa \) and the \( \tilde{\gamma} = 0 \) susceptibility \( \chi \). Thus,

\[ \kappa = -\frac{1}{V} \frac{\partial V}{\partial p}_{T,N} = \frac{1}{n^2} \frac{\partial n}{\partial \mu} \]  

(A12)

where \( p = -\Omega/V \) is the pressure, and

\[ \chi = \mu_B^2 \tilde{N}(\mu) \]  

(A13)

with \( \mu_B \) the Bohr magneton. In a conventional Fermi liquid theory, \( \kappa, \chi, \) and \( C_v \) are all proportional to the dos. At a VHS, this is also true, as will be demonstrated for \( C_v \) below.

The other thermodynamic functions can be similarly computed. The internal energy is

\[ U(T) = U(0) + \Delta U(T), \]  

(A14)

\[ U(0) = \frac{V}{2} \frac{B}{4} + \frac{\mu|\mu|}{B} \ln \left( \frac{eB^2}{4\mu^2} \right), \]  

(A15)

\[ \Delta U(T) = N_1 k_BT [k_BT F\left( \frac{\mu}{k_BT} \right) - \frac{\pi^2}{6}] \]  

\[ + \mu F\left( \frac{\mu}{k_BT} \right) = \frac{(\pi \mu k_BT)^2}{2} \tilde{N}_U, \]  

(A16)

\[ F_U(y) = \int_0^\infty \frac{xdx}{1 + e^x \ln \left( \frac{B^2}{4y^2 - x^2} \right)} \]  

(A17)

\[ \tilde{N}_U \approx N_1 \ln \left( \frac{B}{2eE_U} \right), \]  

(A18)

\[ E_U = \sqrt{\mu^2 - 2\alpha_U \mu k_BT + (\alpha_U k_BT)^2}, \]  

(A19)

where a constant shift has been included to make \( U = 0 \) for the empty band, and \( \alpha_U = 0.756, \alpha_U' = 0.336 \) are numerical constants, evaluated at \( T = 10meV, B = 1eV \).

Equation A18 is an approximation to the numerically calculated \( N_U \) (Fig. 72d); note that \( N_U \) has the form of a thermally broadened dos, Eq. A6. The scaling of \( E_U \) should be compared with that of the resistivity, \( \rho \), Eq. A2.

To calculate the grand canonical potential, it is convenient to integrate Eq. A3 by parts, yielding

\[ \Omega = V(B - 2\mu) - \int_{-B/2}^{B/2} N(E) f(E) dE, \]  

(A20)

\[ N(E) = \int_{-E/2}^E N(E') dE'. \]  

(A21)

Now, \( N(E) = V n(\mu = E, T = 0) \), with \( n \) given by Eq. A3 so

\[ \Omega = \Omega_0 - U, \]  

(A22)

where

\[ \frac{\Omega_0}{V} = B - 2\mu - \int_{-B/2}^{B/2} \left[ 1 + 2E \right] f(E) dE \]  

(A23)

is a nonsingular term. Then the heat capacity \( C_v \) and the entropy \( S \) should both display the divergence of the dos:

\[ C_v = \left( \frac{\partial U}{\partial T} \right)_\mu, = \gamma T, \]  

(A24)

where

\[ \gamma = \frac{\pi^2}{3} k_B^2 \tilde{N}_\gamma \]  

(A25)

is the Sommerfeld constant, and \( \tilde{N}_\gamma \) has the form of Eq. A18, but with \( \alpha = 1.23, \alpha' = 0.60 \).

Note that \( \alpha \approx \alpha_0 / \alpha_0' \approx 1.23, \) and \( \alpha' \approx 0.60 \). This can readily be understood. For \( T < \mu, \Delta U \propto \ln B/\mu \) is independent of \( T \), so \( C_v = d(\gamma T^2/2)/dT = \gamma T \). But for \( \mu = 0, \Delta U \propto \ln B/2e\alpha_0 k_BT \). In this case, \( C_v \) picks up an extra term from differentiating the logarithm, which can be included as \( \gamma \propto \ln B/2e\alpha_0 \ln e^{1/2} k_BT \). Similarly, the entropy \( S = \int_0^T (C_v(T')/T') dT' \) is equal to \( C_v \) when \( \mu >> k_BT \), but differs in the opposite limit. Table VI provides a summary of the logarithmic divergences of various quantities, in the form

\[ X = X_0 \ln \left( \frac{B}{2\gamma X} \right), \]  

(A26)
with

\[ Y = \begin{cases} 
|\mu| & \text{if } |\mu| >> k_B T, \\
\alpha x k_B T & \text{if } |\mu| << k_B T.
\end{cases} \tag{A27} \]

In the expressions for \( \Delta U(T) \),

\[ z = \frac{12}{\pi^2} \int_0^\infty \frac{x \ln x dx}{1 + e^{x}} \simeq 0.546. \tag{A28} \]

The above form for the specific heat was found by Hirsch and Scalapino \[49,229\], while anomalous behavior in \( S \) was pointed out by Wohlfarth (quoted in Rice \[49\]).

From the large-\( y \) limit of \( F(y) \),

\[ \mu \simeq \mu_0 \left[ 1 + \frac{(\pi k_B T)^2}{6 \mu_0^3 \ln \frac{eB}{2|\mu_0|}} \right], \tag{A29} \]

showing a tendency towards phase separation in the region near a VHS. That is, when \( \mu \neq 0 \), the chemical potential is always repelled away from the VHS (\( |\mu| > |\mu_0| \)). This can easily be understood. When \( T \) increases from zero, the Fermi function \( f(E) \) deviates symmetrically from a step function, reducing the occupation probability below the Fermi level and raising it above. But the total electron concentration \( n \) is an integral of \( f(E) \) times the \( N(E) \). For \( E_F < E_c \), the dos is an increasing function of energy, so at finite \( T \) more electrons are created than holes, and the chemical potential must shift below \( E_F \) (i.e., away from the VHS) to compensate, with a larger shift the closer \( E_F \) is to the VHS. Similarly, for \( E_F > E_c \), more holes are created, so \( \mu > E_F \). This same argument, however, shows that if \( E_F \) is exactly at the VHS, the chemical potential does not shift (at least to this order). This result is particularly obvious in the case of a square Fermi surface at half filling, where \( E_F \) must be at the VHS for all temperatures.

**APPENDIX B: \( \tau(x_c) \) IN THE ONE BAND MODEL**

In the VHS model, the doping of optimum \( T_c, x_c \), is the doping \( x \) at which the Fermi level crosses the VHS. Now \( x_c \) can be determined experimentally, and theoretically, it is controlled by the parameter \( \tau \), which determines the curvature of the Fermi surface. Hence, it is convenient to determine \( \tau(x_c) \), the value that \( \tau \) would have to have to reproduce the observed optimal doping. This is easily done by calculating the carrier density for which the Fermi level coincides with the VHS. The carrier density is proportional to the area of the Fermi surface:

\[ 1 - x = \frac{2}{\pi^2} \int_0^\pi \phi_x d\phi_y, \tag{B1} \]

with \( \phi_i = k_i a \), and

\[ \bar{c}_x = -\frac{2\tau + \bar{c}_y}{1 + 2\tau \bar{c}_y}, \tag{B2} \]

The resulting \( \tau(x_c) \) is shown as the solid line in Fig. 73.

An approximate formula can be derived by assuming that the area enclosed by dashed lines in the inset of Fig. 73 is an ellipse. Then, if the point where the ellipse intersects the zone diagonal is \( \phi_x = \phi_y = \pi/2 - \delta \),

\[ x = \delta/2, \tag{B3} \]

\[ \sin \delta = \frac{\sqrt{1 - 4\tau^2} - 1}{2\tau}. \tag{B4} \]

For small \( \tau \), this becomes

\[ \tau = -x(1 - \frac{7}{6}x^2), \tag{B5} \]

the dashed line in Fig. 73. The dot-dashed line is an empirical fit,

\[ \tau = -0.52 \tanh(2.4x). \tag{B6} \]

**APPENDIX C: ELECTRON-PHONON COUPLING**

1. One-band Model, Cu-Cu, O-O Stretch, Octahedral Tilt Modes

In a tight-binding model, the electron-phonon interaction can be calculated from the distance-dependence of the tight-binding parameters. For example, there can be an on-site coupling, to the hole density on site \( i \), \( n_i = c_i^{\dagger} c_i \), by, e.g., modifying the Cu energy level at a particular atomic site, \( R_i \): \( \Delta \rightarrow \Delta(R_i) \), or intersite coupling to the hopping term, \( c_i^{\dagger} c_{i \pm 1} \) by modifying the hopping parameter, \( t \rightarrow t \pm \delta t \) or the exchange, \( J \pm \delta J \) (spin-Peierls coupling).

In analogy to a 1D metal, a first choice for the relevant phonon is the dimerization mode, \( a \rightarrow a \pm \delta a \). However, in 2D metals, the coupling depends sensitively on the particular phonon mode. Following Tang and Hirsch \[49\], we will first study the coupling to a Cu-Cu bond stretching mode, Fig. 44a. In this case, the analysis can be carried out in a one-band model with \( t_1 = 0 \). The strength of the coupling can be estimated by analyzing a static distortion of the same symmetry. Expanding,

\[ t_{ij} = t_0(1 \pm \delta), \tag{C1} \]

with \( t_{ij} > (<) t_0 \) if the \( i-j \) atomic separation is less than (greater than) \( a \). The energy dispersion becomes

\[ E_\pm = \pm 2t_0 \sqrt{(\bar{c}_x + \bar{c}_y)^2 + \delta^2 (\bar{s}_x + \bar{s}_y)^2}. \tag{C2} \]

The total electronic energy, the integral of \( E \) over the occupied states, is lowered by the distortion. By a change of variable \( (k_\pm = (k_x \pm k_y)/2) \), the electronic energy can be written


\[ E = \frac{-16t_0}{\pi^2} \int_0^{\pi/2} (\cos^2 \nu + \delta^2 \sin^2 \nu)^{1/2} d\nu \simeq E_0 - \frac{16t_0}{\pi^2} \delta^2 I, \]

(C3)

with

\[ I \simeq \int_0^{\pi/2 - \delta} \frac{d\nu}{\cos \nu} \simeq \frac{1}{2} \ln \frac{\phi_n}{\delta}, \]

(C4)

where \( \phi_n \) is a cutoff angle. Now the elastic energy increase like \( \delta^2 \), while the electronic energy decreases like \( E - E_0 \propto \delta^2 \ln |\delta| \). Hence, the electronic energy lowering always wins out, just as in the 1D Peierls distortion; the resulting transition temperature has the form of Eq. 1. Indeed, the integrals in Eq. C4 are the same as in the 1D problem. Note the contrast with the molecular JT effect, Eq. 46. Note also that the electronic energy varies like \( \delta^2 \ln |\delta| \), and not like \( \delta^2 \ln^2 |\delta| \), the form expected for a VHS. The reason for this can be seen from the dispersion relation, Eq. C2. For \( \delta = 0 \), the VHS’s are at \( k_x = 0 \), \( k_y = \pi/a \), and equivalent points. The coefficient of the \( \delta^2 \) term is proportional to \( \bar{s}_x \), which vanishes at all of the VHS’s. Thus, the distortion does not split the VHS degeneracy, and hence behaves more like a conventional nesting instability.

On the other hand, an O–O stretch mode does split the VHS degeneracy, and hence produces a much larger energy lowering. This mode was analyzed in the three-band model in Ref. 150. In a one-band model, it does not appear directly, since the O’s are not explicitly included. However, following Zhang and Rice [51], we can replace the Cu’s by effective Cu’s, hybridized with a linear combination of the four surrounding O’s. Then the O–O stretch modes with orthorhombic symmetry become breathing modes, leading to a difference of the on-site Cu potential on the two sublattices, \( \pm 2t_0 \Delta^* \). To best correspond with the 3-band result, \( \Delta^* = n\delta \) (with \( n=2 \) for the 1D stretch mode of Fig. 40). Thus, the dispersion becomes

\[ E_\pm = -4t_1 \bar{c}_x \bar{c}_y \pm 2t_0 \sqrt{(\bar{c}_x + \bar{c}_y)^2 + \Delta^*}, \]

(C5)

where, for variety, a second-neighbor term, \( t_1 \) was included. The net energy lowering becomes, for \( t_1 = 0 \),

\[ E = \frac{-16t_0}{\pi^2} \int_0^{\pi/2} (\cos^2 \nu_x \cos^2 \nu_y + \Delta^* \nu_x \nu_y)^{1/2} d\nu_x d\nu_y \simeq E_0 - \frac{16t_0}{\pi^2} \Delta^* I^2, \]

(C6)

for finite \( t_1 \), the divergence is cut off to \( \sim |\ln \delta| \), as in Eq. 28. Equation C5 is essentially the same as that found in Ref. 176. The pseudogap calculation discussed in Section IX.A, and is consistent with Eq. 28. However, this mode does not seem to be directly involved in the structural instabilities of the cuprates; while the phonons do show signs of softening [76], the actual soft modes found in the cuprates are instead associated with tilting modes – of the CuO\(_6\) octahedra, and (perhaps) of the CuO\(_5\) pyramids in YBCO. Analysis of the tilt mode instabilities led to the VHS Jahn-Teller model for the structural transitions. Once it was realized that short-range order and dynamic JT effects are important, the role of the in-plane stretch modes was reassessed, and it was found that they could still play an important role (Section VII.D).

The quadratically coupled modes can be treated similarly. Thus, the LTT distortion in Fig. 35 couples strongly to the in-plane shear mode, Fig. 35. In the one-band model, the energy dispersion becomes

\[ E = -2t_0 (\bar{c}_x (1 + \delta) + \bar{c}_y (1 - \delta)), \]

(C7)

with \( \delta \propto \Phi^2 \), and \( \Phi \) the octahedral tilt angle. Then

\[ E - E_0 \simeq \frac{-4t_0 \delta}{\pi^2} \int |\bar{c}_x - \bar{c}_y| = -\frac{16t_0 \delta}{\pi^2} \equiv -E^* \Phi^2. \]

(C8)

This does not have a logarithmic divergence, but can still lead to an instability. The phonon energy has the form

\[ E_{ph} = \frac{K}{2} \Phi^2 + \frac{W}{4} \Phi^4. \]

(C9)

Now \( K \sim \hbar \omega_{ph} \), a phonon energy, and hence \( K/2 - E^* \) is likely to be negative; this is indeed the situation found in Ref. 176. This quadratic phonon coupling has also been studied in the three-band model [150, 406]. As discussed in Section VLD.12, it may also play an important role in generating d-wave superconductivity. Normand, et al. [41] also studied this mode, but concentrated on the small, linear coupling which would result below the LTO transition temperature, due to the presence of a finite static tilt.

Equations C3 and C7 were used to calculate the energy dispersions in Figs. 42c and d. The parameters were taken as: for Fig. 42c: \( t_0 = 125\text{meV}, \delta = 0.48 \); for Fig. 42d: \( t_0 = 178\text{meV}, \tau = -0.3, \Delta^*_n = 0.48 \). Note that it has been assumed that \( t_1 \) is unaffected by the structural distortion. In this case, the gap falls at different energies in different parts of the Brillouin zone. Clearly, opening a gap away from the Fermi level costs energy without contributing to the electronic energy lowering. Hence, for the figure, I have assumed an extended-s-wave gap, \( \Delta^* = \Delta^*_0 |\bar{c}_x - \bar{c}_y|/2 \), to minimize the gap away from the Fermi level.

Many studies have employed a simple 2D Holstein model (one band or three band, with on-site phonon coupling), either at the RPA level [21, 105] or by Monte Carlo calculations [22, 23]. The on-site phonon is usually interpreted as a vibration of the apical oxygen above a given Cu site [28]. However, it is also possible to interpret the electronic band as an effective Cu atom, incorporating the coupling to a symmetric superposition of the wave function on the four neighboring O’s (a Zhang-Rice singlet [51]). In this case, the phonon could also be a breathing mode of the planar O’s [129, 169], and hence equivalent to the O–O stretch mode discussed.
above. However, the strong instability of Eq. C3 requires in addition that the Fermi level coincide with the VHS. An inhomogeneous Hartree-Fock calculation [169] finds that intersite phonons have a much stronger effect than intrasite phonons in the three-band model of the CuO$_2$ plane.

2. Three-band Model, O-O Stretch Modes

Even when analyzing only the O-O stretch modes, coupling to the VHS depends sensitively on factors like the inter-row correlations of the stretch, and of coupled X and Y stretch modes. For instance, if the stretch is solely along the $x$ axis, with the same alternation on each row, the associated phonon is at $0.5(\pi/a,0)$, as in the lower mode in Fig. 51b; if instead there is a long-short-long alternation on alternate rows, Fig. 44b, the phonon is at 0.5$Q_0 = 0.5(\pi/a,\pi/a)$. Only the latter mode causes a linear gap at the VHS, Fig. 44b, but it is the former mode which is found to anomalously soften, possibly due to pseudogap formation. (Curiously, this mode has a quadratic coupling to the same in-plane shear mode that couples quadratically to the LTT tilt.)

On the other hand, there can also be simultaneous stretches along $x$ and $y$. There are two phonon modes of 0.5$Q_0$ symmetry. In a breathing mode (Fig. 51a, upper frame), all four short O-lengths are associated with the same Cu, coupling the Cu to a Zhang-Rice combination of the four neighboring O’s. Alternatively, each Cu could have two short and two long O-bonds, with the short bonds alternating along $x$ and $y$ – a quadrupole mode, which is experimentally found to soften, Fig. 51.

In the three-band model, one can compare the coupling of these different modes to the VHS. If the coupling is assumed to be due to modulation of the magnitude of the hopping parameter $t$, then the dispersion for all three modes at 0.5$Q_0$ can be written in a similar fashion (to lowest order in $\delta$, Eq. C2):

$$E = \frac{\Delta}{2} + \sqrt{\frac{\Delta}{2}^2 + W^2},$$  \hspace{1cm} \text{(C10)}

$$W^2 = 4t^2 \pm \sqrt{(2t^2[e_x + e_y])^2 + (2nt\delta)^2},$$ \hspace{1cm} \text{(C11)}

where $n$ is the excess number of short O-bonds between the two inequivalent Cu’s in the distorted unit cell – i.e., $n = 2$ for the $x$-only tilts, 4 for the breathing modes, and 0 for the quadrupole modes. This would say that the largest gap, and hence the strongest JT coupling, is associated with the breathing modes, whereas these modes experimentally show the least anomalous behavior. The breathing mode introduces a unit cell doubling, with a modulation of the occupancy of the Cu d orbitals on the two sublattices, $\psi_{Cu} \rightarrow \psi_{Cu}(1 \pm \alpha)$, with $\alpha = -4t\delta/(E(E-\Delta) - 4t^2)$, to lowest order in $\delta$. Hence, correlation effects near half filling oppose a breathing-type distortion.

To find a strong coupling to the quadrupole mode, it is necessary to examine different forms of electron-phonon coupling – perhaps a coupling to the Cu JT distortion. This would then be similar to the proposed dynamic JT in La$_{1-x}$Sr$_x$MnO$_3$ [167], Section XI.H.5. Note that the relation between the quadrupole mode and the 1D stretch modes is similar to that between the LTO and LTT type distortions, with only the latter coupled to the VHS.

3. JT Parameters

Using the above results, one can estimate what parameters of the breathing mode gap would be required to describe the photoemission studies on underdoped Bi-2212, Section IX.A.2. Thus, using the one-band model, Eq. C2 ($t_1 = 0$). Figure 42a requires $t_0 = (0.5/4)eV = 125meV$, and for the underdoped sample, the shift of the VHS is $2t_0\Delta^* = 250meV$. Thus, for the breathing mode, $\delta = \Delta^*/4 \approx 0.25$. Now $\delta = \delta t_0/t_0 = \beta\delta a/a$, with a the lattice constant and $\beta \geq 6 - 7$ [978, 545] (recall that $t_0 \approx t^2/\Delta$, where $t$ and $\Delta$ are the three-band parameters). Assuming $\beta = 7$, $\delta a/a \approx 1/30$. This should be compared with the expected lattice contraction associated with a localized hole, $O_2^- \rightarrow O^-$, $\delta a/a \approx 0.1$ [150]. A better estimate would be that the hole is delocalized over the four O’s making up the Zhang-Rice singlet, so $\delta a/a \approx 1/40$. [As discussed in Section VIII.E, the electron-phonon interaction near a VHS may not be reduced by correlation effects. In that case, the above estimates should be modified: $t_0 = t^2/\Delta \approx 1.3^2/6 = 0.28$, in which case $\delta$ and $\delta a/a$ would both be reduced by this factor of $\sim 2$.]

Given the above estimate for the gap $\Delta^*$, the net energy lowering is (Eq. C4) $\Delta E \approx 10 - 35meV$, where the uncertainty is due to the different estimates for $t_0$ mentioned above, and $\phi_m$ was assumed to be $\pi/2$. This should be compared to the experimental value $2E_{JT} \approx 70meV$, found in lightly doped cuprates [731], Section XI.B. The underestimate is expected: the above calculation included only the linear effects of the distortion, and hence ignored the important polaronic effects (e.g., band narrowing). Moreover, the molecular and band JT effects differ in form, due to the electronic kinetic energy in the latter case; compare Eqs. 74 and C4. Note, however, that Fehrenbacher [74] has estimated a theoretical $E_{JT} \approx 100-400meV$ for the (1D) breathing mode.

APPENDIX D: RG CALCULATIONS

Following Schulz [5], there are four types of electron-electron interaction constants, $G_1$, for scattering from, e.g., $X,Y \rightarrow Y,X$ (labelling the electrons by the VHS
they are associated with), \( G_2 \): \((X, -X \rightarrow -X, X)\), \( G_3 \): \((X, -X \rightarrow Y, -Y)\), and \( G_4 \): \((X, Y \rightarrow X, Y)\). These coupling constants are renormalized by interaction, and can diverge as the renormalization proceeds. The various density wave and superconducting instabilities are signalled by the divergence of certain linear combinations of the \( G \)'s: \( G_{CDW} = -2G_1 + G_3 - G_4 \), \( G_{SDW} = 2(G_3 + G_4) \), \( G_{sSC} = -2(G_2 + G_3) \), and \( G_{dSC} = -2(G_2 - G_3) \) (the latter for s- or d-wave superconductivity). Additional divergences are possible \([177]\). Related to spin currents and orbital antiferromagnets: \( G_{IS} = -2(G_3 - G_4) \) and \( G_{OAF} = -2(G_1 - G_3 - G_4) \).

In lowest-order perturbation theory, there are divergent corrections to the electron-electron vertices, \( \Gamma \), e.g.: \[ \Gamma_3 = G_3[G_1 + G_2 - 2G_4]I(\epsilon_c) \] (D1) with \[ I(\epsilon_c) = \frac{1}{\pi}i[\ln^2(\frac{\pi^2t}{\omega}) - \ln^2(\frac{\pi^2t}{\epsilon_c})], \] (D2) and \( \epsilon_c \) an ultraviolet cutoff. The renormalization scheme is to reduce the cutoff closer to the Fermi level, and require that the low energy properties remain unchanged. With scaling variable \( l = \frac{\ln^2(\pi^2t/\epsilon_c)}{2\pi} \), the renormalization equations become

\[ G'_1 = -2G_1[G_1 - G_4]\delta, \] (D3)
\[ G'_2 = -G'^2_2 - G'^2_3, \] (D4)
\[ G'_3 = -2G_3[G_2 + (G_1 - 2G_4)\delta], \] (D5)
\[ G'_4 = [G'^2_3 + G'^2_4]\delta, \] (D6)
where the prime means derivative with respect to \( l \), and for now \( \delta = 1 \). These equations are integrated numerically, given the initial values \( G_i = U/4\pi\tau \equiv G_0 \) for the Hubbard model, until one diverges. The competition between various instabilities can be understood by looking at the various \( G \)'s in terms of their initial values: \( G_{SDW} \sim 4G_0 \), \( G_{CDW} \sim G_{sSC} \sim -4G_0 \), and the other three are \( \sim G^0_0 \). Thus, for positive \( U \) (positive \( G_0 \)) \( G_{SDW} \) is dominant, and if it can be suppressed then d-wave superconductivity (or orbital antiferromagnetism or spin currents) becomes possible. On the other hand, if the sign of \( U \) can be changed (by, e.g., boson exchange), then the competition between CDW’s and s-wave superconductivity becomes more favorable, since both terms are of the same order in \( G_0 \). In this Appendix, I will analyze the magnetic case \( U > 0 \) for variety. From Fig. 70a, it can be seen that the SDW instability wins out at half filling, but the dSC and OAF are nearly as singular (they are essentially degenerate with one another), while the other three responses are suppressed by the renormalization. Schulz found that by doping away from half filling (moving away from the VHS), the divergences are reduced or cut off in such a manner that d-wave superconductivity can arise above a critical doping.

However, in the real cuprates, the VHS falls away from half filling, so doping actually moves the system closer to the VHS. Hence, Schulz’s scheme must be modified. I proposed a ‘floating VHS’ model of doping, wherein correlation effects pin the VHS at the Fermi level for all dopings, with the shape of the Fermi surface continually changing to preserve the pinning \([406]\) (see the discussion in Section VII.B). In the present RG scheme, a deviation of the Fermi surface from square means that the inter-VHS scattering \( (G_1, G_3) \) gets cut off from \( \ln^2 \) to \( \ln^4 \), with the cutoff depending on the curvature of the Fermi surface at the VHS, and hence on doping. The terms in Eqs. D3-D6 which are cut off are those proportional to \( \delta \).

To modify the above equations, let \( y = \sqrt{\tau} \). Then, if \( y > y_c \), the cutoff value, Eqs. D3-D6 hold with the prime reinterpreted as derivative with respect to \( y \), if the right hand sides of all four equations are multiplied by \( 2y \). This same perscription will also work for \( y < y_c \), if now \( \delta \rightarrow y_c/2y \). Figure 70b shows that, as \( y_c \) decreases, the SDW divergence is cut off, and ultimately the dSC instability wins out. The OAF is now no longer degenerate with the dSC state, and diverges somewhat more weakly. These results can be converted into a phase diagram of \( T_c \) vs doping by identifying \( \epsilon_c \rightarrow 2\tau \). From Eq. 28 \( y_c = \ln[(1+A)/(1-A)] \). For the one band model, \[ A = \sqrt{\frac{1+2\tau}{1-2\tau}}, \] (D7) so the doping dependence of \( y_c \sim \ln(1/\tau) \) can be found from the results of Appendix B. Since \( y_c = \ln(E/T_c) \), the phase diagram can be calculated; Fig. 71 shows the resulting phases, when \( E \) is adjusted to reproduce the AFM transition at zero doping. The results are very similar to those found by Schulz \([3]\), and are qualitatively similar to the 2D RPA calculations, Fig. 52, although differing in detail.

**Note:** After this Appendix was written, I obtained a preprint of Ref. 396, which contains a similar RG calculation.
## Table I: One Band Model Parameters

<table>
<thead>
<tr>
<th>Material</th>
<th>$t_0$ (eV)</th>
<th>$\tau$</th>
<th>$t_z/t_0$</th>
<th>$x_e$</th>
<th>Ref.</th>
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<td>LSCO</td>
<td>0.24</td>
<td>-0.19</td>
<td>0.16</td>
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<td>[57]</td>
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<tr>
<td>YBCO</td>
<td>0.24</td>
<td>-0.45</td>
<td>0.45 0.53</td>
<td>0.25</td>
<td>[120]</td>
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<tr>
<td></td>
<td>0.35</td>
<td>-0.28</td>
<td>0.40 0.25</td>
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<td>[103]</td>
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## Table II: Three Band Model Parameters

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<th>$t_{OO}$ (eV)</th>
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<td>YBCO</td>
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<td>0.16</td>
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<tr>
<td>Bi-2212</td>
<td>0.35</td>
<td>0.24</td>
<td>0.25</td>
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## Table III: Bare Parameters (eV)

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<th>YBCO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta$</td>
<td>3.6</td>
<td>3.51</td>
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<tr>
<td>$t_{CuO}$</td>
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<td>1.47</td>
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<tr>
<td>$t_{OO}$</td>
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<td>0.61</td>
</tr>
<tr>
<td>$V$</td>
<td>1.2</td>
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## Table IV: Effective Parameter Values of LSCO

<table>
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<th>Parameter</th>
<th>Scaling</th>
<th>Corrected Bare Value (eV)</th>
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<tr>
<td>$t_{CuO}$</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>$\Delta$</td>
<td>$\Delta_0 + 2V$</td>
<td>5-6</td>
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<tr>
<td>$t_{OO}$</td>
<td>$t_{OO}^{1} - X/\Delta$</td>
<td>0.14 (LSCO) 0.3 (YBCO)</td>
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### Table V: Experiments on Phase Separation

<table>
<thead>
<tr>
<th>Material</th>
<th>Doping Range</th>
<th>Property</th>
<th>Section</th>
<th>Refs.</th>
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<tr>
<td><strong>Underdoped Regime</strong></td>
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<td></td>
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<tr>
<td>La₂CuO₄⁺δ</td>
<td>0.06 ≤ δ ≤ 0.11</td>
<td>large period superlattices</td>
<td>XI.A.1</td>
<td>—</td>
</tr>
<tr>
<td>LSCO</td>
<td>x ≤ 0.14</td>
<td>incommensurate diffraction peaks</td>
<td>VI.E.2</td>
<td>341</td>
</tr>
<tr>
<td>LSCO</td>
<td>x ≈ 0</td>
<td>T hole = dielectric polaron</td>
<td>XI.B</td>
<td>—</td>
</tr>
<tr>
<td>LSCO</td>
<td>x ≤ 0.04</td>
<td>magnetic domain size from neutron diffraction</td>
<td>XI.C</td>
<td>736</td>
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<tr>
<td>LSCO</td>
<td>0 ≤ x ≤ 0.08</td>
<td>spin glass</td>
<td>XI.C</td>
<td>743</td>
</tr>
<tr>
<td>LSCO</td>
<td>x ≤ 0.16</td>
<td>magnetic fraction from Mössbauer</td>
<td>XI.D</td>
<td>744</td>
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<tr>
<td>LSCO</td>
<td>x ≤ 0.15</td>
<td>magnetic fraction from μSR</td>
<td>XI.D</td>
<td>748, 747, 267</td>
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<tr>
<td>YBCO</td>
<td>0.0 ≤ δ ≤ 0.7</td>
<td>photoemission doping dependence</td>
<td>VII.D.3</td>
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<td><strong>Paramagnetic Centers (?)</strong></td>
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<tr>
<td>LSCO</td>
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<td>two populations of Cu NQR</td>
<td>XI.F.2</td>
<td>—</td>
</tr>
<tr>
<td>YBCO</td>
<td>δ ≈ 0.6 – 0.7</td>
<td>AF polarons (?)</td>
<td>XI.F.2</td>
<td>733, 734</td>
</tr>
<tr>
<td>LSCO, YBCO</td>
<td>—</td>
<td>EPR (?)</td>
<td>XI.F.3</td>
<td>—</td>
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<tr>
<td>YBCO</td>
<td>—</td>
<td>linear term in specific heat</td>
<td>XI.F.3</td>
<td>231, 780</td>
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<td><strong>Crossover at VHS</strong></td>
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<tr>
<td>LSCO</td>
<td>x ≤ 0.3</td>
<td>( T_c(x) )</td>
<td>VI.D.5</td>
<td>—</td>
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<tr>
<td>LSCO</td>
<td>x ≤ 0.3</td>
<td>Meissner fraction</td>
<td>X.E.1</td>
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<tr>
<td>LSCO</td>
<td>x ≤ 0.3</td>
<td>susceptibility</td>
<td>X.E.2</td>
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<tr>
<td>LSCO</td>
<td>x ≤ 0.3</td>
<td>( T_1 )</td>
<td>X.E.3</td>
<td>758</td>
</tr>
<tr>
<td>LSCO, YBCO</td>
<td>—</td>
<td>intrinsic weak links</td>
<td>X.E.4</td>
<td>—</td>
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<tr>
<td><strong>Overdoped Regime</strong></td>
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<tr>
<td>La₂CuO₄⁺δ</td>
<td>δ ≥ 0.11</td>
<td>‘extra’ superconductivity (60K)</td>
<td>X.F.4</td>
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<tr>
<td>YBCO</td>
<td>δ ≤ 0.1</td>
<td>two ( T_c )’s</td>
<td>X.F.4</td>
<td>—</td>
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<tr>
<td><strong>Macroscopic</strong></td>
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<tr>
<td>La₂CuO₄⁺δ</td>
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<td>mobile O</td>
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<tr>
<td>La₂CuO₄⁺δ</td>
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<td>staging</td>
<td>X.A.1</td>
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<td>YBCO</td>
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<td>X.A.2</td>
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<td>polaronic phase separation O</td>
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<td>159</td>
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<tr>
<td>LBCO</td>
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<tr>
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<tr>
<td>La₂CuO₄</td>
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<td>photodope</td>
<td>X.A.6</td>
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<td>photodope</td>
<td>X.A.6</td>
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<td>δ ≥ 0.7</td>
<td>H-dope (?)</td>
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<td>NCCO</td>
<td>0.1-0.2</td>
<td>sc near miscibility gap</td>
<td>X.V</td>
<td>814</td>
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<td><strong>Nickelates</strong></td>
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<td>LNO</td>
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<td>X.H.1</td>
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<td>XI.H.2</td>
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<td>spin-charge superlattices</td>
<td>XI.H.2</td>
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<td>incommensurate diffuse scattering</td>
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### Table VI: Thermodynamic Functions of Eq. [A26]

<table>
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<tr>
<th>( \chi )</th>
<th>( \chi_0 )</th>
<th>( \chi )</th>
<th>( \alpha \chi )</th>
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<tr>
<td>( N(\mu) )</td>
<td>( N_1 )</td>
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<td>1</td>
</tr>
<tr>
<td>( \Delta U(T) )</td>
<td>( N_1(\varepsilon_{0}k_BT)^2/3 )</td>
<td>( e^{(\varepsilon-1)} = 0.635 )</td>
<td></td>
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<tr>
<td>( C_v )</td>
<td>( N_1(\varepsilon_{0}k_BT)^2/3 )</td>
<td>( 0.635\sqrt{\varepsilon} = 1.047 )</td>
<td></td>
</tr>
<tr>
<td>( S )</td>
<td>( N_1(\varepsilon_{0}k_BT)^2/3 )</td>
<td>( \frac{\sqrt{\varepsilon}}{\pi} = 0.385 )</td>
<td></td>
</tr>
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</table>

---

100
FIG. 1. (a) Energy dispersion of a 2D VHS. Calculations are based on the antibonding band of the 3 band model for the CuO\(_2\) plane, Eqs. 8 and 9, with (renormalized) parameters \(t_{\text{CuO}} = 0.347\) eV, \(\Delta = 0.244\) eV, and \(t_{\text{OO}} = 0.25\) eV (dashed line) or 0 (solid line). (b) Selected Fermi surfaces, corresponding to the two choices for \(t_{\text{OO}}\): \(E_F = 0.7\) eV (squares), \(0.825\) eV \(\equiv E_{\text{VHS}}\) (triangles), or \(0.9\) eV (circles). (c) Corresponding density of states (dos), and (d) total number of electrons per unit cell.

FIG. 2. Model Fermi surface of Ref. [23], showing location of hot spots (heavy black lines), in the immediate vicinity of the VHS’s.

FIG. 3. (a) Schematic Fermi surface of LSCO, \(x = 0.15\), illustrating both conventional \((Q_1, Q_2)\) and VHS \((Q_0)\) nesting. (b) Calculated [28] nesting function, showing the peaks in the joint dos associated with the various nesting vectors [Ref. [16]].

FIG. 4. Modification of dos at VHS, due to interlayer coupling [32]: (a) single layer, (b) four coupled layers, (c) infinite layers (dashed lines: approximate calculations). Inset in (c): calculated dos for Ni, Ref. [3].

FIG. 5. Photoemission-derived CuO\(_2\) antibonding band energy dispersion, for (a) Bi-2212, (b) Bi-2201, (c) YBCO, (d) Y-124, (e) NCCO. [Ref. [104]].

FIG. 6. Experimental Fermi surfaces of Bi-2212: (a) Ref. [3], (b) Ref. [23] – top view: \(\vec{k}_\parallel\) map of photoelectron intensity (logarithmic scale), bottom: sketch of principal features; (c) Ref. [3] – top: Fermi surfaces, including replicas due to incommensurate superlattice (light solid lines), bottom: energy dispersion.

FIG. 7. Theoretical Fermi surfaces of YBCO: (a) Ref. [24], (b) Ref. [25], (c) Ref. [96]. The lower (upper) frames are the \(k_a - k_b\) plane for \(k_c = 0\) (\(\pi/c\)). Dashed lines suggest chain-dominated sections of Fermi surfaces.

FIG. 8. Experimental Fermi surfaces of (twinned) YBCO: (a) Ref. [101], (b) Ref. [11]; and energy dispersions in untwinned (c) YBCO [24] and (d) Y-124 [10] near the extended VHS’s. The theoretical curves are from (a) Ref. [97], (b) Ref. [111], and (c) Ref. [98]. The arrow in (c) illustrates a special inter-VHS scattering between bifurcated VHS’s.

FIG. 9. Contour map of the energy dispersion near an extended VHS in Y-124 of Fig. 5(d).

FIG. 10. Fermi surfaces of NCCO, \(x = 0.15\) (a), 0.22 (b), compared to LDA calculations, after Ref. [104] [Ref. [23]].

FIG. 11. Comparison of the Fermi surfaces of Bi-2201, Bi-2212, and NCCO [Ref. [11]].

FIG. 12. Theoretical Fermi surfaces of LSCO [57] for \(x = 0\) (a), 0.17 – the VHS (b), and 0.2 (c). The Fermi surfaces are shown both in a flattened irreducible wedge (top) and in the extended zone scheme (bottom).

FIG. 13. Theoretical Fermi surfaces of Hg-1223 [58].

FIG. 14. (a) Experimental (circles) [106] and calculated (lines) [115] energy dispersion of SCOC. (b) Comparison of slave boson [113] and cluster Monte Carlo [110,111] calculations of the energy dispersion of a Mott insulator at half filling.

FIG. 15. (a) Calculated energy dispersion of BaBiO\(_3\) [119]. (b) Brillouin zone for simple cubic lattice. (c) Calculated dos, showing Fermi level for \(x=0,0.29\) (assuming uniform doping) [24].

FIG. 16. (a) Calculated Fermi surface of BaBiO\(_3\), at the VHS [121]. (b) Cross sections of the Fermi surface, for a series of energies spanning the VHS.

FIG. 17. Calculated Fermi surface of disorder-averaged \(M_3C_60\) [124].

FIG. 18. Calculated plasma frequency, \(\omega_{\text{pl}}\) (solid line) and dos (dashed line) near a VHS.

FIG. 19. Linearizing the Fermi surface near a VHS, to calculate inter-VHS susceptibility: (a) Perfect nesting, \(\alpha = 45^\circ\); (b) imperfect nesting, \(\alpha < 45^\circ\).

FIG. 20. (a) Discontinuity of heat capacity \(\Delta C/T_c\), plotted vs fractional distance in energy from a VHS, \(\delta/W\) [164]. The two lines are theoretical, with different values assumed for the prefactor of the logarithmic dos, the symbols are data from Refs. [166–169]. (b) Measured heat capacity, including discontinuity at \(T_c\) (diamonds), residual part (circles and dashed line), and sum (solid line) [177].

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FIG. 21. Susceptibility of LSCO (open squares) [99] and YBCO (open circles) [152], with fits to broadened VHS’s, with \( t_x = 2 \) (dot-dashed line), 4 (solid line), 6 (dotted line), and 20 meV (dashed line). The amplitudes of the theoretical curves were taken as adjustable parameters. Filled circles: YBCO data, with a constant term subtracted.

FIG. 22. Hole-hole scattering rate near (but slightly off of) a VHS. Solid lines: theory [252], dashed line: infrared [190], and photoemission [67,90] experimental results.

FIG. 23. (a) ‘Universal’ form of thermopower \( S \) vs \( T \) for different cuprates [202]. (b) ‘Universal’ form of \( S(290 K) \) vs hole doping [202]. (c) Anomalous \( S(T) \) for YBCO [204]. (d) Calculated \( S(T) \) near VHS [207].

FIG. 24. Magnetic breakdown vs switching orbit near a VHS. Frames a-d show the Fermi surfaces (extended zone scheme) of a 2D metal as the Fermi level gradually increases. Frame (d) illustrates a typical situation for magnetic breakdown, from the lens and diamond orbits to the underlying circular orbit. On the other hand, in (b) the metal is at the VHS, and an electron approaching the VHS has a choice of staying on the same orbit (as in (a)) or switching to a hole orbit, as in (c) [222].

FIG. 25. (a) Effective electron-electron interaction potential vs excitation energy \( h\omega \) in BCS theory. (b) Potential vs energy when the Fermi level coincides with a VHS. (c) Coulomb potential vs imaginary frequency \( \nu \) for several values of \( q_\nu/k_c \) at fixed \( q_\nu = 0.05k_c \) (where \( k_c \) is a momentum cutoff). Solid curves: \( E_F = 0 \) (i.e., at the VHS); dotted curves: \( E_F = 0.05B \) (with \( B \) the bandwidth) [239].

FIG. 26. Isotope effect near a VHS. Dotted lines: VHS excitonic superconductivity model [240], dashed line: phase separation model [234], solid lines: guides to the eye; circles: data of Ref. [250], triangles: data of Ref. [251], squares: data of Ref. [252].

FIG. 27. Uemura plot of \( T_c \) vs \( n_d/m_0 \). (a) For cuprates and other high-\( T_c \) superconductors [250,204]. (b) Showing modifications due to overdoping [267]. (c) Expected behavior near a VHS (replotted from Fig. 13, as \( N(E_F) \) vs \( \omega_d^2 \)).

FIG. 28. (a) \( T_c \) vs hole-doping in the cuprates. Lines are calculated from VHS model [261], symbols are experimental data [252]. (b) Universal parabolic dependence of \( T_c \) on doping [262].

FIG. 29. Universal plots of \( T_c \) vs pressure for the cuprates: (a),(b): comparison of the pressure coefficient (a) with the isotope effect coefficient (b) [271]; (c) illustrating effect of overdoping, and the large pressure coefficients which can be obtained if \( T_c \) is sufficiently reduced [272].

FIG. 30. Pressure dependence of \( T_c \) in Hg-12(n-1)n, \( n=1-3 \) [273].

FIG. 31. Incommensurate diffraction peaks in (a) LSCO [327], (b) YBCO [329], and (c) LSNO [330].

FIG. 32. Magnetic energy dispersion in the charge-transfer insulator phase of the 3-band tJ model at half filling: (a) uniform phase, Eq. [24], (b) flat-band nesting flux phase, Eq. [25], (c) VHS-nesting flux phase, Eq. [26] (d-f) are similar to (a-c), with added Néel order, Eq. [85] after [115].

FIG. 33. Slave boson calculations for the cuprates: (a) \( t_B \), (b) \( E_F \), (c) \( n_{VHS} = 1 - x_{VHS} \), and (d) \( \Delta E \), assuming \( \Delta_0 = 4eV \) (solid lines), 5eV (dashed lines), or 6 eV (dotted-dashed lines) [350].

FIG. 34. Dos vs energy, at several different dopings, for LSCO [358]. Fermi levels indicated by short horizontal lines.

FIG. 35. Slave boson calculation (3-band tJ model) of YBCO dispersion as a function of hole doping (solid lines) or electron doping (dashed lines). From bottom to top, curves are for \( x = -0.6, -0.45, -0.3, -0.1 \) (dashed lines), 0, .02, .1, .15, .3, .5 (solid lines).

FIG. 36. \( E_F \) vs doping, comparing slave boson and cluster calculations, for \( \Delta_0/t = 4 (\times) \) [381], 3 (open squares) [382], 2 (open diamonds) [382], and 1 (+) [381]. In terms of the parameters of Scalettar, et al. [382], \( \Delta_0/t = \epsilon + 2V \).

FIG. 37. (a) Comparison of Bi-2212 dispersion to tight binding model, using either bare LDA-derived parameters (dotted lines), or slave boson calculations (solid lines) Dashed lines denote ghost Fermi surfaces. (b) Additional narrowing of VHS peak associated with polaronic correction. [Ref. [150].

FIG. 38. (a) Angle-resolved photoemission spectra showing the ‘1eV’ peak in YBCO [72]. (b) Model dispersion in phase separation model. (c) Shift of the ‘1eV’ peak with doping.

FIG. 39. Angle-resolved photoemission spectra along \( S-Y \) or \( \Gamma-Y \) of (a) Y-124, (b) YBCO6.9 [383], (c) YBCO6.5, (d) YBCO6.3 [72].
FIG. 40. Angle-integrated photoemission spectra of (a) Ca$_{1-x}$Sr$_x$VO$_3$ at several dopings \[389\] and (b) a number of Mott-Hubbard insulators, comparing experiment (symbols) with theory (lines) for the conducting band \[388\].

FIG. 41. Pseudogaps and ‘shadow bands,’ or ‘ghost’ Fermi surfaces: (a) period-doubling Umklapp scattering leading to (b) hole pockets centered on $M = (\pi/2a, \pi/2a)$ \[199\]; (c-e) associated pseudogap developing in dos, for (c) 1D CDW at several temperatures \[110\], (d) 2D CDW in cuprates, at several temperatures \[40\], (e) 2D SDW, in Hubbard model, for several $U$ values \[367\].

FIG. 42. Electronic dispersion in the presence of structural distortion or flux phase: (a),(b) experimental dispersion in underdoped Bi-2212 \[415\]; (c) shear-strain-induced splitting of the VHS degeneracy \[150\]; (d) breathing-mode-induced splitting of the VHS degeneracy; (e) VHS splitting in the flux phase \[14\]. In c-e, the dashed lines show the dispersion from $X$ ($Y$) to $S \equiv (\pi/2a, \pi/2a)$, while the dot-dashed lines show the dispersion near $Y$, where that differs from near $X$. In (e), the heights of the vertical bars indicate the local spectral weights. Parameters used in the calculations are discussed in Appendix C.1

FIG. 43. Octahedral tilt distortions associated with the (a) LTT and (b) LTO phases.

FIG. 44. In-plane phonon stretch modes which affect the Cu-O bond length: (a) Cu-Cu stretch; (b) O-O stretch; (c,d) splitting of electronic band dispersion due to a static distortion of the corresponding symmetry. Dot-dashed lines: dispersion along lines $X-M$. \[150\].

FIG. 45. (a) Calculated energy vs. displacement for a number of $X$-point phonon modes. Inset: contour plot of same data. \[404\]. (b) Self-consistently calculated phonon double well derived from the experimental T-dependence of the soft mode in LSCO \[116\].

FIG. 46. Comparison of anharmonic vs electron-phonon effects in the LTO transition, illustrating phonon softening (a-c) \[406\] and doping dependence of La$_{2-x}$Nd$_x$Sr$_2$CuO$_4$ (d-f) \[150\]. While all models have substantial anharmonicity, the top frames (a,d) have no electron-phonon coupling, middle frames (b,e) have moderate, and bottom frames (c,f) large electron-phonon coupling. In frames (a-c), the dotted lines are guides to the eye; in frames (d-f), the solid lines and open circles are for $y = 0$, the dashed lines and filled circles for $x = 0.15$.

FIG. 47. Tilting mode distortions in LBCO, interpreted as a dynamic JT effect.

FIG. 48. Ferroelectric mode distortions in BaTiO$_3$.

FIG. 49. (a) Soliton model of dynamic JT phase \[454\]. (b) Antiphase boundary of the LTT phase \[457\]. (c) Model of LTT phase, derived from electron microscopic examination \[153\]. (d) Model of incommensurate Bi-2212, derived from EXAFS data \[459\].

FIG. 50. Phonon dispersion curves showing anomalous softening of the O-O stretch modes: (b) LSCO; (c) YBCO; (d) LNO \[174\]. (a) Related phonon distortions: top: breathing mode; bottom: 1D stretch mode.

FIG. 51. Phonon dispersion curves showing anomalies of the planar quadrupolar mode in several cuprates \[174\].

FIG. 52. Pseudogap phase diagram for (a) LSCO \[106\], (b),(c) YBCO \[530,515\], and (d) a combined diagram for both YBCO and LSCO \[105\].

FIG. 53. Pseudogap in the RVB model \[537\].

FIG. 54. NMR in LCO \[547\]. (a,b) Full spectra at several temperatures. In (b), the three data sets were taken at different frequencies. (c) Distribution of tilt angles, $P(\mu)$, with $\mu = \cos \Phi$, required to describe the NMR results.

FIG. 55. Phonon anomaly in YBCO: optical conductivity in phonon region of YBCO$_{6.6}$ \[489\]. Inset: T-dependence of conductivity at 410cm$^{-1}$.

FIG. 56. PDF’s of LBCO \[556\]: theory (a) and experiment (b) for the LTT (solid lines) and LTO (dashed lines) phases.

FIG. 57. Phonon softening in LSCO \[599\]. Solid line shows the result of the VHS theory.

FIG. 58. Schematic phase diagram of nanoscale phase separation, illustrating the free energy vs doping for the bulk phases (a) and the domain phases (b), with the resulting phase diagram (c).

FIG. 59. Comparison between conventional CDW (a), CDW with discommensurations (b), and phase separated CDW (c).
FIG. 60. Phase separation due to combined magnetic and charge transfer mechanisms. Shaded area: 2-phase regime.

FIG. 61. (a) Phase diagram of LCO. Phases are labelled O(T) for orthorhombic (tetragonal). (b) Modified phase diagram of LCO, found for annealed samples. $Fmmn$ phases have recently been identified as regions of stage ordering, as in LNO, Fig. 62.

FIG. 62. Theoretical phase diagram for YBCO, with experimental data of Ref. 708.

FIG. 63. $T_c$ vs hole doping $p$ in Ca and La substituted YBCO. Note that the 60-70K plateau falls at a fixed hole doping, and not at a fixed $\delta$.

FIG. 64. Phase diagram for LSCO (solid and dotted lines) and LBCO (dashed lines). Note change of scale at $T = 100K$. The AFM phase for LSCO is controversial, having been detected by microscopic probes ($\mu$SR, NMR) only – see discussion in Section XIII (dotted curve after Ref. 773). Inset defines $T_f$, $T_{gi}$.

FIG. 65. Roughening transition. While the calculation can be applied in many different situations, for present purposes, it represents a transition between a striped (a) and an island (b) phase, as a function of increasing disorder.

FIG. 66. Magnetic domain fraction $P_{SG}$ in LSCO (a) and YBCO (b), found from Mössbauer measurements.

FIG. 67. (a) Meissner fraction (squares) and diamagnetic phase fraction (circles) vs doping, for LSCO and LBCO (dashed lines). Solid lines are indicative of expected behavior for phase separated material. Long dashed lines in (a): guide to the eyes; short dashed line: LTO-HTT transition.

FIG. 68. Phase diagram of LNO. Filled circles (squares): Néel temperatures of primary (secondary) phases. The magnetic order crosses over from commensurate (C) to incommensurate (I) near $\delta = 0.11$.

FIG. 69. Phase diagram of LSNO. Note change of scale at $T = 100K$. Dashed line shows extent where $x = 1/3$ phase is present. Open squares: Ref. 812; filled squares: Ref. 220; remaining data: Ref. 812 (triangles are actually taken from O-doped LNO).

FIG. 70. Calculation of RG flow of various susceptibilities, near half filling, showing crossover from SDW to d-wave superconductivity, with (a) $y_c = 5$, (b) $y_c = 2.5$. (c) Resulting phase diagram.

FIG. 71. Phase diagram for BKBO.

FIG. 72. Calculated thermodynamic functions: (a) $F(N)$, Eq. A8 (solid line), with two approximate forms described in the text; (b) $\mu(x)$ near a VHS, Eq. A9, using either the exact or approximate form of $F(N)$; (c) temperature-dependent dos of Eq. A10, which enters the expressions for the compressibility $\kappa$ and the susceptibility $\chi$, at $T=0$ (dotted line) or 10meV (solid line), with approximate expression, using small-$y$ limit of $F(y)$ (dashed line); (d) comparing the exact internal energy $\Delta U^* \equiv \Delta U(T)/N(k_B T)^2$, Eqs. A2 and A14 (solid line) with the approximate form, Eq. A13 (dashed line).

FIG. 73. Calculated values for $\tau(x_c)$.

2. Note that, following Belgian custom, Van Hove is spelled with a capital V. I thank his son, M.A. Van Hove, for this information.


