Composition dependence of optical gaps in copper-based Hume-Rothery alloys

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We discuss the composition dependence of a number of critical energy gaps in the Cu-based Hume-Rothery alloys CuZn, CuAl, and CuGe. Our computations, employing the Korringa-Kohn-Rostoker coherent-potential approach, provide a remarkably simple and consistent explanation of a variety of available optical experiments on these systems. Polyvalent impurities are found to influence the spectrum of Cu in a manner which varies strongly from one solute to another.

I. INTRODUCTION

Since the pioneering observation of Hume-Rothery that the phase boundaries of the alloys of noble metals with polyvalent solutes are correlated with the electron per atom ($e/a$) ratio, these alloys have been the subject of numerous investigations. A rigid-band picture has often been invoked in this connection. Here one assumes the alloy to possess a composition-independent band structure (frequently that of the host), which is filled to the appropriate $e/a$ value. The optical-absorption experiments were among the earliest undertaken to gain a microscopic understanding of the electronic spectra of these alloys; more sophisticated differential reflectivity (composition modulation) and piezoreflectance studies have been carried out in recent years. However, no substantial understanding of the rich and varied results of the aforementioned optical experiments exists at this time. Our purpose is to discuss the progress that can be made in this regard on the basis of the modern alloy theory. Insight into the controversial question of assigning spectral features to specific transitions is also obtained. The similarities and differences between the various optical experiments (i.e., total absorption, differential reflectivity, and piezoreflectance) become clear. Different impurities are found to influence the spectrum of Cu in qualitatively different ways, in sharp contrast to a rigid-band-type model for these alloys. It is noteworthy that optical spectra contain information about energy gaps and hence about empty levels within a few eV above the Fermi energy. In contrast, most of the other techniques that have been used widely in connection with alloys (e.g., photoemission, positron annihilation, de Haas—van Alphen, and related experiments) primarily probe the occupied energy levels.

The CuZn, CuAl, and CuGe solid solutions considered here are representative of impurities of valence $Z=2$, 3, and 4, respectively. The major spectral features will be interpreted in terms of direct transitions across critical gaps in the alloy complex band structures. The complex energy bands (as opposed to being real) represent the generalization of the familiar Bloch bands to the alloy problem. Direct transitions have been used frequently in analyzing the optical experiments on perfect crystals. The fact that we are able to explain consistently the composition dependence of a variety of observed features would imply that such an approach continues to be a useful one even in concentrated alloys. The imaginary parts of complex levels, which represent the disorder smearing of states, manifest themselves by broadening the spectral features in an alloy. A proper understanding of this effect requires an analysis of the optical line shapes and thus the more complicated computation of the dielectric response function $\epsilon(\omega)$; its discussion is considered beyond the scope of this paper.

The computational aspects of our coherent-potential approximation (CPA) approach have been discussed elsewhere. The necessary muffin-tin potentials for Cu, Zn, Al, and Ge were constructed via the Mattheiss's overlapping charge-densities prescription and are identical to those used previously. The lattice-expansion effects were incorporated as in Refs. 10 and 13. Also, the value of the muffin-tin zero constant was adjusted to reproduce the measured composition dependence of the optical-absorption edge. This is the only free parameter in the computations and once its value is fixed, the theory predicts all other features of the electronic spectrum uniquely. The physical interpretation of this parameter is not very clear, although it may be thought of as a semi-empirical way of including charge redistribution effects in the atomic potentials upon alloying. In any event the maximum values of the muffin-tin zero shifts used were quite small; they amounted in Cu$_{0.95}$Al$_{0.05}$ and Cu$_{0.9}$Ge$_{0.1}$ to 0.08 and 0.024 Ry, respectively, and no adjustment was necessary in the CuZn computations. More importantly, the results and conclusions of this paper are insensitive to such uncertainties inherent in the first-principles band theory of metals and alloys.

II. RESULTS AND DISCUSSION

We begin by giving a brief description of the overall changes in the band structure of Cu which result on adding polyvalent solutes. Figure 1 shows the CPA complex energy bands in Cu$_{0.9}$Al$_{0.1}$ along with a few principal symmetry directions. The pattern of the energy bands in CuZn and CuGe is similar in the vicinity ($\pm 5$ eV) of the Fermi energy ($E_F$), although substantial differences are present deeper in the spectrum. In particular, approximately 10 eV below $E_F$, an impurity band of $d$ symmetry appears in CuZn, while a band of $s$-$p$ symmetry appears in CuGe. Among other effects, the $s$-$p$-type bands (e.g., $X_4$, $L_2$, $\Gamma_1$) generally move to lower energy, with the
The magnitude of the shift being a strong function of \( \mathbf{k} \) and the type of solute. The Cu-\( d \) bands, on the other hand, are much less affected although their total width decreases on alloying.

The principal transitions in the optical energy range (marked by arrows in Fig. 1) are as follows: upper \( d \) band \( \rightarrow E_F \) (e.g., \( \Delta^a \rightarrow E_F \), \( E_F \rightarrow L^a_1 \), \( L^a_2 \rightarrow L^a_1 \), \( X_1 \rightarrow X_0 \)), and lower \( d \) band \( \rightarrow E_F \) (e.g., \( \Delta^c \rightarrow E_F \)). The calculated composition dependence of these gaps is shown in Fig. 2, together with the relevant experimental results. The absolute values of our theoretical gaps in Cu are in good accord with measurements.\(^{15}\) The various alloys are seen from this figure to differ qualitatively. For example, the \( E_F \rightarrow L^a_1 \) gap decreases rapidly in CuZn and CuAl, but is relatively unaffected in CuGe. The \( L^a_2 \rightarrow L^a_1 \) gap decreases in CuZn and CuAl, whereas it increases substantially in CuGe.

Figure 2 contains rather a large amount of information. For convenience, we will consider the differential reflectivity spectra (DRS) first.\(^{16}\) The DRS is related to the derivative of \( \epsilon(\omega) \) with respect to the impurity concentration. This will be followed by a discussion of the piezoreflectance and the absorption results.

In Fig. 3 we show a typical differential and absorption spectrum in CuZn for illustrative purposes.\(^{1,3}\) The DRS contains sharper features (i.e., \( A, B, C, \) and \( D \)) compared to the absorption spectrum (i.e., \( A', B', D', \) and \( E' \)), as is to be expected. We emphasize that, in general, a single critical gap will yield a double structure in a derivative spectrum. Nastasi-Andrews and Hummel\(^1\) argue that \( B, C, \) and \( D \) in the DRS of the present Cu-based alloys contain information about just two independent gaps; the structure near peak \( C \) being the results of an overlap of two separate contributions. For these reasons, we need only discuss the composition dependence of the structures \( A, B, \) and \( D \).

It is generally agreed that peak \( A \) (or equivalently the edge \( A' \)) marks the onset of transitions from the top of \( d \) bands to the \( E_F \). However, the concentration dependence of this gap (monitored by \( \Delta^c \rightarrow E_F \) or \( \Delta^d \rightarrow E_F \)) is fitted to the experimental values, as is done frequently in the first-principles alloy computations. As emphasized above, even though the agreement in Fig. 2 with respect to the edge transition is a forced one, comparisons for other gaps constitute an independent test of the theory.
The measured changes in the location of structure B in CuZn and CuAl are plotted in Figs. 2(a) and 2(b). This feature is not seen in the differential reflectivity spectra of CuGe alloys. B is assigned to the transition $L_2 \rightarrow L_1^+$ by Nastasi-Andrews and Hummel\(^3\) and to $E_F \rightarrow L_1^+$ by Rosei \textit{et al.}\(^7\) Other critical gaps in this energy range (i.e., 4–5 eV) are $X_5 \rightarrow X_4$ and $\Delta' \rightarrow E_F$. We assign B to the critical gap $E_F \rightarrow L_1^+$. This assignment consistently explains all the aforementioned observations and is seen from Figs. 2(a) and 2(b) to yield a good agreement with the DRS measurements in CuZn and CuAl. In fact, we find that $E_F \rightarrow L_1^+$ is the only gap which varies rapidly enough to account for the experimental decrease in the energy of structure B. This effect conspire to produce this result in the calculations; $E_F$ rises on alloying while $L_1^+$ at the same times moves to lower energies. In contrast, both the initial and the final states in CuZn and CuAl move in the same direction in the case of other gaps (except the edge A) in Figs. 2(a) and 2(b). Finally, Fig. 2(c) shows that in CuGe, $E_F \rightarrow L_1^+$ gap varies almost by a factor of 6 less than in CuZn or CuAl. Since DRS intensities are related to the rate of change of critical gaps with concentration, the contribution of $E_F \rightarrow L_1^+$ gap would, therefore, be correspondingly reduced in CuGe. This effect together with the presence of other natural line-broadening mechanisms (e.g., disorder, temperature, lifetimes, etc.) suggests a remarkably simple explanation of the absence of structure B, noted above, in the DRS spectra of CuGe.

The structure D is assigned to the gap $\Delta' \rightarrow E_F$ by Nastasi-Andrews and Hummel\(^3\) and to $L_2 \rightarrow L_1^+$ by Rosei \textit{et al.}\(^7\) D moves to lower energies in CuZn, but to higher energies in the differential reflectivity spectra of CuGe. (D turns out to be difficult to locate in CuAl. We comment on this point below.) We assign D to the $L_2 \rightarrow L_1^+$ transition. This is the only gap which shows striking, observed differences in its behavior in the various alloys. The computations are in good accord with measurements on D in CuZn [Fig. 2(a)]. In CuGe, however, the nonlinear composition dependence in the data in the dilute limit is not well reproduced. Interestingly, $L_2$ as well as $L_1^+$ both possess some nonlinear concentration dependence in CuGe, which is essentially canceled in the calculation of the transition energy. Since the peak intensity is proportional to the rate of change of the associated gap, the aforementioned nonlinearity in the DRS data should imply a similar rapid change in intensity around $e/a \approx 1.03$. Such an effect, however, is not seen in the measurements, suggesting that a more detailed analysis of the data may yield a less drastic nonlinearity than that shown in Fig. 2(c).

The characteristic differences in the way the $L_2 \rightarrow L_1^+$ gap changes in the various alloys result primarily from the behavior of $L_1^+$ level ($L_2$ moves in a roughly similar manner in all three systems).\(^8\) Physically, this can be understood in terms of a simple picture of the underlying electronic structure presented by Prasad and Bansil.\(^5\) These authors argue that in CuGe the Cu and Ge s and p levels interact to form bonding and antibonding states. The bonding states appear as an impurity level about 10 eV below the $E_F$. The antibonding states, on the other hand, move above the $E_F$ and thus mix with the upper conduction bands. This admixture is what checks the downward movement of $L_1^+$ in CuGe in contrast to CuZn or CuAl, where such a mechanism is not available.

We conclude the discussion of differential reflectivity measurements by commenting further on the question of observability of various critical gaps in this experiment. The relevant factors in this connection are as follows: (1) The rate of change of transition energy with impurity concentration; (2) the disorder smearing of the associated levels; (3) the presence of other transitions in the same energy region; and (4) the oscillator strengths. As noted earlier, structures B and D overlap in energy; D is seen more clearly in CuZn and CuGe compared to CuAl, while B is seen in CuZn and CuAl but not in CuGe. These results may be understood as follows. Although the composition dependence of the relevant gaps $E_F \rightarrow L_1^+$ and $L_2 \rightarrow L_1^+$ is qualitatively similar in CuZn and CuAl, the difference for peak D is that the disorder smearing in CuAl is substantially larger than in CuZn. In fact, D is difficult to locate in CuZn also for high Zn concentrations. The mechanism for D in CuGe, on the other hand, is quite different; the smearing in CuGe and CuAl is comparable, but the structure D is still observable because it is not masked by B, which is absent due presumably to the weak composition dependence of $E_F \rightarrow L_1^+$ gap. Similar reasons of weak concentration dependence and the presence of other structures would make $\Delta' \rightarrow E_F$ difficult to observe. The edge $\Delta' \rightarrow E_F$, however, continues to be clearly visible, despite its relatively slow variation, because it is not masked by other transitions. Finally, $X_5 \rightarrow X_4$ is probably not seen, owing primarily to its weak oscillator strength.\(^15\)

In turning to the piezoreflectance data, we note that the piezoreflectance and differential reflectivity experiments involve different modulation parameters (i.e., stress versus impurity concentration). Therefore, a gap which is unresolved in one experiment can, in principle, become observable in the other. Staines\(^5\) has recently reported piezoreflectance measurements of a number of gaps in the present alloy systems. Figure 2 shows that in CuZn and CuAl, the transitions $L_1^+ \rightarrow E_F$ and $\Delta' \rightarrow E_F$ are well resolved. In CuGe, the transitions $L_1^+ \rightarrow E_F$ and $\Delta' \rightarrow E_F$ are very broad, making direct measurements of them difficult. However, piezoreflectance measurements do not appear to be as sensitive to the details of the electronic structure as differential reflectivity measurements.
CuAl his results are in a good general accord with our computations in all cases. This is particularly gratifying for the \(L_2 \rightarrow L_1^+\) gap in CuAl which, as noted above, is not well resolved in the DRS spectra. In CuGe, however, the agreement with the piezoreflectance data point corresponding to the \(E_F \rightarrow L_1^+\) gap is only qualitative. This discrepancy may be related to the difficulty in analyzing rather broad spectral features in CuGe, due presumably to the high-disorder smearing of states.

It is noteworthy that a weak indication from the \(X_4 \rightarrow X_F\) transition was reported in the piezoreflectance spectra of Ref. 5. Since no other experiment has, to date, observed the \(X_4 \rightarrow X_F\) gap in the present alloys, higher-resolution piezoreflectance measurements would be interesting in this regard.

Finally, we take up the absorptivity and reflectivity measurements. Absorption studies have been carried out by Pells and Montgomery, Bioni and Rayne, and Rayne.\(^{1,20}\) Rea and DeReggi\(^2\) have obtained \(\varepsilon_2\) spectra for CuAl alloys via a Kramers-Kronig analysis of their reflectivity data. We emphasize that these experiments can provide unique information about the electronic spectrum in specific cases. A striking example is the \(\Delta \rightarrow E_F\) gap which, as seen above, is not observed in either the DRS or the piezoreflectance measurements, presumably due to its insensitivity to the modulation parameters. Nevertheless, this transition gives a well-resolved feature \(E'\) (see Fig. 3) in the absorption spectrum of CuZn in good agreement with our calculations [Fig. 2(a)]. Interestingly, \(\Delta' \rightarrow E_F\) and \(L_2 \rightarrow L_1^+\) transitions are quite closely placed in Cu and give a single broad peak in the absorption spectrum. However, these two gaps change with composition (and/or temperature) at different rates, often yielding two well-resolved features (e.g., \(D', E'\) in Fig. 3) in the alloy. Also, a knowledge of the energies of both the \(\Delta \rightarrow E_F\) and \(\Delta' \rightarrow E_F\) (i.e., the optical edge) transitions permits a determination of the magnitude of \(d\)-band narrowing on alloying. Figure 2(a) now shows that the \(d\) bands of Cu narrow by approximately 0.4 eV on the addition of 16 at. % Zn, both theoretically and experimentally.

The experimental variation in the \(\Delta \rightarrow E_F\) gap in CuAl is only reproduced qualitatively in our calculations [Fig. 2(b)]. However, recent angle-resolved-photoemission measurements of the lower \(d\) band (with respect to \(E_F\)) in CuAl and CuGe are in agreement with our predictions,\(^{11}\) in sharp contradiction with the optical results in Fig. 2(b) for CuAl. Perhaps the method of analysis used in Ref. 2 entails some symmetric errors in this regard.

The absorption results are seen from Fig. 2 to confirm that the \(L_2 \rightarrow L_1^+\) gap decreases in CuZn, but increases in CuGe. (In CuAl the corresponding data are not available.) However, the absorption and differential reflectivity results in CuGe differ substantially from each other. Further experimental work towards clarifying the experimental situation in this regard would be useful.

In conclusion, our complex band computations provide for the first time a good overall description of the available optical measurements on the present Cu-based Hume-Rothery system. The underlying electronic structure of this series of alloys is not only a function of the \(e/\hbar\) value but also depends strongly on the type of impurity.

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\(^{14}\) A limited number of additional computations, using different impurity potentials, were also carried out to check this point.

\(^{15}\) Our calculated gaps in Cu are (in eV) as follows: \(\Delta' \rightarrow E_F = 1.9, E_F \rightarrow L_1^+ = 4.0, L_2 \rightarrow L_1^+ = 4.7, X_4 \rightarrow X_F = 3.9,\) and \(\Delta' \rightarrow E_F = 5.1.\)

\(^{16}\) For a recent review of the differential reflectivity technique see Ref. 4. For a general review of modulation spectroscopies, see M. Cardona, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969), Suppl. 11.


\(^{18}\) For example, for an \(e/\hbar\) value of 1.1, the \(L_1^+\) level shifts in CuGe, CuAl, and CuZn, by 0.06, 0.73, and 0.54 eV, respectively.


\(^{20}\) The experimental points given by the inverted triangles for the \(\Delta' \rightarrow E_F\) and \(L_2 \rightarrow L_1^+\) gaps in Fig. 2 were obtained by locating the upper and lower peaks in the absorption spectra of Pells and Montgomery (Ref. 1) (e.g., the peaks \(D'\) and \(E'\) in Fig. 3). We estimate the error in our reading from the curves to be less than 0.2 eV.