STRUCTURE-MAGNETISM CORRELATIONS AND CHEMICAL ORDER-DISORDER TRANSFORMATIONS IN FERROUS L1₀-STRUCTURED COMPOUNDS

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ABSTRACT

Understanding chemical order-disorder transformations and their effects on structure and magnetic properties of ferrous L1₀ intermetallic systems has been a longstanding problem in materials science and solid state chemistry. Herein, the kinetics of ordering and disordering of the L1₀ structure in the FePd and FeNi systems are explored in correlation with their structure and magnetic properties. In many systems, the chemically ordered L1₀ structure forms through an ordering transformation from a chemically disordered parent phase, which is often a face-centered cubic (fcc, A1) solid solution of the two elements (see unit cells of both structures in Figure 1). L1₀ FeNi (a.k.a. tetrataenite) is only found naturally in meteorites that form over 4.5 billion years; to date, it has not been produced in bulk by laboratory methods. The challenge for manufacturing L1₀ FeNi is that it has a critical temperature of 320 °C, below which the fcc chemically disordered phase transforms into the L1₀ chemically ordered phase [1]. Below this critical temperature, the atomic mobilities of Fe and Ni are extremely low (1 atomic jump per 2,600 years [2]) therefore the atomic movement necessary for chemical ordering is limited. On the other hand, the L1₀ structure forms readily in FePd making it a useful model system in which to study the order-disorder transformation [3] (it is noted, however, that the high cost of palladium makes FePd an impractical material for bulk industrial applications). In this dissertation, laboratory-synthesized L1₀ FePd was used as a test-bed system while a variety of meteorites were used as natural sources of L1₀-structured FeNi. The effect of the cooling rate on the A1→L1₀ chemical ordering transformation in FePd is investigated to elucidate the mechanism of chemical ordering. The effect of the heating rate on the L1₀→A1 chemical disordering transformation in
FeNi is investigated to gain understanding of the phase’s stability and order-disorder transformation mechanism. Analysis of the magnetic properties of L1₀ FeNi and L1₀ FePd indicates that the materials have theoretical magnetic energy products comparable to those of today’s best permanent magnets; thus, results from this work may aid future synthesis efforts for advanced permanent magnet applications.

Figure 1: Unit cells of binary alloy AB with (a) the chemically disordered fcc (A1) structure and (b) the chemically ordered L1₀ structure.
## TABLE OF CONTENTS

1 Introduction .......................................................................................................................... 1  
1.1 Motivation .......................................................................................................................... 1  
1.2 Overview of Research ......................................................................................................... 3  
1.3 Organization of Dissertation ............................................................................................ 6  
2 Formalism and Critical Literature Review ........................................................................... 8  
2.1 General Overview of Phase Transformations .................................................................. 9  
2.1.1 Thermodynamics of Phase Transformations ............................................................... 9  
2.1.2 Kinetics of Structural Phase Transformations ............................................................. 17  
2.2 Order-Disorder Transformations ...................................................................................... 26  
2.2.1 Chemical Order and Disorder ...................................................................................... 26  
2.2.2 Magnetic Phase Transitions ......................................................................................... 30  
2.3 Critical Literature Review ............................................................................................... 39  
2.3.1 Overview of L1₀ FePd .................................................................................................. 39  
2.3.2 Overview of L1₀ FeNi (Tetrataenite) ......................................................................... 47  
3 Experimental Methods and Techniques ............................................................................. 55  
3.1 FePd Synthesis and Processing ....................................................................................... 55  
3.2 Meteorite Sample Preparation .......................................................................................... 56  
3.3 Composition and Homogeneity Determination Using Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy (SEM-EDS) ......................................................... 57  
3.4 Characterization of Microstructure and Structure Using Optical Microscopy and X-ray Diffraction (XRD) ....................................................................................................................... 59  
3.5 Methods of Magnetic Domain and Bulk Magnetism Characterization ... 66  
3.5.1 Magnetic Domain Characterization Using Magnetic Force Microscopy (MFM) .................................................................................................................. 66  
3.5.2 Bulk Magnetic Characterization Using Vibrating Sample Magnetometry (VSM) ........ 68  
3.6 Calorimetric Methods ........................................................................................................ 71  
4 FePd Results and Discussion ............................................................................................... 73  
4.1 Characterization of the Structure, Magnetism, and Thermal Stability of L1₀ FePd ............................................................................................................................... 74  
4.1.1 Results from the Characterization of Structure, Magnetism, and Thermal Stability of L1₀ FePd ........................................................................................................... 76
TABLE OF FIGURES

Figure 1: Unit cells of binary alloy AB with (a) the chemically disordered fcc (A1) structure and (b) the chemically ordered L1₀ structure. iv

Figure 2: Unit cells of a binary alloy AB with (a) the chemically ordered tetragonal L1₀ structure and (b) the chemically disordered fcc A1 structure. 2

Figure 3: Thermodynamic characteristics of a) first-order and b) second-order phase transformations. Adapted from [1]. 13

Figure 4: The effect of $\Delta H_{mix}$ and T on $\Delta G_{mix}$ [1]. 16

Figure 5: Classification of structural phase transformations according to growth processes adapted from Christian [15]. 18

Figure 6: Chemical ordering depicted in 2D lattice [2]. 27

Figure 7: The fct and bct representations of the L1₀ lattice. 30

Figure 8: The three orientational domains or variants that form when an fcc crystal orders to L1₀[24]. 30

Figure 9: Schematic representation of hysteresis behavior in a ferromagnetic materials system[30]. 36

Figure 10: Schematic representation of the domain structure in a single crystal of iron. The field $H_{app}$ is applied in the [110] direction[26]. 36

Figure 11: Phase diagram of the binary Fe-Pd system. The L1₀ phase field is labeled as $\gamma_1$[38]. 40

Figure 12: The volume fraction of the ordered phase according to the temperature (°C) and duration of annealing in log(hours)[41]. 42

Figure 13: Schematic representation microtwin formation in FePd [8]. (a) Distribution and alignment of L1₀ precipitates within alternating A1 {110} bands that form during short annealing times. (b) L1₀ microtwin structure after long annealing times showing that each band is a single c-axis variant. 44

Figure 14: Polytwinned microstructure of FePd imaged using bright field transmission electron microscopy (TEM). Inset shows the arrangement of c-axes within the microtwinned lamellae[43]. 44

Figure 15: Selected-area electron diffraction (SAED) results on FePd: (a) fabricated from the disordered equiatomic FePd alloy after severe plastic deformation; (b) subsequent annealing at $T = 450$ °C for 11 h. Two-pike arrows point to the positions of diffraction rings that are common for both electron diffraction patterns. One-pike arrows show the positions of the diffraction rings, those present only in the electron diffraction pattern (b). The values of $d$-spacings are shown above and below the arrows. 46

Figure 16: Yang’s Fe-Ni phase diagram[57]. 50
Figure 17: Schematic representation of energy-dispersive x-ray spectroscopy principles. K, L, and M are the electron shell designations while Kα, Kβ, Lα are the radiation energies emitted when an electron falls from a higher shell to fill a hole in a lower shell[80].

Figure 18: Schematic representation of X-ray diffraction (XRD) operating principles [82].

Figure 19: The stereographic projection[83].

Figure 20: Expected peak positions in a pole figure of a face-centered-cubic crystal measured along the (110) direction.

Figure 21: MFM lift mode principles [87].

Figure 22: Magnetic domain structure of Tetrataenite in the Estherville meteorite.

Figure 23: Phase diagram of Fe-Pd [38] with experimentally important temperatures noted for the 50/50 composition. Experimental annealing temperatures discussed in Section 4.1 are indicated by red circles. The red arrow indicates cooling from 900 °C, through the chemical order-disorder temperature, to room temperature as discussed in Section 4.2.

Figure 24: XRD results from FePd as quenched as as annealed compared to previously reported patterns for L1₀ and fcc FePd.

Figure 25: Scanning probe microscopy measurements showing the (a) topography of quenched FePd, (b) magnetic domains of quenched FePd, (c) topography of annealed FePd, and (d) magnetic domains of annealed FePd. Images (a) and (b) have dimensions of 20 x 20 μm, while (c) and (d) are 50 x 50 μm.

Figure 26: Magnetization as a function of applied field measured at room temperature (Left) and as a function of temperature measured with 20 kOe (Right) for FePd in the quenched (blue) and annealed (red) states.

Figure 27: Differential scanning calorimetry results on annealed FePd subjected to heating at 5, 10, and 20 K/min and subsequently cooled at 20 K/min.

Figure 28: Schematic drawing of the “fir tree” magnetic domain configuration and the relationship of the magnetic domains to crystallographic twins [93]. The arrows in the triangular “branches” of the “fir tree” pattern show that these triangular regions along the twin boundary are magnetized antiparallel to the surrounding regions[93].

Figure 29: Landau fits of experimental $M(T)$ and $\chi_M^{-1}(T)$ data from quenched FePd (a) and annealed FePd (b). Applied field was 20 kOe.

Figure 30: The Curie transition of Nickel measured on heating (purple) and cooling (blue) at 20 K/min by DSC. The heating trace shows $T_C$ as peak-like while the cooling trace shows $T_C$ as a step in the DSC signal.

Figure 31: Optical micrograph of FePd (a) A1-structured FePd after polishing, (b) S2, (c) S1, (d) S0.5. All images are at the same magnification. The scale bar in each image is 100 μm.
Figure 32: XRD results from S2, S1, and S0.5 FePd are compared to previously reported [39] patterns for A1 and L1₀ FePd. The full patterns are in the left window and the (200) and (002) peaks are shown in greater detail in the right window..... 94

Figure 33: Lattice parameters, unit cell volume, and c/a ratio for FePd samples as a function of cooling rate. Values for as-annealed A1 and as-quenched L1₀ FePd, experimentally determined in Section 4.1, are included here for comparison. Lines are drawn to guide the eye.......................................................... 97

Figure 34: Full width at half maximum (FWHM) of the XRD peaks from the (200) and (002) Bragg reflections of FePd. Lines are drawn to guide the eye............... 98

Figure 35: DSC results from three FePd samples initially in the quenched A1 state measured in four steps: 1) heated from room temperature to 900 °C at 20 K/min; 2) slowly cooled from 900 °C to room temperature at 2, 1, or 0.5 K/min; 3) re-heated from room temperature to 900 °C at 10 K/min; 4) cooled from 900 °C to room temperature at 40 K/min................................................. 100

Figure 36: Ratio of the experimentally measured integrated intensity to the expected intensity of the (001) superlattice reflection as a function of cooling rate, measured using XRD on FePd. Line is drawn to guide the eye............. 104

Figure 37: The lattice long range order parameter, LRO₀, calculated from the ratio of lattice parameters determined from fundamental Bragg reflections as a function of cooling rate. ................................................................................. 106

Figure 38: DSC traces for cooling Step 2 and heating Step 3, as described in the main text. The $T_C$, pre-peak onset, peak onset, and peak temperatures are indicated. ............................................................................................................. 108

Figure 39: The Curie temperature with respect to cooling rate as observed in DSC results. ............................................................................................................... 109

Figure 40: Temperatures from calorimetry results on FePd plotted as a function of sample state. The (a) peak-onset and exothermic peak temperatures from the DSC cooling branch, and (b) the peak-onset and peak temperatures from the heating branch are shown. Lines are drawn to guide the eye. ......................... 112

Figure 41: Absolute value of the enthalpy of the high-temperature thermal event as measured on cooling and on heating FePd samples. Lines are drawn to guide the eye only. .......................................................... 113

Figure 42: Comparison of DSC traces taken on heating to show the significance of the pre-peak above the baseline. FePd beginning in the quenched A1 state and in the annealed L1₀ state were both measured at 20 K/min on the same FePd sample. .......................................................... 115

Figure 43: Pre-peak onset temperature of FePd measured on heating in DSC. The x-axis indicates the rate at which the sample was cooled in previous step. Line drawn to guide the eye. .................................................. 115
Figure 44: Breadth of the pre-peak of FePd measured on heating in DSC. The x-axis indicates the rate at which the sample was cooled in previous step. Line drawn to guide the eye. ................................................................. 116

Figure 45: Fraction of the total enthalpy of transformation measured for each FePd sample that is attributed to the peak and to the pre-peak. Lines are drawn to guide the eye. ................................................................. 116

Figure 46: The fraction transformed to the L1_0 phase determined from the relative enthalpy. Line drawn to guide the eye. ................................................................. 117

Figure 47: Effect of fraction transformed (i.e., relative measured enthalpy) on (a) the lattice parameters, (b) unit cell volume, and (c) unit cell tetragonality in FePd determined from the fundamental Bragg reflections. Lines drawn to guide the eye. ................................................................. 118

Figure 48: The relative enthalpy (enthalpies measured during cooling relative to the enthalpy of disordering L1_0) and LRO (the lattice long range order parameter calculated from the unit cell tetragonality) are plotted as functions of the cooling rate................................................................. 119

Figure 49: Polarized light micrograph of two regions of the NWA6259 meteorite. (a) Image taken by the author of this Dissertation. (b) Image taken by collaborators[75]. ................................................................. 125

Figure 50: Pole figure results of NWA6259 meteorite with d-spacings corresponding to L1_0 reflections: a. (111) fundamental, b. (002) fundamental, c. (110) superlattice, d. (201) superlattice, and e. (112) superlattice......................... 127

Figure 51: L1_0 superlattice Bragg peaks of (001), (110), and (003) reflections are clearly observed in NWA 6259 tetrataenite during single-crystal XRD carried at NSLS beamline X20A. The sample was oriented along (a) the (002) direction, and (b) the (220) direction................................. 128

Figure 52: XRD peaks from NWA6259 meteorite measured in the 2θ range corresponding to (a) the (001) superlattice and (b) the (200) fundamental peaks of L1_0 FeNi. Diffraction was measured at varying incident X-ray energies in the vicinity of the iron absorption edge. ................................................................. 129

Figure 53: Integrated intensities of XRD peaks from NWA6259 meteorite in the 2θ range corresponding to (a) the (001) superlattice and (b) the (200) fundamental peaks for L1_0 FeNi, and (b) the ratio of the (001) and (200) integrated intensities....... 130

Figure 54: Magnetic domains of tetrataenite from (a) the Estherville meteorite demonstrate flower-like domains, and (b) the NWA6259 meteorite reveal a complex magnetic structure, as measured by MFM. ........................................ 131

Figure 55: Magnetization of FeNi from the NWA6259 meteorite (a) as a function of applied field, and (b) as a function of temperature. The NWA6259 in the as-received state has higher $H_C$, $M_R$, and $H_K$ than after the 1st and 2nd $M$ vs. $T$ measurements. The $M$ vs. $T$ measured on the as-received state shows a Curie temperature at 557 °C, with $T_C = 467 °C$ during the first cooling branch, and $T_C = 387 °C$ on second heating/cooling $M$ vs. $T$ measurements. ................... 132
Figure 56: The initial magnetization curves NWA6259 meteorite in its as-received state (black) and after being heated to 700 °C (red). Data fit using the Law of Approach to Saturation (LAS) method on the high field portion to estimate the magnetocrystalline anisotropy constant $K_1$. .......................................................... 133

Figure 57: Comparison of the heat flow and magnetization as functions of temperature for two samples extracted from adjacent sites on the NWA6259 meteorite. Both samples in the as-received state exhibit a transformation at ~555 °C. In subsequent heating/cooling steps, both samples show a transition at ~387 °C. .......................................................... 134

Figure 58: Expected reflection positions in a pole figure of a fcc crystal measured along the (110) direction (after Ref. [83]). Yellow triangles mark $\{111\}$ Bragg reflections and pink squares mark $\{100\}$ Bragg reflections. Image rotated so as to roughly match the orientation of the pole figures collected from the NWA6259 meteorite. .................................................................................. 137

Figure 59: Pole figure results modeled as an fct structure with Fitequipoint software [102]. (a) (111) peaks corresponding to fcc crystal with orientation “a”. (b) (200) peaks corresponding to fcc crystal with orientation “a”. ................. 137

Figure 60: XRD pole figures showing the (110) superlattice reflections resulting from the three orthogonal $L1_0$ variants. .................................................................................. 139

Figure 61: Magnetic domain structure of materials with high uniaxial magnetocrystalline anisotropy. (a) NdFeB crystal showing a twin boundary with flower-like magnetic domains in the upper portion of the image and a branching pattern in the lower portion of the image (reproduced from Ref. [92]). (b) Schematic representation of magnetic flux in a high-anisotropy material drawn in side-view showing stray field above the surface (reproduced from Ref. [103]). ... 141

Figure 62: DSC results obtained from meteorite NWA6259 measured at constant heating rates of 1, 5, 10, 20, and 25 K/min. All traces exhibit an asymmetric endothermic peak corresponding to a first-order endothermic chemical-disordering process. .................................................................................. 149

Figure 63: Kissinger plot of DSC results measured at heating rates of 1, 5, 10, 20 and 25 K/min. The clear linear trend has the slope with a linear fit equal to the negative activation energy ($Q_t = 3.08 \pm 0.07$ eV). .................................................................................. 153

Figure 64: DSC data fit using the Michaelsen-Dahms model [19]: (a) model fit to 5 K/min data ($n = 1.27 \pm .01$, $\nu_{Kiss} = 2.99 \pm .01 \times 10^{16}$ s$^{-1}$), and (b) results for $n$ and $\nu$ as a function of heating rate. .................................................................................. 157

Figure 65: Illustration of the incident beam area in the plane of the sample surface for experiments at the NSLS beamline X20A. .......................................................... 196
TABLE OF TABLES

Table 1: The crystal structure designation, Strukturbericht designation, chemically ordered or disordered classification, prototype, space group, Pearson’s symbol and the ball model of the unit cell for various A-B alloys and compounds.... 29

Table 2: Critical exponents of the Universal Scaling Law obtained from different theoretical models [27, 28]................................................................. 34

Table 3: Equilibrium phases in the Fe-Pd system [38].......................................................... 40

Table 4: Previous magnetic studies on meteorites containing Tetrataenite......................... 51

Table 5: EDS results on three FePd samples in the quenched state..................................... 77

Table 6: Lattice parameters of FePd in the quenched and annealed states............................ 79

Table 7: Temperatures of events observed in DSC results on FePd................................. 82

Table 8: Critical exponents determined from $M(T)$ measurements on L1$_0$ and A1 structured FePd samples. Models from the literature [28] are included for comparison. ................................................................. 87

Table 9: Lattice parameters, volume, and $c/a$ ratio of S2, S1, and S0.5 FePd. Experimental values of the as-quenched A1 and as-annealed L1$_0$ FePd phases, established in Section 4.1, are included for comparison. ......................... 95

Table 10: Temperatures of events observed in DSC results on FePd......................... 101

Table 11: The angles of Bragg reflections measured for the three variants in the NWA6259 meteorite at beamline X20A of the NSLS using a point detector with analyzer ($\lambda = 1.54062$ Å). ......................................................... 140

Table 12: The progression of magnetic properties in a NWA6259 sample indicates the presence of three magnetic phases. ......................................................... 144

Table 13: Magnetic properties of permanent magnet materials........................................ 147

Table 14: Summary of DSC measurement results on the chemical-disordering process of tetrataenite in the NWA6259 meteorite. ......................................................... 149

Table 15: Comparison of thermodynamic parameters of material systems with L1$_0$↔A1 transformations: thermodynamic chemical order-disorder temperature $T_{OD}$; enthalpy of transformation $\Delta H_{L1_0 \rightarrow A1}$; driving force $\Delta G$ at 300 °C; and enthalpy of formation of L1$_0$ phase $\Delta H_{L1_0 \rightarrow \text{form}}$ determined experimentally and from calculations in the literature using the generalized gradient approximation (GGA)[111]................................................................. 152

Table 16: Comparison of kinetic parameters of material systems with L1$_0$↔A1 transformations: thermodynamic chemical order-disorder temperature $T_{OD}$; activation energy $Q_i$ of the chemical order-disorder L1$_0$/A1 transformation; activation energies of lattice diffusion $Q_L$ and of grain boundary diffusion $Q_{GB}$ in the disordered phase; lattice and grain boundary diffusivities $D$ at 300 °C in the disordered phase. ..................................................................................... 155
Table 17: Comparison of thermodynamic and kinetic parameters of a selection of material systems with L10↔A1 transformations: thermodynamic chemical order-disorder temperature $T_{OD}$; driving force $\Delta G$ at 300 °C; activation energy $Q_t$ of the chemical order-disorder L10/A1 transformation; activation energies of lattice diffusion $Q_L$ and of grain boundary diffusion $Q_{GB}$ in the disordered phase.......................... 167

Table 18: Long-range-order parameter and distribution of variants calculated for the meteorite NWA6259................................................................. 197
1 Introduction

1.1 Motivation

The overall goal of this Dissertation is to determine the correlations between structure, magnetic properties, and thermal properties of Fe-based L1₀-structured materials and to study the A1↔L1₀ chemical order-disorder transformation. The effect of chemical ordering on magnetic properties and the mechanism of chemical order-disorder transformations are long-standing questions in materials science and solid-state physics. A crystalline chemically ordered phase is one in which each elemental species resides at particular specified lattice positions. Chemically disordered phases are solid solutions in which the probability of finding a particular element at any lattice position is equal to its concentration. Chemical order-disorder transformations are typically 1st-order thermodynamically in systems with face-centered cubic unit cells (fcc), and thus show a discontinuity in the first derivatives of the Gibbs free energy with respect to temperature and pressure. An exothermic latent heat accompanies the chemical-ordering transformation because the ordered phase has lower energy. Only local rearrangement of the atoms is required for chemical ordering; thus, the rate of transformation is dependent upon the difference in free energy between the chemically ordered and disordered phases at a given temperature and upon the rate at which atoms are able to change lattice positions. Nominally equiatomic Fe-based intermetallics with the L1₀ crystal structure (see Figure 2(a)) form from the A1 crystal structure (see Figure 2(b)) via a chemical-ordering transformation and exhibit hard magnetic properties.
Figure 2: Unit cells of a binary alloy AB with (a) the chemically ordered tetragonal \( \text{L1}_0 \) structure and (b) the chemically disordered fcc A1 structure.

In this Dissertation, the FePd and FeNi material systems have been chosen for study because they both exhibit \( \text{A1} \leftrightarrow \text{L1}_0 \) chemical order-disorder transformations. Additionally, their \( \text{L1}_0 \) structures are reported to possess high magnetocrystalline anisotropies and high magnetizations, which make them promising candidates for future permanent magnet applications. \( \text{L1}_0 \) FeNi (a.k.a. tetrataenite) is only found naturally in meteorites that form over 4.5 billion years; to date, it has not been produced in bulk by laboratory methods. The challenge for manufacturing \( \text{L1}_0 \) FeNi is that it has a critical temperature of 320 °C, below which the fcc chemically disordered phase transforms into the \( \text{L1}_0 \) chemically ordered phase [1]. Below this critical temperature, the atomic mobilities of Fe and Ni are extremely low (1 atomic jump per 2,600 years [2]) therefore the atomic movement necessary for chemical ordering is kinetically limited. On the other hand, the \( \text{L1}_0 \) structure forms readily in FePd making it a useful model system in which to study the order-disorder transformation [3]. It is noted, however, that the high cost of palladium makes FePd an impractical material for bulk industrial applications.

The magnetic character of FePd is not well understood. In particular, reported values of the Curie temperature, \( T_C \), of \( \text{A1 Fe}_{50}\text{Pd}_{50} \) are spread over nearly one hundred degrees and there is disagreement on whether chemical ordering causes \( T_C \) to increase or decrease [4, 5]. There have been several studies on the microstructural evolution during \( \text{L1}_0 \)-phase
growth in FePd [6-8], but information on the enthalpy of transformation is limited and the kinetic mechanism of the transformation is not well understood.

While the crystal structure of L1₀ FeNi has been studied in meteorites, little magnetic characterization has been conducted since the phase was first discovered in the 1960s [9-11]. The thermodynamic and kinetic parameters of the chemical order-disorder phase transformation are also unknown. Therefore, it is of great interest to study the magnetic properties of FeNi and to gain an understanding of the thermodynamics and kinetics involved in its L1₀-A1 chemical-order-disorder transformation.

L1₀ FeNi is a particularly promising material for next-generation rare-earth-free permanent magnets as Fe and Ni are both inexpensive, readily available, and amenable to standard metallurgical processing techniques. Collaborative efforts carried out during the course of this work demonstrated that meteoritic L1₀ FeNi has properties that make it competitive with the best rare-earth permanent magnets at room temperature and, furthermore, outperforms many rare-earth permanent magnets at elevated temperatures [12]. It is anticipated that the results from this work will inform future synthesis efforts of L1₀-structured FeNi-based materials for permanent magnet applications.

1.2 Overview of Research

The aim of this Dissertation is to obtain a fundamental understanding of the correlations between chemical ordering and the magnetic properties in the FePd and FeNi systems and to elucidate the mechanisms of the chemical ordering and disordering transformations.
The following characteristics are examined:

(a) Structure: microstructure, crystal structure, long range order
(b) Magnetic properties: saturation magnetization, anisotropy constant, $T_C$
(c) Thermodynamics: enthalpy of transformation, enthalpy of formation, driving force for transformation
(d) Kinetics: activation energy for transformation, mechanism

Laboratory-synthesized FePd is used as a test-bed material system in this work and L1$_0$ FeNi (tetrataenite) extracted from the NWA6259 meteorite is utilized as a natural source of the chemically ordered phase (43 ± 1 at.% Ni composition). FePd samples were formed by arc-melting elemental materials to form an alloy and subjecting the alloy to varying heat treatments to form the A1 and L1$_0$ structures. To detect the L1$_0$ phase and analyze the magnetic characteristics, meteoritic and laboratory-prepared samples were probed by a variety of techniques including energy-dispersive X-ray spectroscopy (EDS), optical microscopy, X-ray diffraction (XRD), magnetic force microscopy (MFM), vibrating sample magnetometry (VSM), and differential scanning calorimetry (DSC).

The objectives of this Dissertation are pursued in the FePd materials system in two steps. First, A1-structured and L1$_0$-structured FePd are characterized to determine the structural and magnetic properties and the thermal stabilities of the two phases. The magnetic domain structures, Curie transition behavior, and enthalpies of formation of the A1-structured and L1$_0$-structured FePd are compared. Second, thermal and structural developments during the A1→L1$_0$ chemical-ordering transformation are observed at different cooling rates for FePd samples that are slowly cooled through the order-disorder
transformation temperature. The effect of cooling rate on the chemical-ordering transformation in FePd is examined.

The objectives of this Dissertation are also pursued through study of the FeNi materials system in two steps. First, the structural and magnetic characteristics of L1₀ FeNi (tetrataenite) extracted from meteoritic materials are characterized and correlations between the structure and magnetism are discussed. Second, calorimetric changes are studied as functions of heating rate to quantitatively determine the thermodynamic and kinetic parameters of the L1₀→A1 chemical-disordering transformation and to add insight into the kinetic mechanisms of the transformation.

Results from investigations on FePd can be summarized as follows. The magnetic domain patterns obtained for L1₀-type FePd indicate that this material has uniaxial magnetic anisotropy with a twinned microstructure. Bulk magnetic measurements confirmed that L1₀-structure FePd has a high magnetic anisotropy and further showed that behavior of the magnetization through the Curie transition is consistent with the tricritical mean-field theory. The enthalpy of transformation from the L1₀ phase to the A1 phase in FePd was experimentally determined as 2.4 ± 0.2 kJ/g-atom and the enthalpy of formation for L1₀ FePd is \( \Delta H_{\text{form}}^{li} = -9.4 \) kJ/g-atom. The chemical disordering transformation is not kinetically-limited under the conditions tested in this work. Overall the results provide insight into the structure, magnetism, and thermal attributes of the A1 and L1₀ phases. Structural analysis of FePd slowly cooled through the order-disorder temperature reveals a mixture of the L1₀ phase and a chemically disordered tetragonal phase. Structural and magnetic results in this Dissertation are presented in relation to two proposed mechanisms of the chemical-ordering transformation.
Results from experimental studies carried out on FeNi are summarized here. The microstructure is found to consist of regions ~50 μm wide with a tetragonal crystal structure confirmed to be the L1₀-type structure. Magnetic results indicate that tetrataenite has strong uniaxial magnetic anisotropy and a high observed $T_C \approx 560$ °C. Calorimetry showed that tetrataenite chemically disorders at the same temperature as the observed $T_C$, indicating the occurrence of a simultaneous chemical disordering transition (from the tetragonal L1₀ structure to the cubic A1 structure upon heating) and magnetic transition (the Curie transition from ferromagnetic to paramagnetic behavior upon heating). Thus the disordering transformation in tetratatenite is a magnetostructural phase transition. The chemical order-disorder enthalpy of transformation is $\Delta H_{L1_0 \rightarrow A1} \approx 4.0 \pm 0.2 \text{ kJ/g·atom}$. The experimentally-determined heat of formation of L1₀ FeNi suggests that tetrataenite may be more stable than previously reported. The activation energy of chemical disordering is found to be comparable to the activation energy of lattice diffusion in Fe-Ni. Overall these results indicate that the chemical-disordering process in tetrataenite is a kinetically-limited and thermally-activated phase transformation that is likely limited by the creation and movement of atomic vacancies.

1.3 Organization of Dissertation

This Dissertation contains seven main chapters: (1) Introduction (current chapter); (2) Formalism and Critical Literature Review; (3) Experimental Methods; (4) FePd Results and Discussion; (5) FeNi Results and Discussion; (6) Conclusions; and (7) Recommendations for Future Work. Chapter 2 – “Formalism and Critical Literature Review” – provides the reader with fundamental background regarding thermodynamic and kinetic aspects of phase transformations. Special attention is paid to chemical order-
disorder transformations and magnetic order-disorder transitions. Additionally, the FePd and FeNi material systems are introduced and previous work concerning the L1₀ structure in these systems is reviewed. In Chapter 3 – “Experimental Methods” – the experimental techniques and apparatuses used to characterize the chemical, structural, magnetic, and thermal properties of the FePd and FeNi samples are discussed. Chapter 4 – “FePd Results and Discussion” – is sub-divided into two sections. In the first section, experimental data pertaining to studies aimed at characterizing the structure, magnetism, and thermal stability of A1- and L1₀-structured FePd are presented and interpreted. The second section of Chapter 4 is focused on examining the effect of cooling rate on the A1→L1₀ chemical ordering transformation in FePd. Chapter 5 – “FeNi Results and Discussion” – is also sub-divided into two sections. The first section investigates the structural and magnetic properties of L1₀ FeNi extracted from meteorites. In the second section of Chapter 5, experimental results from studies aimed at understanding the thermal stability and kinetic mechanism of the disordering transformation of the L1₀ FeNi phase are presented and analyzed. Conclusions derived from the results achieved in this Dissertation are concisely summarized in Chapter 6 – “Conclusions”. Finally, recommendations for future experiments are discussed in Chapter 7 – “Recommendations for Future Work”.

7
2 Formalism and Critical Literature Review

Understanding phase transformations, both structural and magnetic, in equiatomic chemically-ordered L1₀ intermetallic compounds is at the core of this Dissertation work. To that end, this formalism and critical literature review discusses three main topics: 1) fundamental thermodynamics and kinetics of phase transformations, 2) chemical and magnetic order-disorder transitions, and 3) previous work performed on the L1₀-type structure in FePd and FeNi studying phase properties, stability, and formation.

The basic thermodynamic and kinetic fundamentals that are required for an appreciation of chemical and magnetic order-disorder phase transformations are discussed in Section 2.1. Section 2.1.1 lays a foundation for understanding the thermodynamic conditions that govern phase transformations. This discussion is extended in Section 2.1.2 by addressing kinetic mechanisms of structural phase transformations.

An overview of order-disorder transformations, both chemical and magnetic, is given in Section 2.2. Definitions of chemical order-disorder and an overview of the phases of concern in this work are shown in Section 2.2.1. Concepts central to magnetism and magnetic phase transitions, with a focus on permanent ferromagnets, are introduced in Section 2.2.2.

Previous work on the specific material systems of interest is summarized in Section 2.3. A review of known structural and magnetic properties of FePd with the L1₀ structure, as well as prior literature on the formation mechanism of this test-bed system is presented in Section 2.3.1. A critical literature review of L1₀ FeNi is presented in Section 2.3.2 with an emphasis on L1₀ FeNi phase stability, structural and magnetic properties, and formation routes.
2.1 General Overview of Phase Transformations

The fundamentals of thermodynamics and kinetics of phase transformations are presented in this section. An overview of thermodynamics is provided in Section 2.1.1. The distinction between 1st-order versus 2nd-order transformations is given, followed by thermodynamic concerns that are specific to binary alloys and compounds. The kinetics of structural phase transformations (2.1.2) are discussed in terms of nucleation and growth models relevant to chemical order-disorder transformations.

2.1.1 Thermodynamics of Phase Transformations

Phase transformations occur because the initial state of a given system is unstable relative to the final state at that temperature and pressure. For transformations that occur at constant temperature and pressure, the stability of a single-component system is determined by its Gibbs free energy $G(T,P)$. The Gibbs free energy of a system is defined by:

$$G(T,P) = U + PV - TS = H - TS$$  \hspace{1cm} (2.1)

where: $G$ = Gibbs free energy (Joules, J)

$U$ = internal energy of the system (J)

$P$ = pressure (Atmospheres, atm)

$V$ = volume (Liters, L)

$T$ = temperature (Kelvin, K)

$S$ = entropy (J/K)
\[ H = \text{enthalpy (J)} \]

For a magnetic material, there is an additional term in the Gibbs free energy expression that accounts for the energy of different magnetic phases and the interactions of electrons in those phases [1]. In this circumstance the Gibbs free energy becomes

\[ G(T,P) = H - TS + \Xi \]  

(2.2)

where: \( \Xi = \) free energy contribution due to the presence of magnetism in the system (Joules).

2.1.1.1 First-order vs. Second-order Transformations

Phase transformations that take a system from an initial state to a final state are classified by Ehrenfest as \( n \)th order where the \( n \)th derivative results in a discontinuity in Gibbs free energy with respect to at least one state variable \([13, 14]\). The Gibbs free energy \( G(T,P) \) is a continuous function with respect to temperature and pressure; a first-order phase transition exhibits a discontinuity in the first derivative of Gibbs free energy with respect to temperature and pressure. This distinction is shown mathematically below and graphically in Figure 3 [1].

\[
\left. \frac{\partial(G_2-G_1)}{\partial T} \right|_P = S_1 - S_2 \neq 0
\]

\[
\left. \frac{\partial(G_2-G_1)}{\partial P} \right|_T = V_2 - V_1 \neq 0
\]

(2.3)

where: \( G_1 = \) Gibbs free energy of phase 1 (J)

\( G_2 = \) Gibbs free energy of phase 2 (J)
\( S_1 = \text{entropy of phase 1 (J/K)} \)

\( S_2 = \text{entropy of phase 1 (J/K)} \)

\( V_1 = \text{volume of phase 1 (L)} \)

\( V_2 = \text{volume of phase 2 (L)} \)

The heat lost or gained during a first-ordered transition is known as the enthalpy or heat of transformation, also known as the latent heat \( \Delta H \), and it follows from the second law of thermodynamics that for a closed system

\[
\Delta H_{1 \leftrightarrow 2} = T(S_2 - S_1) \tag{2.4}
\]

where: \( \Delta H_{1 \leftrightarrow 2} = \text{Latent heat of transformation (Joules)} \)

By combining Equations (2.3) and (2.4) the change in the Gibbs free energy during a first-ordered phase transition can be related to the latent heat of the system by

\[
\frac{\partial (G_2 - G_1)}{\partial T} \Bigg|_P = \frac{\partial (S_1 - S_2)}{\partial T} = \frac{-\Delta H_{1 \leftrightarrow 2}}{T} \tag{2.5}
\]

In this way it is possible to monitor the response of a system during a first-order transition by monitoring the heat uptake or release in a system [1].

A second-order phase transition occurs when \( G(T,P) \) and its first derivative are continuous but the second derivative with respect to temperature and pressure is discontinuous.

\[
\frac{\partial^2 (G_2 - G_1)}{\partial T^2} \Bigg|_P = \frac{\partial (S_1 - S_2)}{\partial T} \Bigg|_P = \frac{C_{P_1} - C_{P_2}}{T} \neq 0
\]
\[
\frac{\partial^2 (G_2 - G_1)}{\partial P^2} \bigg|_T = \frac{\partial (V_1 - V_2)}{\partial P} \bigg|_T \neq 0
\]  

(2.6)

where: \(C_{P,1}\) = heat capacity at constant pressure of phase 1 (J/K)

\(C_{P,2}\) = heat capacity at constant pressure of phase 2 (J/K)

Since the entropy change is continuous in a second-order phase transition, there is no latent heat \(\Delta H_{1\rightarrow2}\) released. A second-order phase transition can be observed by the change in specific heat [1].

Magnetic phase transformations, such as a Curie transition where a ferromagnetic phase becomes paramagnetic upon heating through a critical temperature (the Curie temperature), are second order transformations as can be seen by examining the magnetic contribution to the free energy:

\[
d\mathcal{E} = -\mu_0 MV dH_{\text{app}}
\]

(2.7)

\[
\frac{\partial (G_2 - G_1)}{\partial T} \bigg|_{P,H_{\text{app}}} = S
\]

(2.8)

\[
\frac{\partial^2 (G_2 - G_1)}{\partial T^2} \bigg|_{P,H_{\text{app}}} = \frac{\partial (S_1 - S_2)}{\partial T} \bigg|_{P,H_{\text{app}}} = \frac{C_{P,H_{\text{app}}}^{-1} - C_{P,H_{\text{app}}^2}}{T} \neq 0
\]

(2.9)

where: \(\mu_0\) = permeability of free space

\(M\) = magnetization per unit volume or per unit mass

\(H_{\text{app}}\) = applied magnetic field

Unlike a structural transformation, the first derivative of \(G\) with respect to temperature is continuous. There is a discontinuity in the constant field specific heat at the
ferromagnetic to paramagnetic phase transition so the transition is characterized as second order.

Figure 3: Thermodynamic characteristics of a) first-order and b) second-order phase transformations. Adapted from [1].

2.1.1.2 Heat of Mixing, Heat of Formation, Heat of Transformation, Driving Force for Transformation in Binary Solutions and Compounds:

This Dissertation is concerned with nominally equiatomic binary alloys and compounds therefore salient aspects of thermodynamics of binary systems are summarized here. In an A-B binary solution, where A and B are elemental species, the
Gibbs free energy of the system is a function of the Gibbs free energy of each component, their molar fractions, and the change in Gibbs free energy due to mixing.

\[ G(T, P, X) = X_A G_A + X_B G_B + \Delta G_{mix} \]  

(2.10)

where: \( G \) = Gibbs free energy of the binary solution (J)

\( X_A \) = mole fraction of A

\( X_B \) = mole fraction of B

\( G_A \) = Gibbs free energy of component A (J)

\( G_B \) = Gibbs free energy of component B (J)

\( \Delta G_{mix} \) = change in Gibbs free energy due to mixing (J)

The change in Gibbs free energy due to mixing is the difference in energy between the unmixed and mixed states and it can be expressed as

\[ \Delta G_{mix}(T, P, X) = \Delta H_{mix} - T \Delta S_{mix} + \Delta \Xi_{mix} \]  

(2.11)

where: \( \Delta G_{mix} \) = change in Gibbs free energy due to mixing (J)

\( \Delta H_{mix} \) = heat of solution (J)

\( \Delta S_{mix} \) = difference in entropy between the mixed and unmixed states (J/K)

\( \Delta \Xi_{mix} \) = change in magnetic free energy term due to mixing (J)

Each of the terms in Equation (2.11) is briefly addressed as follows. The heat of solution \( \Delta H_{mix} \) represents the difference in internal energy in the system before and after
mixing. $\Delta H_{\text{mix}}$ depends upon the energies of A-B bonds relative to those of the A-A and B-B bonds and the number of bonds of each type. $\Delta H_{\text{mix}}$ also depends on the length and strength of the bonds and the number of bonds per atom. Based on these factors, $\Delta H_{\text{mix}}$ may be positive or negative. The second term in the above equation, $-T\Delta S_{\text{mix}}$, is always be negative. $\Delta S_{\text{mix}}$ describes the change in entropy due to configurational changes that occur during mixing. The magnetic free energy $\Delta \Xi_{\text{mix}}$ is known to change dramatically as a function of composition. The interplay between the first and second terms and their effect on $\Delta G_{\text{mix}}$ for a non-magnetic material is shown for a binary A-B alloy in Figure 4 [1]. As can be seen in Figure 4, $\Delta G_{\text{mix}}$ is only be positive if $\Delta H_{\text{mix}}$ is positive with larger amplitude than the contribution of $(-T\Delta S_{\text{mix}})$ in the non-magnetic material. However, in a magnetic material, $\Delta G_{\text{mix}}$ may be positive, even if $\Delta H_{\text{mix}}$ is negative, if the magnetic free energy term is positive and sufficiently large. When $\Delta G_{\text{mix}}$ is positive, the solution is unstable and segregation is favored [14].
Figure 4: The effect of $\Delta H_{\text{mix}}$ and $T$ on $\Delta G_{\text{mix}}$ [1].

The heat, or enthalpy, of formation $\Delta H_{\text{form}}$ of an AB binary compound represents the relative thermodynamic stability of the phase, is equal to the energy difference between the phase and the total energy of its constituents in their elemental ground state volumes and crystal structures. The heat of transformation $\Delta H_{1\leftrightarrow2}$ represents the enthalpy difference between two phases. When composition is held constant and the enthalpies are assumed to be temperature independent, the enthalpies of formation of phases 1 and 2 are related to the enthalpy of transformation by

$$\Delta H_{1\leftrightarrow2} = \left| \Delta H_{\text{form}}^1 - \Delta H_{\text{form}}^2 \right|$$

(2.12)

The volume driving force for transformation $\Delta G_V$ is the difference in free energy between two phases at a certain temperature, $T$, and is approximated as a function of the enthalpy of transformation and the undercooling/superheating.
\[
\Delta G_f \approx \frac{\Delta H_{fus}' [T_f - T]}{T_c}
\]  

(2.13)

where \( T_f \) is the transformation temperature. The quantity \((T_f - T)\) is either the undercooling or superheating.

### 2.1.2 Kinetics of Structural Phase Transformations

This Dissertation is concerned with the rate and mechanism of chemical order-disorder transformations, which are governed by kinetics. The classification of kinetic growth processes and the importance of vacancies for phase transformations are discussed in this section. Subsections describe kinetic models of nucleation (Section 2.1.2.1) and growth (Section 2.1.2.2) for thermodynamically 1\(^{st}\)-order transformations.

Phase transitions can be classified based on their growth processes according to Christian [15] as shown in Figure 3. Thermodynamically 1\(^{st}\)-order transitions typically proceed discontinuously by nucleation and growth processes in which fluctuations in the Gibbs free energy are drastic at localized volumes such that nuclei of a new phase grow when the activation energy for growth is overcome. The growth of the product phase in 1\(^{st}\)-order transformations can be categorized as athermal (such as for many martensitic transformations), heat-transport-controlled (such as for solidification and melting), or thermally-activated. This Dissertation is primarily interested in thermally-activated growth that describes a transformation in which the rate of growth of the product phase is a function of the temperature. Thermodynamically 2\(^{nd}\)-order transitions are characterized by subtle periodic fluctuations in the Gibbs free energy throughout large volumes that produces continuous changes such that the transformation is considered to occur everywhere in the system.
This Dissertation is chiefly concerned with chemical order-disorder transformations (these transformations are discussed in Section 2.2) and as can be seen by the classification in Figure 3, these transformations may be thermodynamically 1<sup>st</sup>- or 2<sup>nd</sup>-order in nature. Chemical order-disorder transformations in body-centered cubic lattices, such as that found in the equiatomic CuZn alloy, may be 2<sup>nd</sup>-order in character but order-disorder transformations in face-centered cubic lattices, such as is the focus of this Dissertation, are generally of 1<sup>st</sup>-order thermodynamic character and are therefore characterized by nucleation and growth processes.

![Classification of structural phase transformations according to growth processes adapted from Christian [15].](image)

Whether a phase transition may be described as thermodynamically 1<sup>st</sup>- or 2<sup>nd</sup>-order in nature, chemical order-disorder transformations occur by a process of local atomic rearrangement, in which atoms exchange places with neighboring atoms to form a
chemically ordered lattice (see Section 2.2 on chemical order-disorder). The rate at which an atom successfully changes lattice positions is given by the atomic jump frequency \[ \Gamma \] that depends upon the energy in the system and the lattice sites available for the atom to move into

\[
\Gamma = \nu z C_v \exp \left( \frac{\Delta G_m}{RT} \right)
\]  

(2.14)

where: \( \nu \) = temperature-independent atomic vibration frequency

\( z \) = number of nearest neighbors

\( C_v \) = concentration of vacancies

\( \Delta G_m \) = activation free energy of vacancy migration

\( R \) = ideal gas constant

It is observed in Eq. (2.14) that the atomic jump frequency is directly related to the concentration of vacancies in the system. Experimental data on the motion of atoms is typically published in terms of the diffusivity \( D_i \), which is a function of the jump frequency, the average jump distance, and the number of directions in which the atom can jump \((1/6)\) [14].

\[
D_i = \frac{1}{6} \delta^2 \Gamma_i
\]  

(2.15)

where: \( \delta \) = average jump distance (m)

\( \Gamma_i \) = number of successful jumps by species \( i \) in one second (#/s)
The diffusivity is temperature dependent with an Arrhenius-type relationship and is expressed for substitutional movement of atoms through the lattice of a crystalline solid by [14]

\[
D = \frac{1}{6} \delta^2 z v C_r \exp \left( \frac{-\left(\Delta G_m + \Delta G_f\right)}{RT} \right) = D_0 \exp \left( \frac{-\left(Q_m + Q_f\right)}{RT} \right)
\]

where: 
- \( D = \text{diffusivity (cm}^2/\text{s)} \)
- \( D_0 = \text{diffusion constant (cm}^2/\text{s)} \)
- \( \Delta G_m = \text{activation free energy for vacancy migration (J/mol)} \)
- \( \Delta G_f = \text{activation free energy for vacancy formation (J/mol)} \)
- \( Q_m = \text{activation energy for vacancy migration (J/mol)} \)
- \( Q_f = \text{activation energy for vacancy formation (J/mol)} \)
- \( R = \text{ideal gas constant (J/mol} \cdot \text{K)} \)

The total activation energy for diffusion in a lattice, \( Q_L \), is approximately equal to the sum of the activation energies for vacancy formation and vacancy migration. Vacancies are easily created and annihilated at grain boundaries, thus the activation energy for diffusion at a grain boundary, \( Q_{GB} \), is only dependent upon the vacancy migration process, and is roughly equal to half the magnitude of \( Q_L \) [16].
2.1.2.1 Nucleation Models of Structural Transformations

Nucleation describes the local formation of a thermodynamic state, or phase, that is different from the parent phase. The new phase may have a different crystal structure, different magnetic behavior, or a different composition as compared to those of the parent phase. The free energy change associated with the nucleation process is given by [14]

\[ \Delta G_N = -V \Delta G_V + A \gamma + V \Delta G_S - \Delta G_d \]  

(2.17)

where: \( \Delta G_N \) = Gibbs free energy change associated with the nucleation process (J)

\( V \) = volume of the nucleated phase (m\(^3\))

\( \Delta G_V \) = driving force per volume (J/m\(^3\))

\( A \) = area of interface between phases (m\(^2\))

\( \gamma \) = interfacial strain (J/ m\(^2\))

\( \Delta G_S \) = misfit strain energy per volume (J/ m\(^2\))

\( \Delta G_d \) = free energy due to destruction of defects (J)

Each term in Equation (2.17) is briefly described for the nucleation of a phase 2 from a parent phase 1. The driving force \( \Delta G_V \) is the difference in free energy between phase 1 and phase 2 per unit volume of the nucleated phase. At temperatures where phase 2 is stable, the creation of a volume of phase 2 reduces the free energy by an amount equivalent to the product \( V \Delta G_V \). The second term represents in Eq. (2.17) strain introduced by interface between the phases that increases the free energy. The interfacial strain \( \gamma \) is written here as a single isotropic value for simplicity. However, \( \gamma \) can vary
greatly depending on the type of interface and therefore the second term in Eq. (2.17) can be written as the summation over all nucleus surfaces as \( \Sigma \gamma_i A_i \). The third term in Eq. (2.17) arises from the difference in volume between the nucleated and parent phases that produces a strain energy \( \Delta G_S \) per unit volume of the nucleated phase that increases the free energy. Lastly, the creation of a nucleus may remove a defect, resulting in a reduction in free energy by an amount \( \Delta G_d \). Due to the last term in Eq. (2.17), nucleation prefers to occur at defects such as free surfaces, grain boundaries and interphase boundaries, stacking faults, dislocations, and vacancies [1].

### 2.1.2.2 Kinetic Growth Models of Transformations with First-order Thermodynamics

The growth process in most phase transformations is either diffusion-controlled, interface-controlled, or a combination of diffusion and interface controlled. The transformation is typically diffusion-controlled when there is a change in composition such that long-range diffusion of atoms through the lattice is required. The growth is interface-controlled when atoms are not able to easily cross the inter-phase interface. Typically interface-controlled growth occurs when the product phase has the same composition as the parent phase so that long-range diffusion is not required or when the product and parent lattices have a coherent or semicoherent relationship[14]. A combination of diffusion and interface controlled growth occurs in some systems, for example, the oxidation of silicon is interface-controlled at short time scales but becomes diffusion-controlled at longer time scales [17]. Chemical order-disorder transformations (see Section 2.2) generally do not involve a change in composition and the interfaces between ordered and disordered phases are usually coherent, therefore an interface-controlled mechanism is expected.
Interface-controlled growth assumes that diffusion within each phase is relatively fast compared to the movement of atoms across the interface between the phases. There is little free volume at coherent and semi-coherent interfaces so that atoms at the boundary cannot be easily accommodated on the boundary of the nucleated phase. This situation results in a low rate of successful atomic jumps, $\Gamma$ at the interface and a slow flux of atoms across the interface [14].

The fraction transformed from the parent phase to the nucleated phase during isothermal heat treatment can be described by the Johnson-Mehl-Avrami-Kolmogorov (JMAK) formulation [14], allowing further insight to be gained into the mechanism of transformation. The volume fraction transformed to the product phase, assuming spatially random nuclei and linear growth with respect to time, is expressed as:

$$X_V = 1 - \exp\left(- \left(K_{JMAK} t\right)^n\right)$$

(2.18)

where: $X_V = \text{volume fraction transformed}$

$K_{JMAK} = \text{is a constant at a given temperature (1/s)}$

$t = \text{time (s)}$

$n = \text{the transformation order, the Avrami exponent (unitless)}$

The Avrami exponent, $n$, represents the transformation order is expressed as [15]

$$n = \text{nucleation condition} + (\text{growth dimensionality} \times \text{growth mechanism})$$

(2.19)
where: the nucleation condition is either site-saturated nucleation (0) or constant nucleation rate (1); the growth is one-, two-, or thre-dimensional; and the growth mechanism is either diffusion controlled (½) or interface controlled (1).

In this Dissertation, constant heating rate experiments are conducted, rather than isothermal measurements, for better signal to noise. Calorimetry measures heat flow, \( \phi \), which is related to the growth rate (transformed volume fraction, \( X_V \), with respect to temperature), enthalpy of transformation, \( \Delta H \), and heating rate, \( \beta \).

\[
\frac{dX_V}{dT} = \frac{\phi}{\Delta H \beta}
\]  \hspace{1cm} (2.20)

The peak in calorimetry data measured as a function of temperature with constant heating rate corresponds to the temperature at which the growth rate of the product phase is a maximum. This equivalence allows the activation energy for growth of the product phase to be determined from peak temperatures observed during the phase transformation achieved under different heating rates \([18-20]\). Equation (2.21) has the form of the equation derived by Kissinger for chemical kinetics, and thus the activation energy can be determined using a Kissinger type analysis.

\[
\ln \left( \frac{\beta}{T_{peak}^2} \right) \approx \ln \left( \nu_{Kiss} \frac{k_B}{Q_i} \right) - \frac{Q_i}{k_B T_{peak}}
\]  \hspace{1cm} (2.21)

where: \( T_{peak} \) = temperature corresponding to the peak in calorimetry data (K)

\( \beta = \) heating rate (K/s)
\( v_{kiss} = \) frequency factor (1/s)

\( Q_t = \) activation energy for transformation (eV/atom)

Michaelsen and Dahms [19] developed a model for characterizing nucleation and growth transformations in terms of three kinetic parameters (activation energy, transformation order, and frequency factor) that can be determined from calorimetry experiments measured with a constant heating rate. The rate of transformation is given by Eq. (2.22). The activation energy and frequency factor are determined from the slope and intercept of the linear fit of experimental results when \( \ln(\beta/T_{peak}^2) \) is plotted versus \((k_B T_{peak})^{-1}\) using the Kissinger analysis in Eq. (2.22). Determination of the exponent \( n \) is accomplished by fitting the transformation rate, converted from calorimetry results using Eq. (2.21), with the Michaelsen and Dahms model [19]:

\[
\frac{dX_v}{dT} \approx n \left( \frac{v_{kiss}}{\beta} \right)^n \exp \left( - \frac{nQ_t}{k_B T} \left( \frac{k_B T^2}{Q_t} \right)^{n-1} \right) \exp \left[ - \left( \frac{v_{kiss}}{\beta} \right)^n \exp \left( - \frac{nQ_t}{k_B T} \left( \frac{k_B T^2}{Q_t} \right)^n \right) \right] \quad (2.22)
\]

The Michaelsen and Dahms analysis makes use of the following three assumptions. First, it is assumed that only two states exist in the system: the untransformed state and the transformed state, and that these two states have a fixed enthalpy difference that is independent of temperature and time. Second, it is assumed that nucleation sites have a random spatial distribution and a fixed density. Then, the activation energy of the transformation given by Michaelsen and Dahms is equivalent to the activation energy of growth of the product phase and neglects the activation energy of nucleation of the product phase.
2.2 Order-Disorder Transformations

This Dissertation is concerned with two types of long-range order: chemical order and magnetic order. A chemical ordering transformation describes the process of randomly-distributed atoms rearranging in a crystal lattice to form an organized structure in well-defined atomic lattice positions such that the alloy changes from a solid solution to a compound, as described in Section 2.2.1. Magnetic order describes the coupling of magnetic moments within a material that can result in ferromagnetic behavior as described in Section 2.2.2.

2.2.1 Chemical Order and Disorder

In a binary A-B solid solution, where A and B are elemental species, the probability of a species existing on a specific lattice site is equivalent to the atomic fraction of the species in the solution. In a chemically-ordered compound, each species resides at particular specified lattice positions.

Chemical ordering can occur in an A-B binary alloy when A-B bonds have lower energy than A-A or B-B bonds, such that $\Delta H_{mix}$ (A-B) is negative, and $\Delta G_{mix}$ is also negative (as in Figure 4b). A atoms prefer to be surrounded by B atoms and vice versa when the A-B bonds are the most stable. The result of this chemical ordering is represented by the 2D lattice in Figure 6 [21].
Figure 6: Chemical ordering depicted in 2D lattice [2].

The degree of long-range chemical ordering is given by the order parameter $LRO$, which is a measure of how completely the specific lattice sites for A atoms ($\alpha$-sites) are occupied by $A$ atoms and the specific lattice sites for B atoms ($\beta$-sites) by B atoms [21]. The $LRO$ parameter of unity represents perfect chemical order and the $LRO$ parameter of zero represents complete disorder. This parameter answers the question: are the right atoms in the correct lattice positions? Details of the calculation of $LRO$ from X-ray diffraction data are given in Appendix A. $LRO$ is defined [13, 21] as

$$LRO = \frac{r_\alpha - X_A}{Y_A} = \frac{r_\beta - X_B}{Y_B}$$

(2.23)

where: $r_\alpha =$ fraction of $\alpha$-sites rightly occupied by $A$ atoms

$r_\beta =$ fraction of $\beta$-sites rightly occupied by $B$ atoms

$X_A, X_B =$ fraction of atoms that are $A$ atoms, $B$ atoms

$Y_A, Y_B =$ fraction of lattice sites that are $\alpha$-sites, $\beta$-sites

Many systems undergo chemical order-disorder transformations; this Dissertation is concerned with details that control the $L1_0 \leftrightarrow A1$ transformation in the ferrous systems.
FePd and FeNi. The A1 phase has a face-centered-cubic (fcc) chemically disordered lattice shown in Table 1 with the likelihood of a particular element occupying a particular lattice site equal to that species molar fraction (indicated in drawing by dual-colored atoms). The A1 unit cell is shown in Table 1 along with alternative ways of referring to this structure such as the γ-phase, space group Fm-3m, and Pearson’s nomenclature of cF4. The Strukturbericht notations are used in this Dissertation for clarity and correctness.

The L1₀ phase (see Table 1) is chemically ordered, meaning that ideally atom A occupies only α-lattice sites and B atoms occupies only β-lattice sites. In the L1₀ structure, A atoms occupy all four corners and two opposite faces of the unit cell while B atoms occupy the remaining four face-centered positions. Chemical ordering causes the L1₀ unit cell to become tetragonal so that the lattice parameters $a = b \neq c$ and all the structural angles are 90°. The tetragonality may be such that $c/a < 1$ or $c/a > 1$ and both structures are shown in the table. The L1₀ phase forms in the near-equiatomic stoichiometry ranges in many material systems including AuCu, FePt, FeCo, FePd, and FeNi through a chemical ordering process from the A1 phase.

Two additional phases of relevance to this Dissertation are the L1₂ and A6 crystal structures. The L1₂ structure adopts the chemically-ordered fcc arrangement with four corners of the cube occupied by A atoms while all six faces are occupied by B atoms. This phase forms from the A1 phase at stoichiometries near AB₃. The A6 phase is a chemically disordered face-centered tetragonal phase that may have $c/a < 1$ or $c/a > 1$ (see Section 2.3.1 for more details on the A6 phase in FePd).
The L1₀ and A6 phases technically have body-centered tetragonal (bct) Bravais lattices, however they are discussed in this Dissertation, and frequently in the literature, in terms of a face-centered tetragonal (fct) lattice. The fct representation allows for easy comparison to the A1 parent phase. The relationship between the fct and bct unit cell representations is shown in Figure 7.

**Table 1: The crystal structure designation, Strukturbericht designation, chemically ordered or disordered classification, prototype, space group, Pearson’s symbol and the ball model of the unit cell for various A-B alloys and compounds.**

<table>
<thead>
<tr>
<th>Phase</th>
<th>Strukturbericht Designation</th>
<th>Chemical order-disorder</th>
<th>Cubic / Tetragonal</th>
<th>Space Group</th>
<th>Pearson’s Symbol</th>
<th>Unit Cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma) ((A,B))</td>
<td>A1</td>
<td>Disordered</td>
<td>Cubic</td>
<td>Fm-3m</td>
<td>cF4</td>
<td><img src="image" alt="cF4" /></td>
</tr>
<tr>
<td>AB</td>
<td>L1₀</td>
<td>Ordered</td>
<td>Tetragonal</td>
<td>P4/mmm</td>
<td>tP4</td>
<td><img src="image" alt="tP4" /></td>
</tr>
<tr>
<td>AB₃</td>
<td>L1₂</td>
<td>Ordered</td>
<td>Cubic</td>
<td>Pm-3m</td>
<td>cP4</td>
<td><img src="image" alt="cP4" /></td>
</tr>
<tr>
<td>(\alpha_2) ((A,B))</td>
<td>A6</td>
<td>Disordered</td>
<td>Tetragonal</td>
<td>I4/mmm</td>
<td>tI2</td>
<td><img src="image" alt="tI2" /></td>
</tr>
</tbody>
</table>
During the Al → L1₀ phase transition the tetragonal L1₀ phase may form with the individual c-axes of the constituent crystallites arranged in a manner that is coherent with the [100], [010], or [001] directions of the parent phase so that three crystal lattice variants are possible as shown in Figure 8[6, 22-24]. These three crystallographic variants can have a coherent relationship that results in crystal twinning and that reduces interfacial strain.

2.2.2 Magnetic Phase Transitions

This Dissertation is concerned with ferromagnetic materials, their magnetic order-disorder transitions, and changes in magnetic structure related to the crystal structure. In this section, ferromagnetism is defined and salient features of ferromagnetic materials are
discussed in terms of the magnetic order-disorder transition (Section 2.2.2.1) and the characteristics of hard and soft ferromagnets (Section 2.2.2.2).

Magnetism stems from the quantized motion of electrons. The magnetic moment of a free electron is a fundamental quantity called a Bohr magneton $\mu_B$ of value $9.27 \times 10^{-21}$ erg/G that arises from combinations of the orbital and spin motion of the electron. In general, the total magnetic moment an atom is described two electronic contributions: the spin angular momentum and the orbital angular momentum [25, 26]. Materials can be roughly classified according to the response of a magnetic moment ($m$) to an externally applied magnetic field ($H_{\text{app}}$); this is known as the magnetic susceptibility ($\chi_M$). Common types of magnetic materials include: 1) paramagnetic ($\chi_M > 0$); 2) diamagnetic ($\chi_M < 0$); 3) antiferromagnetic (anti-parallel electron spins); and 4) ferromagnetic (parallel electron spins). This Dissertation is concerned with ferromagnetic materials. The specific interactions between spins of electrons is an exclusively quantum mechanical effect but the proper relations and temperature dependences of a ferromagnetic material can be given by the mean-field theory (Weiss theory) of ferromagnetism, which considers only generalized average behavior. In a ferromagnetic material, the atomic moments couple to each other to produce a positive net magnetization, $M$, and cooperatively align so that there is a long-range ordering of the atomic moments, according to the mean-field theory ferromagnetism[25]. The maximum magnetization that a ferromagnetic material can have is known as the saturation magnetization, $M_S$, and is an intrinsic property of the material.

### 2.2.2.1 The Curie Transition: Magnetic Order-Disorder

The magnetic phase transition from ferromagnetism to paramagnetism, equivalent to a change from long-range ordering to disordering, is called the Curie transition. The
Curie temperature $T_C$ is the ferromagnetic order-disorder temperature. Magnetic moments in the ferromagnetic material are coupled and aligned causing a positive net magnetic moment below $T_C$. As the temperature increases towards $T_C$, entropy effects cause disordering of magnetic moments. The magnetic moments are uncoupled above $T_C$ [26].

In this Dissertation, the Curie transition and the behavior of the magnetization in the vicinity of the Curie transition are analyzed using Universal Scaling Laws developed from Landau’s classical theory describing 2nd order phase transitions. Landau’s theory assumes that the free energy of a system can be expressed as a power law function of some order parameter. The magnetic moment $M$ serves as an order parameter for ferromagnetic materials. The free energy of a system is equivalent whether the material is magnetized positively or negatively therefore the free energy power law need only include even powers. The Gibbs free energy can be expressed as

$$G = G_0 - \frac{1}{2} a_T (T - T_C) M^2 + \frac{1}{4} b_T (M)^4$$  \hspace{1cm} (2.24)$$

Free energy is minimized when

$$M = \begin{cases} 
0 & (T > T_C) \\
\pm \left[ \frac{a(T - T_C)}{b} \right]^{1/2} & (T < T_C)
\end{cases}$$  \hspace{1cm} (2.25)$$

Experimental measurements of magnetization as a function of temperature, $M$ vs. $T$, can be described by Eq. (2.25) when the material has magnetic interactions described by the mean-field theory.
The Universal Scaling Laws expand Landau’s theory to describe magnetic behavior in the vicinity of the Curie temperature for other models of magnetism such as the Ising model and Heisenberg model[27]. The Ising model treats spin parallel or antiparallel to a given direction while the Heisenberg model treats spins as isotropically interacting unit vectors in three dimensional space[27]. The equations of the Universal Scaling Laws relevant to $M$ vs. $T$ experiments are[28]:

$$
M = M_0 (T_C - T)^{\beta_{MT}}
$$

$$
\chi_M^{-1} = \frac{h_0}{M_0} (T - T_C)^{\gamma_{MT}}
$$

$$
\delta_{MT} = 1 + \frac{\gamma_{MT}}{\beta_{MT}}
$$

(2.26)

where: $T_C$ = Curie temperature

$M$ = magnetization at temperature $T$

$M_0$ = magnetization at zero Kelvin

$\chi_M$ = magnetic susceptibility

$h_0$ = critical amplitude

$\beta_{MT}$ = critical exponent

$\gamma_{MT}$ = critical exponent

$\delta_{MT}$ = critical exponent
Critical exponents evaluated for certain models of ferromagnetism are given in Table 2. The nature of magnetic interactions in a material is informed by comparing experimental critical exponents, found by fitting $M$ vs. $T$ data using Eq. (2.26), to the critical exponents expected for theories of ferromagnetism [27, 28].

**Table 2: Critical exponents of the Universal Scaling Law obtained from different theoretical models [27, 28].**

<table>
<thead>
<tr>
<th>Theory</th>
<th>$\beta_{MT}$</th>
<th>$\gamma_{MT}$</th>
<th>$\delta_{MT}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Field Theory</td>
<td>0.5</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Ising Model</td>
<td>0.325</td>
<td>1.24</td>
<td>4.82</td>
</tr>
<tr>
<td>XY Ising Model</td>
<td>0.331</td>
<td>1.292</td>
<td>4.84</td>
</tr>
<tr>
<td>3D Heisenberg Model</td>
<td>0.365</td>
<td>1.336</td>
<td>4.8</td>
</tr>
<tr>
<td>Tri-critical Mean-Field Theory</td>
<td>0.25</td>
<td>1.0</td>
<td>5.0</td>
</tr>
</tbody>
</table>

**2.2.2.2 Hard and Soft Ferromagnets: the Hysteresis Loop, Magnetocrystalline Anisotropy, and Permanent Magnets**

A ferromagnetic material may be characterized by the dependence of the magnetization $M$ upon an applied magnetic field, $H_{app}$. The features of the magnetic hysteresis loop, $M$ vs. $H_{app}$, are discussed in Section 2.2.2.2.1. The shape of the hysteresis loop is determined by intrinsic and extrinsic factors. The magnetocrystalline anisotropy constant $K$ is one of the three intrinsic factors ($T_C$, $M_S$, and $K$) that influences the hysteresis loop and it is defined in Section 2.2.2.2.2. The extrinsic magnetic properties of ferromagnetic materials are dependent upon many factors including microstructure, defects and stress, the angle between the applied field and the easy axis, and the shape of
the sample. Criteria for a ferromagnetic material to be used in permanent magnet applications are discussed in Section 2.2.2.2.3.

2.2.2.2.1 The Hysteresis Loop and Magnetic Domains

The hysteresis loop (Figure 9) describes bulk magnetic behavior while magnetic domains (Figure 10) describe the magnetic microstructure. Magnetic domains are regions of a ferromagnetic material where the atomic moments are aligned parallel. A ferromagnet begins in the demagnetized state shown by point 0 at the origin in the hysteresis loop (Figure 9) when measuring magnetization as a function of applied field. Each domain is spontaneously magnetized to saturation in an easy axis (see Section 2.2.2.2.2) in the absence of an applied field so there is no net magnetization as is shown in Figure 10(a). Domains with a large magnetization component in the direction of an applied field grow at the expense of neighboring domains in a process known as domain wall motion as depicted in Figure 10(b). Domain wall motion, in a low field, occurs until there are only two domains left (Figure 10(c)). The only way in which the magnetization can increase further is by rotation of the $M_S$ vector of each domain until it is parallel with the applied field. As larger fields are applied, the net magnetization increases until saturation is achieved at point 1 in Figure 9. The ferromagnetic material may retain some net magnetization call remanence $M_R$ when the applied field is removed (point 2). A negative field called the coercivity $H_C$ must be applied in order to demagnetize the ferromagnet (point 3). The ferromagnet can be driven to saturation in the negative direction with a magnetization of -$M_S$ (point 4). The material is said to be “soft” when saturation magnetization is achieved in weak applied fields. Conversely, the material is “hard” when a large applied field is required to reach saturation [29].
Figure 9: Schematic representation of hysteresis behavior in a ferromagnetic materials system[30].

Figure 10: Schematic representation of the domain structure in a single crystal of iron. The field $H_{app}$ is applied in the [110] direction[26].
2.2.2.2 Magnetocrystalline Anisotropy

In a crystal lattice, the electron magnetic moment is affected by the interatomic bonds and some orientations of the electron moment may be energetically favorable causing magnetization to occur along particular crystal axes known as the easy directions. The magnetocrystalline anisotropy energy $E_K$ is the energy stored in a crystal when it is magnetized to saturation in a non-easy direction. The material is a “soft” ferromagnet when the anisotropy energy is small because it is easily magnetized in a direction other than the easy axis. “Hard” ferromagnet have large anisotropy.

The directional dependence of the anisotropy can be expressed by the anisotropy energy $E_K$ as a function of the anisotropy constants ($K_0, K_1, K_2, \ldots$) and directional cosines ($\alpha_1, \alpha_2, \alpha_3$) describing the angles between $M_S$ and the crystal axes.

$$E = K_0 + K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2(\alpha_1^2\alpha_2^2\alpha_3^2) + \cdots \quad (2.27)$$

It can be shown that for a cubic crystal such as the A1 structure (Table 1):

$$K_0 = E_{100}$$

$$K_1 = 4(E_{110} - E_{100})$$

$$K_2 = 27(E_{111} - E_{100}) - 36(E_{110} - E_{100}) \quad (2.28)$$

where: $E_{hkl}$ is the anisotropy energy measured along the $[hkl]$ axis

For a uniaxial material such as the L1$_0$ structure (Table 1), the anisotropy energy depends on only a single angle, the angle $\theta$ between the $M_S$ vector and the $c$-axis. Therefore,
The anisotropy constants can be evaluated by combining measured magnetometry data with Equations (2.27-29) [26]. Details of this calculation using experimental data are in Section 3.5.2.

2.2.2.2.3 Permanent Magnets

The ferromagnets studied in this Dissertation have potential use in permanent magnets applications. Permanent magnets retain a large remanence $M_R$ in the absence of an applied magnetic field and display a large coercivity $H_C$ such that once magnetized along the easy axis, they resist being demagnetized. Permanent magnets can be regarded as energy-storage devices because energy put into them when they are first magnetized remains in the magnet indefinitely as long as the material is not heated past its Curie point. A large magnetic anisotropy, among other factors, can result in a large remanence and coercivity necessary for an advanced permanent magnet[29]. The figure of merit for a permanent magnet is its maximum energy product $(BH)_{\text{max}}$, which is the product of its magnetic flux $B$ (also called induction) multiplied by the applied field. The total magnetic flux density in a material, also known as the magnetic induction ($B$), is related to the magnetization ($M$) [26]:

$$B = H_{\text{app}} + 4\pi M$$

where: $B = \text{magnetic flux or induction (Gauss, G)}$

$$M = \text{magnetization (electromagnetic units / cubic centimeter, emu/cc)}$$
The maximum energy product \((BH)_{\text{max}}\) can be determined from the plot of magnetic induction \((B)\) versus applied field \((H_{\text{app}})\) as the largest rectangle that can be drawn in the second quadrant.

2.3 Critical Literature Review

This dissertation is primarily concerned with the A1 and L1\(_0\) crystal structures in the FePd and FeNi material systems. Specific structural and magnetic properties of A1- and L1\(_0\)-structured FePd and FeNi are discussed in the following sections along with known information of the chemical order-disorder processes in these systems. The FePd material system is discussed first in Section 2.3.1 followed by the FeNi system in Section 2.3.2.

2.3.1 Overview of L1\(_0\) FePd

Prior literature that addresses the thermal stability, structural and magnetic properties, and formation of the L1\(_0\)-structure in FePd is reviewed in this section. This discussion focuses on reported results concerning synthesis of L1\(_0\) FePd bulk samples of the approximate Fe\(_{50}\)Pd\(_{50}\) composition\([3, 31-33]\) although the L1\(_0\) phase has also been studied in films\([34, 35]\) and nanoparticles\([36, 37]\).

Stability of the L1\(_0\) phase in FePd is examined in the context of the FePd phase diagram. The equilibrium phases of the Fe-Pd system, as shown in the equilibrium phase diagram in Figure 11 and Table 3, are as follows \([38]\): (1) \(L\), the liquid phase exists above 1310 °C at the equiatomic concentration; (2) \(\delta\)-Fe, a high temperature body-centered-cubic (bcc) phase between 1394 and 1538 °C and 0-3.7 at% Pd; (3) \(\gamma(\text{FePd})\), the A1 (fcc) solid solution stable across all compositions from the liquidus to ~800 °C; (4) \(\alpha\)-Fe, the low-temperature bcc phase existing below 912 C with up to 3.5% Pd; (5) \(\gamma_1\), the L1\(_0\)
phase with equilibrium chemical order-disorder temperature ($T_{\text{OD}}$) that ranges from 605 °C (48.5 at% Pd) to 790 °C (~60 at% Pd); (6) $\gamma_2$, the L12 phase with ~62 to 85 at% Pd with a maximum $T_{\text{OD}}$ of 820 °C at ~66 at% Pd. At 50 at% Pd, the L10 phase exists in a two-phase region from 700 to 660 °C and as the single stable phase for $T < 660$ °C.

Figure 11: Phase diagram of the binary Fe-Pd system. The L10 phase field is labeled as $\gamma_1$.[38]

Table 3: Equilibrium phases in the Fe-Pd system [38].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition range at% Pd</th>
<th>Structure</th>
<th>Magnetism</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L$</td>
<td>0 - 100</td>
<td>Liquid</td>
<td></td>
</tr>
<tr>
<td>$\delta$-Fe</td>
<td>0 - 3.7</td>
<td>A2 (bcc)</td>
<td></td>
</tr>
<tr>
<td>$\alpha$-Fe</td>
<td>0 - 3.5</td>
<td>A2 (bcc)</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>0 - 100</td>
<td>A1 (fcc)</td>
<td>Paramagnetic</td>
</tr>
<tr>
<td>$\gamma_1$</td>
<td>48.5 - 60</td>
<td>L10</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>$\gamma_2$</td>
<td>62 - 85</td>
<td>L12</td>
<td></td>
</tr>
</tbody>
</table>
The L1₀ phase of the equiatomic composition FePd has reported lattice parameters $a = 3.852 \text{ Å}, \ c = 3.723 \text{ Å}, \ c/a = 0.967$ while the A1 phase of the same composition has reported lattice parameter $a = 3.80 \text{ Å}$ [39]. The saturation magnetization $M_S$ of both the A1 and L1₀ structures of FePd is reported as 110 emu/g[3]. The L1₀ FePd phase has a large uniaxial magnetic anisotropy (anisotropy constant $K = 2.6 \times 10^7 \text{ erg/cc}$) with the easy-axis in the [001] crystallographic direction while the A1 phase has very low magnetic anisotropy ($K \approx 10^4 \text{ erg/cc}$) [3].

The reported Curie temperatures of A1 and L1₀ FePd vary greatly. Curie temperatures from 400 - 480 °C have been reported for the 50/50 composition of A1 FePd while the $T_C$ of the analogous L1₀ phase varies from 420 - 490 °C [4, 5]. Several authors [4, 40] report that $T_C$ (L1₀) > $T_C$ (A1) for a given FePd composition while other authors observe the opposite trend [6]. It has been hypothesized that the Curie temperature of FePd is highly dependent upon both lattice strain and on the degree of short-range chemical ordering, both of which depend upon processing conditions. A motivation for the work in this Dissertation is to better understand the relationship between processing conditions, crystal structure, chemical ordering, microstructure, and the Curie temperature.

The literature reports L1₀ phase formation in FePd achieved by isothermal annealing procedures carried out at $T < T_{OD}$, with information deduced on the time required to complete the phase transformation at different annealing temperatures, as shown in Figure 12. L1₀ phase formation proceeds most rapidly at annealing temperatures of ~500 – 525 °C as shown by the nose of the time-temperature-transformation (T-T-T) diagram.
where each curve represents an indicated volume fraction transformed to the L1₀ according to the temperature and duration of annealing.

![Graph of volume fraction against temperature and duration of annealing.](image)

**Figure 12:** The volume fraction of the ordered phase according to the temperature (°C) and duration of annealing in log(hours)[41].

Isothermal annealing studies have characterized changes in the FePd microstructure as a function of annealing time. The early stages of the A1→L₁₀ transformation, observed in an A1 single crystal FePd sample annealed at 550 °C for 4 h, are characterized by realization of a “tweed contrast” microstructure [42]. The tweed contrast is ascribed to the existence of waves of elastic displacement of atoms that periodically distort the initial crystal lattice, which are caused by intragrain transformations that are either indicative of nuclei of a new coherent phase within the matrix [42] or a pre-transition state [4]. The later stages of the chemical ordering transformation are characterized by a “polytwinned” microstructure consisting of microtwins (nano-scale) and macrotwins (micron-scale)[8, 31].
Zhang et al. [8] attribute observed microstructure features formed during isothermal annealing of FePd at 500-650 °C to nucleation and growth of the L1₀ phase. The tweed contrast is attributed to nucleation of the L1₀ phase occurring in three directions coherent to the parent A1 lattice (supported in TEM results)[8]. The difference in lattice parameters between the parent A1 and product L1₀ phases causes lattice strain and bands of microtwins form along the {110} planes in the A1 lattice to accommodate the strain[8]. Two orientations of the L1₀ precipitates are preferred due to the lattice strain. The {110} A1 microtwin bands are shown in Figure 13 with coherent L1₀ precipitates forming within each band[8]. The L1₀ phase grows and impinges within each {110} twin such that each microtwin band corresponds to a single c-axis variant (merohedral twins) and the twin boundaries are orthogonal variant boundaries [8, 24]. Antiphase boundaries (APBs), where the c-axis of an L1₀ crystallite is off-set by half a unit cell relative to its neighbors, are present within each microtwin band[8]. A micrograph and schematic diagram of the polytwinned microstructure are shown in Figure 14 where the macrotwin plates, or bands, each consist of packets of microtwins [43]. The arrows in the inset mark the c-axis directions of the variants in the microtwins [43].
Figure 13: Schematic representation microtwin formation in FePd [8]. (a) Distribution and alignment of L1₀ precipitates within alternating A1 {110} bands that form during short annealing times. (b) L1₀ microtwin structure after long annealing times showing that each band is a single c-axis variant.

Figure 14: Polytwinned microstructure of FePd imaged using bright field transmission electron microscopy (TEM). Inset shows the arrangement of c-axes within the microtwinned lamellae[43].

Vlasova et al. agree with the microstructural changes observed by Zhang et al., however Vlasova et al. propose that the A1→L1₀ chemical ordering transformation in FePd occurs via a two-stage process in which an intermediate A6 phase is formed [7, 44]. The A6 phase is a tetragonal chemically disordered phase (see Section 2.2.1) that is
predicted to be a distinct metastable phase in FePd and is not simply a distortion of the A1 phase. It is proposed that the A1→A6 transformation occurs via cooperative displacement (diffusionless) while the A6→L1₀ transformation is a chemical ordering process [7, 44]. Evidence of the A6 phase is shown in selected-area electron diffraction patterns of single-crystal FePd annealed at 550-600 °C for 15 min – 100 h [44] and in FePd subjected to high pressure torsion [7]. The results from high pressure torsion are shown in Figure 15 where the as-deformed sample (a) shows evidence of a tetragonal structure by the splitting of the (200) and (002) fundamental Bragg reflections (d-spacing = 0.185, 0.192) but no evidence of chemical ordering indicated by the absence of (001) and (110) superlattice Bragg reflections (d-spacing = 0.368, 0.274). Furthermore, Vlasova et al. propose that the FePd system (as well as CoPt and FePt) exhibits ferroelasticity [44]. Vlasova et al. define a ferroelastic phase as having a crystal that may be found in two or more orientational states with different but structurally identical arrangements of atoms. The effect of ferroelasticity consists in the emergence of macroscopic spontaneous deformation of a crystal upon a phase transition. The ferroelastic phase transition may be induced by a mechanical stress and may exhibit a mechanical hysteresis (analogous to the magnetic hysteresis loop of ferromagnets in Section 2.2.2.2.1)[44]. The evidence of ferroelasticity in FePd is given by polarized light observations in Ref. [44]. Short annealing times show ferroelastic domains (polytwinned structure) however longer annealing leads to the growth of single structural domains (reduction of twinning).
Figure 15: Selected-area electron diffraction (SAED) results on FePd: (a) fabricated from the disordered equiatomic FePd alloy after severe plastic deformation; (b) subsequent annealing at $T = 450$ °C for 11 h. Two-pike arrows point to the positions of diffraction rings that are common for both electron diffraction patterns. One-pike arrows show the positions of the diffraction rings, those present only in the electron diffraction pattern (b). The values of $d$-spacings are shown above and below the arrows.

Alteration of the rate of $L1_0$ transformation and its microstructure has been reported in samples processed by cold rolling, by application of uniaxial compression, and by applied magnetic fields. Cold-rolling and other severe plastic deformation methods have been shown to enhance the rate of chemical ordering in FePd and result in $\{111\}$ lattice twins. A cooperative reaction of chemical ordering and recrystallization has been explored as a mechanism for enhanced transformation rate in cold-rolled samples[45]. Applications of uniaxial pressure, or large magnetic fields, during annealing have been shown to result in a single c-axis orientation of $L1_0$ during the chemical ordering transformation[23].
2.3.2 Overview of $L_1^0$ FeNi (Tetrataenite)

Laboratory synthesis and study of $L_1^0$ FeNi are hampered by the extremely sluggish kinetics of formation of the chemically-ordered phase. In this section, the reported formation methods of $L_1^0$ FeNi are presented followed by information on the phase stability and the low-temperature FeNi phase diagram. Structural and magnetic properties determined from studies of meteorites and of irradiated samples are presented. Finally, the kinetics of Fe-Ni system and barriers to chemical ordering in this system are discussed.

To date, $L_1^0$ FeNi formation has only been reported in samples subjected to high-energy neutron or electron irradiation, in selected meteorites and terrestrial rocks, and recently in thin films formed by monatomic layer epitaxial deposition [10, 11, 46-49]. Neutron and electron irradiation were key to the realization of $L_1^0$-type FeNi by Paulevé and Néel et al. in the 1960s, delivering sufficiently large energy to create atomic vacancies that enabled short-range atomic rearrangement into the chemically-ordered phase below the reported chemical order-disorder temperature of 320 °C.[11, 50] In the late 1970s, $L_1^0$ FeNi was detected in the complicated microstructures of the many slowly-cooled iron, stony-iron and stony meteorites.[9, 10] Meteorites provide a unique opportunity to study the Fe-Ni system as they have cooled over timescales approaching a billion years, some with cooling rates on the order of 0.1 K per million years;[51, 52] this timescale allows for low-temperature phase transformation under very small driving forces. A recent report describing attainment of $L_1^0$ FeNi through severe plastic deformation[53] is encouraging but lacks consideration of easily-formed iron oxides that have peaks at many of the same positions as $L_1^0$ FeNi. A better understanding of the
energy required for phase formation and the kinetic mechanism(s) of transformation will greatly aid terrestrial bulk synthesis efforts.

While the thermodynamic stability of L1\textsubscript{0} FeNi (tetrataenite) has been informed by studies performed on both irradiated and meteoritic samples, it is still an open question whether L1\textsubscript{0}-type FeNi is a stable\textsuperscript{[54-56]} or is a metastable\textsuperscript{[1]} phase. The chemical order-disorder temperature $T_{\text{OD}}$ identifying the FeNi A1–L1\textsubscript{0} structural transformation temperature was established by study of neutron-irradiated specimens as 320 °C \textsuperscript{[11]}. Subsequent studies corroborated these findings and showed evidence of L1\textsubscript{0} phase formation in Fe-Ni samples with initial average compositions in the range 31 - 70 at\% Ni irradiated in the temperature range 200 – 400 °C.\textsuperscript{[54-56]}

The most recent and most complete phase diagram of the low temperature Fe-Ni system was published by Yang and Goldstein in 1996 (Figure 16)\textsuperscript{[57]}. The key features of the phase diagram are described here. A martensitic transition is noted by its start temperature ($M_{\text{start}}$) shown as a dash-dot-dotted line. The Curie temperature of the A1 phase is indicated by the dash-dotted line labeled $T_{C\gamma}$ and varies considerably with composition. The magnetic contribution to the free energy induces a miscibility gap, at a point known as a tricritical point that occurs at 48.8 wt\% Ni and 462 °C. Below the tricritical point, the $\gamma$-phase splits into the low Ni content paramagnetic $\gamma_1$-phase, and a high Ni content ferromagnetic $\gamma_2$-phase. The spinodal is indicated by hashed lines while the miscibility gap is shown by dashed lines. The $\gamma''$-phase is the L1\textsubscript{0} and is shown on Yang and Goldstein’s phase diagram as a metastable phase existing on the high Ni content boundary of the miscibility gap. The critical chemical order-disorder temperature of the $\gamma''$-phase is indicated by a small horizontal dashed line at $T_{C\gamma''} = 320$ °C. Yang et al.
argued that tetrataenite is a metastable phase in the Fe-Ni system based on chemical information derived from microprobe measurements performed on meteoritic samples showing the presence of the A2-type phase (bcc α-Fe with up to 7 at% Ni, also known as kamacite) bordering the L12 phase (FeNi3 with the AuCu3-type structure, also known as awaruite), strongly suggesting that these two phases are in equilibrium with each other. These observations allowed Yang et al. to conclude that the L10 phase was not present as an equilibrium phase during the cooling history of the meteorite[1]. Further, Chuang et al. and Reuter et al. argued that a significant magnetic contribution to the free energy of the Fe-Ni system reduces phase stability and may produce a miscibility gap in the vicinity of ~30-50 at% Ni composition for T < 462 °C.[58, 59] Computational studies of the stability of L10-type FeNi have differed in both initial assumptions and results but Cacciamani et al. and Barabash et al. argue that the L10 structure is the stable ground state configuration[60-62]. Overall, there are not sufficient experimental data to date to fully understand the phase stability of L10-type FeNi.
Figure 16: Yang's Fe-Ni phase diagram[57].

The structure and magnetic properties of L1₀ FeNi have been informed examination of meteorites. Since Fe and Ni have similar atomic radii the lattice parameters have a ratio of \( c/a = 1.0036 \pm 0.0002 \) with \( c = 3.5890 \pm 0.0005 \) Å and \( a = 3.5761 \pm 0.0005 \) Å[63]. Magnetic investigations in meteorites have reported Curie temperatures 535-580 °C and widely varying coercivities (see Table 4) with the greatest coercivity (2800 Oe) reported for the Santa Catharina meteorite[64]. It is important to note that previously tested meteorites contained many other phases including other Fe-Ni phases as well as non-metallic minerals.
Table 4: Previous magnetic studies on meteorites containing Tetrataenite

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Type of Meteorite</th>
<th>Estimated % tetrataenite phase</th>
<th>Magnetization (emu/g)</th>
<th>Coercivity $H_C$ (Oe)</th>
<th>Curie Temp. °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>300 K 4.2 K</td>
<td>300 K 4.2 K</td>
<td></td>
<td></td>
</tr>
<tr>
<td>St. Séverin</td>
<td>LL6</td>
<td>42</td>
<td></td>
<td></td>
<td>765</td>
<td>565</td>
</tr>
<tr>
<td>Appley Bridge</td>
<td>LL6</td>
<td>43</td>
<td></td>
<td></td>
<td>160</td>
<td>190</td>
</tr>
<tr>
<td>Tuxtuac</td>
<td>LL5</td>
<td></td>
<td></td>
<td></td>
<td>40</td>
<td>90</td>
</tr>
<tr>
<td>Y-74160</td>
<td>LL7</td>
<td></td>
<td></td>
<td></td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>ALH-77260</td>
<td>L3</td>
<td></td>
<td></td>
<td></td>
<td>83</td>
<td>86</td>
</tr>
<tr>
<td>ALH-77219</td>
<td>Mesosiderite</td>
<td></td>
<td></td>
<td></td>
<td>560</td>
<td></td>
</tr>
<tr>
<td>Olivenza</td>
<td>LL6</td>
<td>46</td>
<td>2.42</td>
<td>3.05</td>
<td>1245</td>
<td>780</td>
</tr>
<tr>
<td>Yamato-74160</td>
<td>LL6</td>
<td></td>
<td></td>
<td></td>
<td>255</td>
<td>226</td>
</tr>
<tr>
<td>ALH-76260</td>
<td>L3</td>
<td></td>
<td></td>
<td></td>
<td>185</td>
<td>580</td>
</tr>
<tr>
<td>Nova Petrópolis</td>
<td>Medium octahedrite</td>
<td>IIA</td>
<td></td>
<td></td>
<td>5.5</td>
<td>535</td>
</tr>
<tr>
<td>Santa Catharina</td>
<td>Ni-rich ataxite</td>
<td></td>
<td></td>
<td></td>
<td>51</td>
<td>81</td>
</tr>
<tr>
<td>Twin City</td>
<td>Ni-rich ataxite</td>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td>83</td>
</tr>
<tr>
<td>San Cristobal</td>
<td>Ni-rich ataxite</td>
<td></td>
<td></td>
<td></td>
<td>8</td>
<td>109</td>
</tr>
<tr>
<td>NWA-6259</td>
<td>Ni-rich ataxite</td>
<td></td>
<td></td>
<td></td>
<td>95</td>
<td>144</td>
</tr>
</tbody>
</table>

FeNi with the nominally-equiatomic L1₀ structure has attracted great interest in the physics community [48, 70] due to early reports of high magnetocrystalline anisotropy ($K_1 = 1.3 \times 10^7$ ergs/cc) and high saturation magnetization ($M_S = 1300$ emu/cc) in neutron irradiated FeNi samples [11, 71]. The good abundance and low cost of the constituent elements, together with intriguing magnetic properties that include a high theoretical
maximum energy product \((BH)_{\text{max}} = 42 \text{ MGOe}\), make \(L1_0\) FeNi an ideal candidate to replace lower energy-density ferrite and Alnico magnets or as an alternative to dysprosium-containing NdFeB permanent magnets in elevated-temperature applications[12].

On the question of kinetics of \(L1_0\)-type FeNi phase formation, all literature reports agree that it happens extraordinarily slowly. The process of chemical ordering or disordering requires local atomic rearrangement, which is facilitated by the presence of atomic vacancies or other defects to allow atomic motion.[15, 72] The interdiffusion coefficient \(D\) of fcc \(\text{Fe}_{50}\text{Ni}_{50}\) at 300 °C, just below \(T_{OD}\), is estimated as \(D \approx 1 \times 10^{-27} \text{ cm}^2/\text{sec}\), which translates to the occurrence of 1 atomic jump every 2,600 years at 300 °C.[2] Yang and Goldstein proposed that magnetic interactions in Fe-Ni alloys make vacancy formation less favorable and vacancy migration more favorable, with the net effect that diffusion is greatly reduced for temperatures below the alloy Curie temperature.[2] With such a low atomic jump frequency, the FeNi \(L1_0\) phase cannot be made in laboratory time scales employing standard metallurgical techniques. However, once formed, the slow atomic movement in Fe-Ni makes the \(L1_0\) phase very kinetically stable. Recently Dos Santos et al. sought to characterize the kinetics of the chemical disordering process of tetrataenite using magnetic remanence as a proxy for \(L1_0\) phase fraction in the Santa Catharina and Guidder meteorites. Their results provided experimental time-temperature-transformation (T-T-T) information on the behavior of tetrataenite and found that complete disordering took seconds at 600 °C, but well over one month at 400 °C.[73] Despite these reports, quantitative determination of the kinetic
barriers inherent to the chemical ordering and chemical disordering processes in tetrataenite have not been provided to date in the published literature.

In this Dissertation, tetrataenite was extracted from the meteorite known as NWA 6259 (named for its location of discovery, Northwest Africa), which was discovered in 2010 and verified to consist of largely single-phase tetrataenite. NWA 6259 is a high-Ni ataxite with an overall composition of 42.6 wt.% (41.4 at%) Ni [74], which is the second highest Ni content of all known iron meteorites. Collaborative work carried out in parallel with this Dissertation utilized electron probe microanalysis to confirm the average chemical composition of the matrix of NWA 6259 to be 43.5 to 45 wt% (± 0.5) (43 ± 1 at%) Ni[12]. Transmission electron microscopy confirmed the presence of L1₀-structured FeNi in NWA6259 by identification of the {001} superlattice Bragg reflections. The microstructure was investigated using electron backscattered diffraction (EBSD) which identified regions near the center of the meteorite as having a single orientation and absence of grain boundaries[75]. EBSD could not detect the slight tetragonality of the L1₀-phase and is not sensitive to chemical ordering; results are interpreted as indicating that a single-crystal of the fcc A1 phase was first formed in the meteorite’s cooling history and that L1₀ variants formed coherently in the meteorite during further cooling[75].

Additionally, magnetic domain information was collected from tetrataenite in the Estherville meteorite in work carried out in this Dissertation. The Estherville meteorite fell in Estherville, Iowa, USA in 1879 [76]. It is classified as a mesosiderite, which is a type of stony-iron meteorite containing approximately equal parts metallic nickel-iron and silicate and is estimated to have cooled at a rate of ~0.5 Kelvin per million years [76,
The metallic regions of Estherville consist of zones of the mineral Kamacite (bcc $\alpha$-Fe with $<$7 wt.% Ni), zones of tetrataenite, and zones of tetrataenite islands in a kamacite honeycomb matrix [77].
3 Experimental Methods and Techniques

The operating principles and experimental details used in the course of this Dissertation are presented here. Synthesis and sample preparation methods of FePd samples are shown in Section 3.1.1 followed by sample preparation methods used for meteoritic samples in Section 3.1.2. The compositions were determined using scanning electron microscope energy-dispersive x-ray spectroscopy (SEM-EDS), which is detailed in Section 3.1.3. The microstructure and crystal structure were measured using optical microscopy and x-ray diffraction (XRD) as presented in Section 3.1.4. Magnetic domain characterization employed magnetic force microscopy (MFM) while bulk magnetic characteristics were probed by vibrating sample magnetometry (VSM) as shown in Section 3.1.5. Enthalpic changes are measured using differential scanning calorimetry (DSC), which is presented in Section 3.1.6.

3.1 FePd Synthesis and Processing

Bulk material production for this research employed arc-melting followed by annealing. A plasma arc-melter is a furnace that heats materials by means of an argon plasma and was used to melt elemental stocks to form an alloy. In this method, a DC current is applied between a tungsten tip and a water-cooled copper plate in an argon atmosphere to create sustained plasma that reaches a temperature of 3500 °C. Sample material on the copper plate is melted by the argon plasma, then cools slowly and solidifies when the plasma is removed. Annealing is a heat treatment process during which a material is exposed to an elevated temperature for an extended time period to promote diffusion and phase transformations[14].
Sample surfaces were prepared by grinding and polishing. Grinding is a metallurgy technique in which features on the sample surface are worn down by coarse and subsequently finer abrasives adhered to a work wheel. Polishing further refines the sample surface using a polishing cloth adhered to a work wheel and applying a very fine abrasive solution. A milling machine and slow speed saw were employed to cut the sample down to a size compatible with the characterization techniques. The specific heat treatments performed on FePd samples are given in Chapter 4.

3.2 Meteorite Sample Preparation

Meteorites containing the tetrataenite phase were selected with the assistance of meteorite expert and collaborator Dr. J. I. Goldstein (University of Massachusetts Amherst). With the exception of MFM results from the Estherville meteorite, all results reported in this Dissertation are obtained from the NWA6259 meteorite.

Meteorites were prepared for MFM measurement by mounting, polishing, and in some cases etching (at both NEU and UMass) to understand the microstructure and locate the tetrataenite-containing regions. Mounting the meteoritic sample for polishing and examination was accomplished by placing the sample in a one-inch-diameter mold filled with epoxy (Epothin Epoxy prepared by mixing 1.95 g of hardener with 5 g of resin) and allowed to cure for forty-two hours. The meteorite encased in epoxy was then removed from the mold, ground, and polished for examination. A Struers LaboPol-5 and LaboDoser polishing wheel assembly with abrasives progressing from coarse to fine and polishing cloths with alumina powders of 3 µm, 1 µm, and 0.05 µm were used to achieve a mirror finish on the meteorite sample surface. Nital, a solution of alcohol and nitric acid, was used on the Estherville meteorite sample as an etchant to reveal the
microstructure. Tetrataenite etches at a slower rate than other meteoritic phases and thus was revealed and identified after etching[78]. Optical microscopy was utilized to locate regions of the Estherville meteoritic sample containing tetrataenite for study.

Regions of Estherville and NWA6259 meteorites containing tetrataenite were isolated using a machinist’s end mill with a 1/16” bit to cut 4- and 6-mm diameter cylindrical cores; this process was carried out at the University of Massachusetts, Amherst. Further, a MTI Corporation SYJ-150 Precision Low Speed Diamond Saw was employed at NEU to slice small samples from the NWA6259 meteorite with approximate dimensions 4 x 4 x 1 mm for VSM and DSC measurements.

3.3 Composition and Homogeneity Determination Using Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy (SEM-EDS)

Scanning electron microscope energy-dispersive x-ray spectroscopy (SEM-EDS) was used to confirm compositions and determine degree of homogeneity. EDS is an elemental characterization technique that uses a high-energy electron beam to stimulate the emission of characteristic x-rays from a sample. This technique enables identification of the elements in a sample and their relative abundances. By focusing on different areas and at different magnifications, compositional profiles across samples may be determined and compared[79].

The mechanism that underlies EDS is described as follows: a large applied voltage is used to accelerate high-energy electrons, which in turn bombard a sample and excite specimen electrons. Excited inner shell electrons are then ejected from the shell, creating vacancies (as shown in Figure 17). When an electron from a higher energy shell fills the
vacancy, excess energy is emitted as an x-ray with energy equal to the difference in shell energies; this is shown in the figure as $K_{\alpha}$ as an example. The x-ray energy is characteristic of the element from which it was emitted. The energies and relative intensities of emitted x-rays are measured by an energy-dispersive spectrometer and that data can be related to the relative abundance in the sample of elements having those characteristic energies [79].

![Diagram of electron shell and radiation emissions](image)

**Figure 17:** Schematic representation of energy-dispersive x-ray spectroscopy principles. K, L, and M are the electron shell designations while $K_{\alpha}$, $K_{\beta}$, $L_{\alpha}$ are the radiation energies emitted when an electron falls from a higher shell to fill a hole in a lower shell[80].

Compositions of FePd samples were confirmed using a Hitachi S4800 scanning electron microscope (SEM) with energy-dispersive x-ray spectroscopy (EDS) capability (standardless). The limit of detection of EDS is approximately ± 0.5 weight percent. The in the determination of relative abundances of elements may be as much as 5% of the
measured value for standardless EDS. Furthermore, the accuracy of the relative abundance determination decreases when there are elements with overlapping characteristic energies [79]. Homogeneity was determined by measuring and averaging the composition of three different areas of three FePd disk samples cut from the same initially arc-melted ingot.

The composition of tetrataenite from the NWA6259 meteorite was determined by collaborators J. I. Goldstein and A. Mubarok (UMass Amherst) using microprobe analysis. The microprobe experiments were performed on a thin slice originating from the same meteorite, NWA6259, however it was obtained separately from the mass of NWA6259 used in all other experiments presented in this Dissertation.

3.4 Characterization of Microstructure and Structure Using Optical Microscopy and X-ray Diffraction (XRD)

In this Dissertation, sample microstructures were examined using optical light microscopy while the crystal structures were investigated using X-ray diffraction. This section gives an overview of the operating principles of optical microscopy and X-ray diffraction and the specific details of experiments carried out in the course of this Dissertation.

Optical light microscopy was utilized in this Dissertation to observe microstructure features of the samples. Light microscopy produces a magnified visual of the sample surface by passing visible light through a system of lenses. The magnification of the image is changed by exchanging objective lenses and the focal depth is adjusted by changing the lens to sample distance. Polarized light microscopy was used in this
Dissertation to detect the L1\(_0\) phase. The L1\(_0\) phase has a tetragonal lattice which exhibits birefringence, meaning that the refractive index is dependent upon the polarization and propagation direction of light relative to the crystal lattice. Polarized light microscopy uses a filter on the incident beam to polarize the light, which then interacts with crystallites in the sample, and the reflected light passes through a second polarizing filter placed before the objective lens. Birefringent crystallites with different orientations are observed as different colors in polarized light microscopy[81].

The microstructure of FePd was examined using a Leice DMILM Inverted Optical Microscope with a 100x objective lens. The microstructure of NWA6259 was examined using optical microscopy with a 20x objective lens and polarized light. Both systems used built-in digital cameras to capture the images.

X-ray diffraction is a method of determining the arrangement of atoms within a material, in which an incident beam of x-rays is diffracted into specific directions by lattice planes in a crystal. This technique enables identification of many factors including phase content, degree of crystallinity, crystal structure, lattice parameters, grain size, and strain. X-rays incident on a crystalline sample are elastically scattered by the atoms in the sample in certain angles. Bragg’s law predicts that x-rays diffracted from a crystalline material constructively interfere when:

\[ n\lambda = 2d\sin \theta \]  

(3.1)

where: \( d \) = interplanar spacing (Å)

\( \lambda \) = wavelength of incoming radiation (Å)
\[ \theta = \text{angle of incidence (degrees)} \]

\[ n = \text{an integer corresponding to the number of coherent planes (unitless)} \]

The angles at which x-rays are diffracted are known as Bragg angles and correspond to a certain crystallographic planes with an interplanar spacing equal to \( d \). By keeping the radiation wavelength constant and varying the angle of incidence, the crystallographic planes can be known.

**Figure 18: Schematic representation of X-ray diffraction (XRD) operating principles [82].**

For a \( \theta/2\theta \) diffractometer scan, a filament is heated to produce electrons that bombard a target and produce x-rays in the same manner as described in Section 3.3. The x-ray source orbits the sample so that the path of the x-ray beam is at an angle \( \theta \) with the sample surface while the x-ray detector simultaneously rotates to maintain an angle of \( 2\theta \) (as shown in Figure 18) and records the intensity of the diffracted x-rays. The collected data of measured intensity as a function of \( 2\theta \) can be used to determine the phases present, the degree of crystallinity in the sample, and the degree of chemical
Four-circle single crystal diffractometers allow for controlled movement of the sample’s rotation about the center of the sample’s axis (angle $\varphi$) and the tilt of the sample surface relative to the incident beam (angle $\chi$).

Pole figure measurements on a four-circle diffractometer were conducted in this Dissertation to determine the orientation of crystallites in the sample. In this method, the $\chi$ and $\varphi$ angles are systematically varied for each $2\theta$ setting to create a set of stereographic projections (see Figure 19), which shows the variation in pole density with pole orientation. Each diffracting plane can be represented by a normal vector radiating from the center of the crystal onto a reference sphere about the crystal. The pole of the plane is given by the position of the normal vector on the reference sphere. The reference sphere is represented in two dimensions using a projection where a diameter is drawn on the sphere such that the projection plane is tangent to the sphere at one end of the diameter while the other end is the point of projection. A plane with pole $P$ on the reference sphere becomes point $P'$ on the projection plane; point $P'$ is found by drawing a line from the point of projection, through $P$, onto the projection plane. A pole figure of a face-centered-cubic crystal, measured along the (110) direction, would exhibit Bragg diffraction peaks at the positions indicated in Figure 20. The radius of the pole figure corresponds to $\chi$ while the angle is given by $\varphi$. 
Figure 19: The stereographic projection[83].

Figure 20: Expected peak positions in a pole figure of a face-centered-cubic crystal measured along the (110) direction.
X-ray diffraction (XRD) was used to probe meteoritic and FePd samples to identify the phases present and lattice parameters were determined from XRD data using a least-squares method [84]. Specifically, structural characterization of FePd was carried out using the PANanalytical X’Pert PRO MPD Theta-2Theta Systems Laboratory-based Diffractometer at Northeastern, which employs a Cu target and Ni filter to produce monochromatic Cu-Kα radiation with a wavelength of 1.5418 Å. An ω offset was used during XRD measurements on the FePd fcc and ordered on cooling samples to maximize the (200) peak. Contributions from the Cu-Kα2 radiation were stripped using the instrument software. The full width at half maximum (FWHM) was corrected for instrumental broadening, determined from the FWHM of several Bragg reflections of a Si standard. The average crystallite size in FePd samples was estimated through application of the Scherrer formula to the Bragg peaks in each diffraction pattern. Scherrer analysis attributes XRD peak broadening to finite size effects and is valid for crystallites sizes of ~100 nm or less with insignificant strain. The Scherrer crystallite size, $d^*$, is calculated as a function of shape factor assumed to be 0.9, the X-ray wavelength $\lambda$, the full width at half maximum corrected for instrumental broadening $B^*$, and the Bragg angle of the reflection $\theta$ using Eq. (3.2).

$$
\frac{d^*}{B^* \cos \theta} = \frac{0.9 \lambda}{B^* \cos \theta}
$$

(3.2)

Synchrotron four-circle x-ray diffraction at beamline X20A of the National Synchrotron Light Source (NSLS) at Brookhaven National Lab was used in the course of this work to probe the L1₀ phase in meteoritic samples. The crystallographic orientation of tetrataenite regions in the NWA6259 meteorite was probed using synchrotron single
crystal XRD pole figures ($2\theta$: 36-69°; $\chi$: 0-89°; $\varphi$: 0-360°; $\omega$=0°) with incident X-ray energy of 8.0477 keV (wavelength of 1.5406 Å) using a linear detector and Ge (111) monochromator. A point detector with Ge (111) analyzer and with Ge (111) monochromator was used with incident X-ray energy 8.0477 keV (wavelength of 1.5406 Å) in $\theta$-2$\theta$ scans that were conducted at selected sample orientations based on the pole figure results. The experimental data was measured in detector counts per 10,000 monitor counts. Additional scans were conducted with the point detector setup and varying the energy from 6.70 to 7.16 keV (1.85 – 1.73 Å wavelength), calibrated at 7.000559 keV.

The slits on the incident beam were 2 x 2 mm while the detector slits were 4 mm vertical x 3 mm horizontal and the sample to detector distance was 794 mm for $\theta$-2$\theta$ measurements. Lattice parameters of both FePd and meteoritic samples were calculated by fitting each diffraction peak in $\theta$-2$\theta$ scans with a pseudovoight fit then using the peak positions in least-squares methods developed by Novak and Colville for cubic and tetragonal crystals [84].

Long-range order parameters ($LRO$) were calculated for FePd and tetrataenite from the XRD results (definitions and details of the calculations are given in Appendix A). Evaluation of the crystallographic long-range order parameter of FePd used the tetragonality of the unit cell compared to the lattice parameters from Hultgren [39] as an indication of the L1$_0$ structure (See Appendix A) [85, 86]. The chemical long-range order parameter of tetrataenite and the distribution of L1$_0$ c-axis variants were calculated from the relative intensities of the superlattice and fundamental Bragg reflections (see Appendix A). Anomalous diffraction was used to increase the intensity of the superlattice Bragg reflections relative to the fundamental Bragg reflections (see Appendix A).
3.5 Methods of Magnetic Domain and Bulk Magnetism Characterization

The magnetic character of a material provides unique information concerning the magnetic order. The fundamentals of magnetism were discussed in Section 2.1.3; the methods used to probe the magnetic response of studied meteorites and Fe-Pd samples is addressed in this section. Magnetic domain characteristics were probed by magnetic force microscopy (MFM). The bulk magnetic response was measured using vibrating sample magnetometry (VSM), which allowed the anisotropy and energy product to be calculated.

3.5.1 Magnetic Domain Characterization Using Magnetic Force Microscopy (MFM)

Magnetic force microscopy (MFM) is a technique that measures the magnetic interactions as a magnetized tip scans the surface of a magnetized sample to produce an image representing the magnetic domain structure of the sample surface. During MFM operation, a magnetized tip scans a sample’s surface. The tip is at the end of a cantilever and oscillates at a resonant frequency. The tip experiences atomic and magnetic interactions near the sample surface that either attract the tip to or repel it from the sample surface. The tip’s movements are detected by an infrared laser and converted to data shown as an image. During an MFM measurement the instrument first performs a topographic line scan in the operation mode known as atomic force microscopy (AFM) and then repeats the same line scan but at an offset height (typically 30-100 nm) (shown in Figure 21). The response of the tip is only due to magnetic interactions while scanning at the offset height. MFM can reveal magnetic domain information including whether the magnetization direction is in-plane or out-of-plane. These measurements elucidate the size and orientation of the domains of the samples in this Dissertation (see Section 2.1.3).
An MFM image of tetrataenite in the Estherville meteorite is shown in Figure 22. The dark regions indicate the tip is strongly attracted to the sample indicating magnetic domains oriented with the easy-axis out-of-plane (a low coercivity tip was use: MESP-LC). The light areas indicate less attraction of the tip to the sample and suggest the magnetic domains of the sample are oriented with easy-axis in-plane. The brightest lines delineate magnetic domain walls where the tip is repelled from the sample surface [87].

Figure 21: MFM lift mode principles [87].

1. Cantilever traces surface topography on first trace.
2. Cantilever retraces surface topography on first retrace.
3. Cantilever ascends to Lift scan height.
4. Lifted cantilever profiles topography while responding to magnetic influences (second trace).
5. Lifted cantilever reprofiles topography while responding to magnetic influences (second retrace).
Figure 22: Magnetic domain structure of Tetrataenite in the Estherville meteorite.

Magnetic domain microstructures of the FePd and meteoritic samples were probed using magnetic force microscopy (MFM). The Bruker Multimode V8 system used in this work for MFM measurements has a lateral resolution of ~5-10 nm for topographical measurements and ~30-50 nm for magnetic measurement [87]. A lift height of ~50 nm was used for magnetic measurements on most samples. Bruker tips with magnetic coatings, known as MESP and MESP-LC, were used [88].

3.5.2 Bulk Magnetic Characterization Using Vibrating Sample Magnetometry (VSM)

The bulk magnetic properties of meteoritic and FePd samples were characterized by measuring the change in magnetization as a function of the applied field or as a function of temperature using vibrating sample magnetometry (VSM). Magnetometry provides information on saturation magnetization, remanence, coercivity, and Curie temperature (these parameters were defined Section 2.1.3). Additionally, magnetometry allows
determination of magnetocrystalline anisotropy constants and the maximum energy product (defined in Section 2.1.3).

Vibrating sample magnetometry (VSM), detects volume-averaged sample magnetization as a function of field and temperature. The operating principle is based on the flux change in a coil when a magnetized sample is vibrated near it. The sample is attached to a rod, the other end of which is attached to a mechanical vibrator. The oscillating magnetic field of the moving sample induces an alternating electromagnetic field in the detection coils, which has a magnitude proportional to the magnetic moment of the sample. The alternating electromagnetic field is amplified with a lock-in amplifier that is sensitive only to signals at the vibration frequency. By measuring in the field of an external electromagnet, the hysteresis loop of a material can be obtained.

Magnetization as a function of applied field and temperature $M(H,T)$ was investigated using vibrating sample magnetometry (VSM) to measure the saturation magnetization $M_s$, coercivity $H_C$, remanence $M_R$, and Curie temperature $T_C$. A Quantum Design VersaLab-free VSM, a Quantum Design Physical Property Measurement System (PPMS) with VSM option, and a Microsense VSM were used to study volume-averaged magnetic behavior from room temperature to 727 °C. The Quantum Design VersaLab-free VSM operates in temperatures from -223 °C to 727 °C (50 – 1000 K) and has a 30 kOe maximum applied field parallel to the sample’s movement [89]. The Quantum Design PPMS with VSM option is capable of applying magnetic fields up to 90 kOe parallel to the sample’s movement from -271 to 727 °C (2 K to 1000 K). The Microsense VSM has a 22 kOe maximum field applied perpendicular to the sample’s movement and operates in the -196 - 700 °C (77 – 973 K) temperature range [90]. In order to obtain the
Curie temperature ($T_C$), measurements of magnetization as a function of temperature, $M(T)$, were carried out using VSM on meteorites and FePd samples. The Curie temperature was determined as the inflection point in the $M(T)$ curve. The critical exponent of the temperature dependent magnetization was determined using the Landau theory of phase transitions (see Section 2.1.3).

The magnetocrystalline anisotropy constant ($K$), which describes the preference for magnetization to lie along a particular crystallographic direction, was calculated using the Law of Approach to Saturation method [25], which models the high field portion of the initial magnetization curve where magnetization occurs by rotation away from the easy axis. The Law of Approach to Saturation is given by:

$$M = M_s \left(1 - \frac{a_{LAS}}{H_{app}} - \frac{b_{LAS}}{H_{app}^2} \frac{K_1^2}{M_s^2} - \cdots \right) + \chi_0 H$$

$$\frac{dM}{dH} = M_s \left(\frac{a_{LAS}}{H_{app}^2} - \frac{b_{LAS}}{H_{app}^3} \frac{K_1^2}{M_s^2} - \cdots \right) + \chi_0$$

(3.3)

where: $M =$ magnetization

$M_s =$ saturation magnetization

$H_{app} =$ applied field

$K =$ anisotropy constant

$a_{LAS} =$ term due to voids and impurities

$b_{LAS} = 8/105$ for cubic, $4/15$ for uniaxial

$\chi_0 =$ paramagnetic contribution
The anisotropy field and saturation magnetization of L1₀-structured FePd were determined by fitting the measured field dependent magnetization data and extrapolating the curve to a magnetization equal to $M_S$ of the A1 phase using Eq. (3.3).

### 3.6 Calorimetric Methods

Determination of the temperatures and enthalpies of phase transformation allows for study of transformation behavior including thermodynamic attributes and kinetic mechanisms. In this Dissertation, differential scanning calorimetry (DSC) was employed to detect and study chemical and magnetic phase transitions. DSC is a thermo-analytical technique that measures the heat input required to reach a temperature in a sample as compared to a reference and is a useful technique for determining transition temperatures, latent heats, and activation energies. Structural transformations are either endothermic or exothermic, so that the instrument must supply more, or less, heat during the transition, which appears as a positive or negative peak in the DSC data. The onset of the exothermic or endothermic peak indicates the start of the transition and the peak observed in DSC indicates the temperature of maximum transformation rate. The area encompassed by the DSC peak, integrated with respect to time, provides a measure of the energy associated with that transition. The transition temperatures thus determined may be mapped onto a phase diagram to extract structural information and phase relationships appropriate to the sample. DSC was also used to determine the Curie temperature, which appears as a change in slope in data of heat flow versus temperature and can be seen more clearly as a discontinuity in the first derivative of the heating data[26].

Calorimetric changes in the samples of this Dissertation were studied using a Netzsch STA 449 F3 Jupiter Simultaneous TG-DTA/DSC Apparatus with the flux
differential scanning calorimetry (DSC) option [91]. Calibration for temperature, sensitivity, and thermal-lag was performed using several standard reference materials. Heating rates of 1 – 25 K/min were employed with alumina liners in platinum-rhodium crucibles with UHP Ar flow gas. Controlled cooling from 900 °C to 100 °C was carried out with cooling rates of 0.5 to 40 K/min. The enthalpy of transformation was found by integrating the DSC data with respect to time utilizing NETZSCH Proteus® software.

The enthalpies of the thermal changes occurring in FePd samples during DSC measurement were determined as the area between the DSC trace and a baseline integrated with respect to time. The data had already been corrected for instrumental effects by subtracting thermal data obtained from measurement of the response of an empty crucible; however the DSC baseline was still not at zero so a second baseline was created analytically from a linear fit of the high temperature portion of the DSC trace where the trace appears steady with no thermal events. The enthalpy of the high temperature endothermic peak was further corrected by subtracting the contribution from the mid-temperature event. The enthalpy of the pre-peak in the heating steps, where the DSC trace deviates from the baseline before increasing to the peak, was found as the total area of the DSC trace minus the contribution from the mid temperature event and the high temperature peak.
4 FePd Results and Discussion

The FePd system was used in this Dissertation as a model system to study the magnetic properties and thermal stability of the L1₀ structure and to study the mechanism of the chemical-ordering transformation. These objectives were pursued in two steps:

1) Studying A1-structured and L1₀-structured FePd to determine structure-magnetism correlations and thermal stabilities of the two phases. The magnetic domain structures, Curie transition behavior, and enthalpies of formation of A1-structured and L1₀-structured FePd are reported and compared in Section 4.1.

2) Observing the thermal and structural developments during the A1→ L1₀ chemical ordering transformation was accomplished by slowly cooling the A1-structured FePd through the order-disorder transformation temperature. The effect of cooling rate on the chemical ordering transformation in FePd is reported and examined in Section 4.2.

In Section 4.1, magnetic domains of A1-structured FePd are consistent with domains of a soft ferromagnet with cubic anisotropy while those of L1₀-structured FePd were indicative of uniaxial magnetic anisotropy with a twinned lattice microstructure. Analysis of the Curie transition in these materials showed that the transition in the A1-structured FePd is consistent with three-dimensional (3D) Heisenberg behavior with localized magnetic interactions while the L1₀-structured FePd exhibits magnetic behavior described by the tricritical mean-field theory. Calorimetric results provide the enthalpy of transformation between the L1₀ and A1 phases and analyses show that the chemical disordering process is not kinetically-limited in FePd under the conditions tested. Overall
the results provide insight into the structure, magnetism, and thermal attributes of the A1 and L1₀ phases.

In Section 4.2, structural analysis of FePd samples that were slowly cooled through the order-disorder temperature reveals that the microstructure consists of a mixture of the L1₀ phase and a chemically-disordered tetragonal phase. Results presented in Section 4.2 of this Dissertation are consistent with a chemical ordering mechanism in which nucleating regions of the L1₀ phase cause a tetragonal distortion of the parent A1 phase. Measured changes in Curie temperature are linked to lattice strain. The results provided in this section inform the mechanism of the chemical ordering transformation in FePd.

4.1 Characterization of the Structure, Magnetism, and Thermal Stability of L1₀ FePd

In this section, A1-structured and L1₀-structured FePd were investigated to study relationships of magnetism and structure and to determine the thermal stability of the A1 and L1₀- phases in FePd. Details of the FePd sample synthesis and preparation are presented first. Experimental results are shown in Section 4.1.1 followed by discussion in Section 4.1.2. Conclusions in this section regarding structure-magnetism correlations and thermal stability of the A1 and L1₀ phases are given in Section 4.1.3.

The rationale for the FePd heat treatment steps chosen in this study are based on the phase diagram of Fe-Pd at the 50/50 composition, with the goal of producing a chemically-disordered A1-structured sample and making comparisons to a fully-chemically-ordered L1₀-structured sample. The phase diagram in Figure 23 shows that Fe₅₀Pd₅₀ has the A1 (γ, fcc) structure exists above ~700 °C, a two-phase A1 + L1₀ region
that exists from 700 °C to 660 °C, with the L1₀ structure stable below 660 °C. Based on this information, it was expected that samples annealed at 1000 °C would form the A1 structure and retain the A1 structure when quenched to room temperature, and samples annealed at 500 °C would form the L1₀ structure that is the equilibrium phase at 500 °C and 50 at.% Pd. The specifics of the synthesis and processing steps based on this rationale are discussed below.

![Phase diagram of Fe-Pd](image)

**Figure 23:** Phase diagram of Fe-Pd [38] with experimentally important temperatures noted for the 50/50 composition. Experimental annealing temperatures discussed in Section 4.1 are indicated by red circles. The red arrow indicates cooling from 900 °C, through the chemical order-disorder temperature, to room temperature as discussed in Section 4.2.

An initial 1.5 g FePd alloy was formed by arc-melting Fe and Pd granules into an alloyed ingot. The FePd ingot was annealed at 1000 °C for 100 h in an evacuated quartz tube placed in a tube furnace, quenched using liquid nitrogen, then sliced with a slow
speed saw and polished with a final grit size of 0.5 μm. The resulting samples are referred to as “quenched” and consist of disks approximately 6 mm in diameter by 1 mm thick plus oddments. FePd samples were then subjected to annealing at 500 °C for 100 hours in evacuated quartz tubes placed in a tube furnace to form the “annealed” state. The quenched and annealed samples were characterized using electron dispersive X-ray spectroscopy (EDS), X-ray diffraction (XRD), atomic and magnetic force microscopies (AFM, MFM), and vibrating sample magnetometry (VSM). Enthalpy changes between the L1₀ and A1 phases were studied by performing differential scanning calorimetry (DSC) measurements on annealed FePd using heating rates of 5, 10, and 20 K/min.

The composition of synthesized samples was investigated using SEM with EDS to confirm equiatomic composition. The crystallographic phases present in quenched and annealed samples were investigated using XRD. Magnetic characterization was performed to observe the effect of crystal structure on magnetic domain structure, hysteresis behavior, and Curie transition behavior. Lastly, calorimetric studies were carried out on annealed FePd to determine the enthalpic difference between the L1₀ and A1 phases and to elucidate the kinetic mechanisms of the L1₀ → A1 chemical disordering process.

4.1.1 Results from the Characterization of Structure, Magnetism, and Thermal Stability of L1₀ FePd

Results of experiments to characterize the properties of FePd samples in the quenched and annealed states are presented in this section. For organizational clarity, this
section has been divided into five parts: chemical results (4.1.1.1); structural results (4.1.1.2); magnetic results (4.1.1.3); and calorimetric results (4.1.1.4).

4.1.1.1 Chemical Results

The composition of FePd was informed by results from SEM with EDS (see Section 3.3 for details on this technique). EDS results confirm the intended equiatomic compositions for three samples measured in the quenched state. Three measurements were taken on each sample with the average for each sample presented in Table 5. The standard deviation of the composition was small and much less than the estimated instrumental error of 5% (given in parenthesis).

<table>
<thead>
<tr>
<th>Quenched FePd</th>
<th>at% Pd</th>
<th>at% Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>49.7 ± 0.6 (± 2)</td>
<td>50.3 ± 0.6 (± 3)</td>
</tr>
<tr>
<td>#2</td>
<td>50.7 ± 0.3 (± 3)</td>
<td>49.3 ± 0.3 (± 2)</td>
</tr>
<tr>
<td>#3</td>
<td>50.4 ± 0.9 (± 3)</td>
<td>49.6 ± 0.9 (± 2)</td>
</tr>
<tr>
<td>Average</td>
<td>50.3 ± 0.7 (± 3)</td>
<td>49.7 ± 0.7 (± 2)</td>
</tr>
</tbody>
</table>

4.1.1.2 Structure Results

X-ray diffraction results obtained on quenched and annealed FePd are shown in Figure 24 with comparisons to standard XRD patterns for the A1 and L10 FePd phases as reported by Hultgren [39]. The quenched sample shows Bragg peak positions that match closely to the peak positions of Hutgren’s fcc-structured XRD pattern but are shifted to lower 2θ, with very different peak intensities, confirming (200) texture in the samples synthesized in this current work. Bragg peaks of the annealed sample appear to be very similar in position to those of Hultgren’s L10 pattern. The lattice parameters, unit cell volumes, and c/a ratios of quenched and annealed FePd are shown in Table 6. The
annealed sample exhibited $a$-parameter greater than that of the quenched sample and $c$-parameter less than that of the quenched sample. The unit cell volume of the annealed sample was $\sim 0.6\%$ smaller than the quenched sample. The tetragonality of the unit cell is described by the ratio $c/a$, which is equal to unity for the cubic quenched sample and decreases to $c/a = 0.966 \pm .001$ for the annealed sample. Based on comparisons of the XRD results to Hultgren’s patterns for FePd, it is clear that quenched FePd is $A1$-structured and annealed FePd is $L1_0$-structured.

![XRD results from FePd as quenched as as annealed compared to previously reported patterns for $L1_0$ and fcc FePd.](image)

**Figure 24:** XRD results from FePd as quenched as as annealed compared to previously reported patterns for $L1_0$ and fcc FePd.
Table 6: Lattice parameters of FePd in the quenched and annealed states.

<table>
<thead>
<tr>
<th>State</th>
<th>Lattice parameters</th>
<th>Volume (Å³)</th>
<th>c/a</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>a (Å)</td>
<td>c (Å)</td>
<td></td>
</tr>
<tr>
<td>Quenched</td>
<td>3.815 ± 0.004</td>
<td>55.5 ± 0.1</td>
<td>1</td>
</tr>
<tr>
<td>Annealed</td>
<td>3.849 ± 0.005</td>
<td>3.721 ± 0.005</td>
<td>55.16 ± 0.01</td>
</tr>
</tbody>
</table>

4.1.1.3 Magnetic Results

The magnetic domain structure and bulk magnetic properties of FePd were probed using MFM and VSM.

The topographic and magnetic domain structures of FePd in the quenched and annealed states are displayed in Figure 25 as measured using AFM and MFM. The topography of quenched FePd is shown in Figure 25(a) to consist of stripes ~ 1 μm wide, a few dust particles, and no other features. The magnetic domains of quenched FePd appear maze-like with each path of the maze extending tentacle-like projections in all directions. The topography of annealed FePd displays a regular set of ridges ~ 10 μm wide and a few scratch-like features (Figure 25(c)). The magnetic domains of annealed FePd present light and dark stripes corresponding to the ridges observed in the topographic data such that each ridge is magnetically attracting the tip (dark) on one side and magnetically repelling the tip (light) on the other side. Within each dark magnetic stripe in Figure 25(d) there is a set of bright triangular features that have corresponding dark triangles in the accompanying light magnetic stripe.

Field- and temperature-dependent magnetization behavior was measured for FePd samples in the quenched and annealed states (Figure 26). The room-temperature hysteresis loop of quenched FePd possessed a $M_s$ of $110 \pm 1$ emu/g and a negligibly
small coercivity value of 6 Oe. The magnetization of annealed FePd did not reach saturation at the maximum field of the instrument and coercivity was 84 Oe, as observed in the hysteresis loop. A saturation magnetization $M_S = 108 \pm 2$ emu/g and anisotropy field $H_K \approx 35 \pm 5$ kOe were estimated for annealed FePd based on extrapolation of the Law of Approach to Saturation fit to the hysteresis data (see Section 3.5.2). Quenched FePd has an experimental $T_C = 474$ °C shown in blue in Figure 26 (right) while annealed FePd has $T_C = 477$ °C shown in red.

![Quenched and Annealed FePd](image)

**Figure 25:** Scanning probe microscopy measurements showing the (a) topography of quenched FePd, (b) magnetic domains of quenched FePd, (c) topography of annealed FePd, and (d) magnetic domains of annealed FePd. Images (a) and (b) have dimensions of 20 x 20 μm, while (c) and (d) are 50 x 50 μm.
4.1.1.4 **Calorimetric Results**

Differential scanning calorimetry (DSC) results, Figure 27, are examined in two steps beginning in the annealed state. In the heating step, samples are heated at 5, 10, and 20 K/min from room temperature to 900 °C. In the cooling step, all samples were cooled from 900 °C to room temperature at 20 K/min.

A minor thermal event is observed in the temperature range 430 – 475 °C in all samples. This event appears as a small asymmetric peak-like feature. The temperature of this event is given for each sample in Table 10. A prominent high temperature thermal event in is noted in the heating step. The large endothermic peak begins as an increase in DSC signal from the baseline that persists over a large temperature range and culminates in a peak. The peak temperatures are provided in Table 10.
Figure 27: Differential scanning calorimetry results on annealed FePd subjected to heating at 5, 10, and 20 K/min and subsequently cooled at 20 K/min.

Table 7: Temperatures of events observed in DSC results on FePd.

<table>
<thead>
<tr>
<th>Step</th>
<th>heat/cool rate (K/min)</th>
<th>Mid-Temp Event (°C)</th>
<th>High-Temp Event (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>heating</td>
<td>5</td>
<td>453.8 ± 3</td>
<td>658 ± 3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>454.8 ± 3</td>
<td>660 ± 3</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>457.5 ± 3</td>
<td>663 ± 3</td>
</tr>
<tr>
<td>cooling</td>
<td>20</td>
<td>439.8 ± 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>443.4 ± 3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>443.1 ± 3</td>
<td></td>
</tr>
</tbody>
</table>
4.1.2 Discussion from the Characterization of Structure, Magnetism, and Thermal Stability of L1₀ FePd

Analysis of the magnetic and calorimetric results MFM, VSM, and DSC is be presented in Sections 4.1.2.1 and 4.1.2.2, respectively. The magnetic analysis first discusses the magnetic domain structure of A1-type and L1₀-type FePd followed by an examination of the bulk magnetothermal behavior of these two phases. Features in the calorimetry results are attributed to a Curie transition and a chemical order-disorder transition.

4.1.2.1 Magnetic Analysis

The differences in the magnetic behavior between A1-type and L1₀-type (quenched and annealed) FePd are exhibited by their respective magnetic domain structures observed via MFM. The small feature size and branching pattern with branches diverging at ~90° angles observed in MFM results on quenched FePd are indicative of a soft ferromagnetic material with weak cubic anisotropy [92] as expected for the A1 phase. The topographic image of annealed FePd shows ridges ~10 μm across that were also observed in the slowly-cooled FePd samples and is discussed in Section 4.2.2.1. The MFM results obtained from annealed FePd are consistent with the so-called “fir tree” domain arrangement typically observed for twinned structures with uniaxial magnetocrystalline anisotropy as shown in Figure 28 [92, 93]. The diagonal lines represent the twin boundaries between crystal lattice variants. Thick arrows indicate the easy axes of magnetization, which are the [100] and [010] directions in the case of Ni₂MnGa for which the schematic was drawn. Thin arrows in the triangular “branches” of the fir tree pattern show that these triangular regions along the twin boundary are
magnetized antiparallel to the surrounding regions[93]. The similarity between the observed MFM pattern for annealed FePd and the fir tree pattern indicate that annealed FePd has both uniaxial magnetocrystalline anisotropy and crystallographic twins.

![Diagram of a fir tree magnetic domain configuration]

**Figure 28:** Schematic drawing of the “fir tree” magnetic domain configuration and the relationship of the magnetic domains to crystallographic twins [93]. The arrows in the triangular “branches” of the “fir tree” pattern show that these triangular regions along the twin boundary are magnetized antiparallel to the surrounding regions[93].

Field-dependent magnetization results obtained on quenched FePd showed that FePd reaches magnetic saturation under very low applied fields and displays negligible coercivity and remanence indicating that quenched FePd is a soft ferromagnetic material, as expected for A1-structured FePd. The hysteresis loops of annealed FePd shows that the sample does not reach saturation even at high applied magnetic fields, indicating that annealed FePd displays hard ferromagnetic behavior consistent with previous reports on L1₀ FePd [3]. The low remanence and coercivity values are consistent with a polycrystalline hard ferromagnet comprised of magnetically interacting crystallites [25].

The critical exponents of the magnetothermal data in the vicinity of the Curie transition were determined through application of Landau theory (see Section 2.2.2.1). Fits of the Landau equations to experimental $M(T)$ and $\chi M^{-1}(T)$ are shown in Figure 29.
and values for the fit parameters are given in Table 8. Comparison of these experimentally-derived critical exponent values, $\beta_{MT}$ and $\gamma_{MT}$, with those obtained from known models provides insight into the magnetic structure in the two sample states. The quenched FePd sample has a $\beta_{MT}$ value ($0.357 \pm 0.003$) comparable to that of the 3D Heisenberg model that is appropriate to materials with short-range magnetic interactions (where a $\beta_{MT} = 0.365$, see Table 8). The $\gamma_{MT}$ value of quenched FePd ($1.01 \pm 0.02$) is consistent with that resulting from application of the mean-field theory ($\gamma_{MT} = 1.0$, see Table 8). Achievement of a combination of $\beta_{MT}$ consistent with that of the 3D Heisenberg model and $\gamma_{MT}$ close to that of mean-field theory has been observed in other systems, such as La$_{0.7}$Ca$_{0.2}$Sr$_{0.1}$MnO$_3$ [28]. These results may be attributed to the existence of magnetic inhomogeneity in a polycrystalline sample and to short-range spin clusters, or nanosized ferromagnetic clusters, that persist above $T_C$. The critical exponents for the annealed FePd sample ($\beta_{MT} = 0.262 \pm 0.006$, $\gamma_{MT} = 0.96 \pm 0.02$) are very close to the values of their counterparts realized in the tricritical mean-field theory ($\beta_{MT} = 0.25$, $\gamma_{MT} = 1.0$) [28]. Tricritical mean-field theory is applicable to systems that undergo a thermodynamically first-order phase transition under certain conditions but experience a second-order phase transition under different conditions (e.g., temperature, pressure, compositions, magnetization) [94]. The tricritical point occurs at the cross-over between conditions resulting in a first-order transformation and conditions causing a second-order transformation [94]. There are no reports of a first-order magnetic phase transition in FePd therefore experimentally-derived critical exponents consistent with the existence of a tricritical point in this system are unexpected. Reported AC susceptibility measurements of single-crystal L1$_0$-structured FePd have shown “anomalous” behavior.
that the authors attributed to the existence of local regions in the crystal possessing anomalous exchange interactions near the Curie temperature that were substantially different from average exchange interactions over the sample volume [4]; Vlasova et al. did not consider whether this observed anomalous behavior could be attributed to a first-order or to a tricritical point phase transition [4]. The critical exponents for annealed FePd determined in this Dissertation work suggest that the magnetic state of the sample is at a tricritical point and that a first-order magnetic transition may occur in the system under slightly different conditions.

Figure 29: Landau fits of experimental \( M(T) \) and \( \chi_M^{-1}(T) \) data from quenched FePd (a) and annealed FePd (b). Applied field was 20 kOe.
### Table 8: Critical exponents determined from $M(T)$ measurements on L1$_0$ and A1 structured FePd samples. Models from the literature [28] are included for comparison.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_C$</td>
<td>474 °C</td>
<td>477 °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$M_0$</td>
<td>135.1 ± 0.7</td>
<td>120 ± 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta_{MT}$</td>
<td>0.357 ± 0.003</td>
<td>0.262 ± 0.006</td>
<td>0.5</td>
<td>0.365</td>
<td>0.325</td>
<td>0.25</td>
</tr>
<tr>
<td>$\gamma_{MT}$</td>
<td>1.01 ± 0.02</td>
<td>0.96 ± 0.02</td>
<td>1.0</td>
<td>1.336</td>
<td>1.241</td>
<td>1.0</td>
</tr>
<tr>
<td>$\delta_{MT}$</td>
<td>3.84 ± 0.08</td>
<td>4.7 ± 0.1</td>
<td>3.0</td>
<td>4.80</td>
<td>4.82</td>
<td>5.0</td>
</tr>
</tbody>
</table>

#### 4.1.2.2 Calorimetry Analysis

Analysis of the calorimetry results obtained from the FePd samples produces a number of conclusions. The first conclusion attributes the observed intermediate-temperature event (Section 4.1.1.4) to a Curie transition and the high-temperature event observed upon heating to a chemical-disordering transformation. The enthalpy of transformation and enthalpies of formation of the A1 and L1$_0$ phases are calculated based on calorimetry results. Lastly, the mechanism of chemical disordereding in FePd is discussed.

The temperature of the mid-temperature event observed in DSC experiments carried out on FePd falls within the broad range of Curie temperatures reported for A1 and L1$_0$ FePd in previous work [4, 5]. The shape of the mid-temperature event observed in DSC measurements is also consistent with the shape of a Curie transition [95]. Measurements performed on a piece of high-purity nickel stock with a confirmed Curie temperature of 356.6 ± 3 °C confirmed that its Curie transition appears to be peak-like on heating while it has step-like character upon cooling in the DSC signal (see Figure 30).
The $T_C$ of the A1-type FePd is $440 \pm 3 \, ^\circ C$ while that of the L1$_0$ phase is $455 \pm 3 \, ^\circ C$ as determined from DSC measurements of the quenched sample and the annealed sample, respectively. Both of these Curie temperatures are lower by ~25-35 degrees than the $T_C$ values measured using VSM. A large applied field of 20 kOe was used during VSM measurement, which caused the Curie transition to appear broad in temperature; high applied magnetic fields are known to shift the observed Curie point to higher temperatures [28]. In contrast, DSC measurements are conducted in zero applied magnetic field, which may provide a better reading of the true Curie point.

![DSC Signal](image)

**Figure 30:** The Curie transition of Nickel measured on heating (purple) and cooling (blue) at 20 K/min by DSC. The heating trace shows $T_C$ as peak-like while the cooling trace shows $T_C$ as a step in the DSC signal.

The annealed FePd sample is confirmed to adopt the L1$_0$ structure as determined by XRD results, thus the endothermic peak observed upon heating corresponds to chemical disordering of the annealed samples. Assuming that the annealed sample consists of a single phase with the fully-chemically-ordered L1$_0$ structure, the enthalpy measured upon heating this sample in the DSC characterizes the enthalpy of transformation between the
L1$_0$ and A1 states $\Delta H_{L1_0 \rightarrow A1}$ (FePd) = 2.4 ± 0.2 kJ/g·atom. The enthalpy of formation of the L1$_0$ phase itself is then calculated as $\Delta H_{\text{form}}^{L1_0}$ = -11.8 kJ/g·atom, based on $\Delta H_{L1_0 \leftrightarrow A1}$ and $\Delta H_{\text{form}}^{A1}$ = -9.4 kJ/g·atom [96] according to Eq. (2.12).

The peak temperature observed in the DSC results, corresponding to the chemical-disordering transformation, did not change with heating rate indicating that the chemical-disordering transformation is not kinetically-limited under the conditions of the measurement. The peak temperature observed in the DSC results are equal to the chemical order-disorder temperature reported for Fe$_{50}$Pd$_{50}$ according to the phase diagram[38], suggesting that the L1$_0$→A1 transformation occurs at the equilibrium transition temperature.

4.1.3 Significance of Work from the Characterization of Structure, Magnetism, and Thermal Stability of L1$_0$ FePd

The magnetic domain patterns obtained for L1$_0$-type FePd indicate that this material has uniaxial magnetic anisotropy with a twinned microstructure. Bulk magnetic measurements confirmed that L1$_0$-structure FePd has a high magnetic anisotropy and further showed that behavior of the magnetization through the Curie transition is consistent with the tricritical mean-field theory. The enthalpy of transformation from the L1$_0$ phase to the A1 phase in FePd was experimentally determined as 2.4 ± 0.2 kJ/g·atom and the enthalpy of formation for L1$_0$ FePd is $\Delta H_{\text{form}}^{L1_0}$ = -11.8 kJ/g·atom. The chemical disordering transformation is not kinetically-limited under the conditions tested in this work.
Critical exponents characterizing the A1-L1₀ FePd phase transformation that were obtained from a fit to experimental data in this Dissertation indicated that the annealed FePd sample is at a thermodynamic tricritical point. This means that a slight change in composition or structure might cause the Curie transition to become thermodynamically first-order in nature. Previous reports on the Curie transition in L1₀-structured FePd have been limited but the few reports that have been published give disagreeing Curie temperatures and provide evidence of an unexplored “anomalous” behavior of the AC susceptibility [4, 5]. The existence of a tricritical point in Gibbs free energy of L1₀-structured FePd, as indicated by the results presented in this section, may be the reason for the inconsistencies in the literature. Small difference in composition or processing techniques used by different authors may result in a different thermodynamic nature of the Curie transition.

4.2 **The Effect of Cooling Rate on the A1→L1₀ Chemical Ordering Transformation in FePd**

The goal of Dissertation work addressed in this section is to gain understanding of the chemical-ordering transformation mechanism in FePd. To that end, structural and calorimetric changes in FePd were studied as functions of sample processing to determine the effect of slow cooling rates on the A1→L1₀ chemical-ordering transformation. Samples of equiatomic FePd composition cooled from 900 °C to room temperature are expected to transform from the A1 phase to the L1₀ phase based on the FePd binary phase diagram (Figure 23). The work presented in this section seeks to observe, characterize and understand that chemical-ordering transformation.
Details of synthesis and processing steps carried out to study chemical ordering as a function of cooling rate are described here. The quenched equiatomic FePd samples confirmed to have the A1 structure (see Section 4.1.1.2) were heated from room temperature to 900 °C at 20 K/min in a DSC, held at 900 °C for 30 min to allow for instrument equilibration, and then slowly cooled to room temperature at rates of 2, 1, and 0.5 K/min (DSC results shown in 4.2.1.2). Samples formed in this way are referred to as S2, S1, and S0.5 based on the rate of slow cooling in DSC. The microstructures of S2, S1, and S0.5 were observed using optical microscopy while the crystal structures were characterized using XRD. DSC was utilized to measure thermal changes during the slow cooling step and during the subsequent heating step (4.2.1.2). Structural and calorimetric results are presented in Section 4.2.1 followed by a discussion in Section 4.2.2 and conclusions in 4.2.3.

4.2.1 Results from the Effect of Cooling Rate on the A1→L1₀ Chemical Ordering Transformation in FePd

Experimental results on FePd (S2, S1, S0.5) are categorized into chemical and structural, magnetic, and calorimetric results. Microstructural and structural results, comprised of observations and data collected from optical microscopy and XRD are presented in Section 4.2.1.1. Calorimetric results from DSC measurements are displayed in Section 4.2.1.2.

4.2.1.1 Structural Results

Optical microscopy was utilized to observe changes in the samples’ microstructures at the surface as a function of slow cooling rate. The microstructures of A1, S2, S1, and
S0.5 FePd samples are compared in Figure 31. The as-polished A1 FePd, shown in Figure 31(a) for comparison, is largely featureless with only a few light lines making a cross-hatch pattern. The S2 (Figure 31(b)), S1 (Figure 31(c)), and S0.5 (Figure 31(d)) samples show both strongly- and weakly-defined grain boundaries. The S0.5 sample displayed a greater number of weakly-defined grain boundaries than the other slowly-cooled samples. S2 FePd, Figure 31(d), exhibited grains more equiaxed in dimension than the S1 and S0.5 samples. Stripe-like features were observed within each grain of widths ~10 µm (light + dark = 1 stripe). During optical microscopy examination the stripes were identified as topographic features. These stripes, or ridges, were observed in S2, S1, and S0.5 but were most prominent in S2. The direction of the ridges is unique to each grain and some grains appeared to show overlapping intersecting ridges in two different directions. Additionally, some larger topographic ridges were present in S2 that spanned across multiple grains and had a width of ~50 µm. Grains in S1 FePd, Figure 31(c), had average widths of 100 µm and average lengths greater than 500 µm. S0.5 FePd, Figure 31(d), showed a mixture of smaller (50 µm x 50 µm) grains and larger elongated grains (100 µm x 500 µm). The grains in observed S1 and S0.5 different levels of brightness from grain to grain, such that some grains appeared darker and some grains appeared lighter, whereas grains in S2 were uniformly colored.
Figure 31: Optical micrograph of FePd (a) A1-structured FePd after polishing, (b) S2, (c) S1, (d) S0.5. All images are at the same magnification. The scale bar in each image is 100 μm.

X-ray diffraction results obtained from S2, S1, and S0.5 FePd are shown in Figure 32 with comparisons to standard patterns included for the A1 and L1₀ FePd phases from Hultgren [39]. FePd samples subjected to cooling at 2, 1, and 0.5 K/min show room-temperature Bragg peaks consistent with those of Hultgren’s tetragonal L1₀ phase, but of (200) texture. The slowest-cooled S0.5 sample displays (200) and (002) Bragg peaks that are clearly separated but merge in the most quickly cooled S2 sample, Figure 32.
Figure 32: XRD results from S2, S1, and S0.5 FePd are compared to previously reported [39] patterns for A1 and L1₀ FePd. The full patterns are in the left window and the (200) and (002) peaks are shown in greater detail in the right window.
Table 9: Lattice parameters, volume, and $c/a$ ratio of S2, S1, and S0.5 FePd. Experimental values of the as-quenched A1 and as-annealed L1$_0$ FePd phases, established in Section 4.1, are included for comparison.

<table>
<thead>
<tr>
<th>Cooling rate</th>
<th>Lattice parameters</th>
<th>Volume ($\text{Å}^3$)</th>
<th>$c/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$a_{\text{fund}}$ (Å)</td>
<td>$c_{\text{fund}}$ (Å)</td>
<td>$a_{\text{sup}}$ (Å)</td>
</tr>
<tr>
<td>A1</td>
<td>3.815 ± 0.004</td>
<td></td>
<td>55.5 ± 0.1</td>
</tr>
<tr>
<td>S2</td>
<td>3.840 ± 0.006</td>
<td>3.771 ± 0.006</td>
<td>3.853 ± 0.007</td>
</tr>
<tr>
<td>S1</td>
<td>3.855 ± 0.002</td>
<td>3.732 ± 0.004</td>
<td>3.840 ± 0.006</td>
</tr>
<tr>
<td>S0.5</td>
<td>3.853 ± 0.002</td>
<td>3.723 ± 0.002</td>
<td>3.849 ± 0.002</td>
</tr>
<tr>
<td>L1$_0$</td>
<td>3.849 ± 0.002</td>
<td>3.723 ± 0.002</td>
<td>3.853 ± 0.002</td>
</tr>
</tbody>
</table>

Two sets of lattice parameters are calculated based on the XRD results. The first set, denoted $fund$, is calculated from the fundamental Bragg reflections (111), (200), and (002). The second set, denoted $sup$, is calculated from the superlattice Bragg reflections (001) and (110). The measured fundamental peaks show a split of the (200) and (002) Bragg reflections indicating that the lattice is tetragonal. The presence of the superlattice peaks indicates chemical ordering. The superlattice peaks can only be due to the L1$_0$ phase whereas the fundamental peaks can have contributions from the L1$_0$, the A1, or possibly the A6 phases.

The calculated lattice parameters, unit cell volumes and $c/a$ ratios are summarized in Table 9 and are plotted as a function of cooling rate in Figure 33. The lattice parameters determined from fundamental reflections for the S1, S0.5, and as-annealed L1$_0$ samples were the same within error as those determined from the superlattice reflections. The $c$ lattice parameter calculated for the S2 sample was 0.058 Å higher when calculated from the fundamental reflections than from the superlattice reflections. The unit cell volume
calculated from the fundamental lattice parameters decreases slightly with decreasing cooling rate but these changes are within the measurement error. The volume from the superlattice lattice parameters is lowest for S2, highest for S1, and equivalent to $V_{\text{fund}}$ for S0.5 and L1$_0$. The $c/a$ ratio provides a measure of the tetragonality of the unit cell; the $c/a$ ratio is equal to unity for the cubic A1-structured FePd. The unit cell determined from fundamental Bragg reflections becomes significantly more tetragonal, $(c/a)_{\text{fund}}$ decreases, with decreasing cooling rate; however, $(c/a)_{\text{sup}}$ did not change with cooling rate. The significance of the changes in lattice parameters, volume, and $c/a$ are discussed in Section 4.2.2.1.

The full width at half maximum (FWHM) intensity of the XRD peaks, representing the peak breadth, decreases with decreasing cooling rate for both the (200) and (002) Bragg reflections as shown in Figure 34 for the S2, S1, and S0.5 samples. The FWHM of the (200) Bragg reflection shown in the XRD results decreases monotonically from 0.295 $\pm$ .005° for S2 to 0.213 $\pm$ .002° for S0.5. The FWHM of the (002) Bragg peak was far larger than that of the (200) peak. The FWHM of the (002) peak was 0.9 $\pm$ 0.2° for S2 and decreased monotonically to 0.314 $\pm$ 0.008° for S0.5. The crystallite size of the L1$_0$ phase was calculated as 6.0 $\pm$ 0.3 nm in S2, 5 $\pm$ 3 nm in S1, and 17.8 $\pm$ 0.3 nm in S0.5, by applying the Scherrer formula [Eq. (3.2)] to the (001) superlattice Bragg peaks.
Figure 33: Lattice parameters, unit cell volume, and $c/a$ ratio for FePd samples as a function of cooling rate. Values for as-annealed A1 and as-quenched L1$_0$ FePd, experimentally determined in Section 4.1, are included here for comparison. Lines are drawn to guide the eye.
4.2.1.2 Calorimetric Results

DSC was utilized to observe thermal changes in the FePd samples while slowly cooling them through the reported chemical order-disorder temperature as well as on subsequent re-heating. The goal of these experiments is to elucidate aspects of the chemical-ordering transformation on cooling and of the chemical-disordering transformation on heating. Results are reported here from DSC measurements obtained from three different FePd samples initially in the quenched A1 state conducted in four distinct steps that are described as follows: 1) heating from room temperature to 900 °C at 20 K/min; 2) slowly cooling from 900 °C to room temperature at 2, 1, or 0.5 K/min; 3)
re-heating from room temperature to 900 °C at 10 K/min; 4) cooling from 900 °C to room temperature at 40 K/min.

A minor thermal event is observed in the temperature range 430 °C — 475 °C in the data measured from all samples in all DSC steps. This event corresponds to a Curie transition (see Section 4.1.2.2) and $T_C$ is given for each DSC step in Table 10.

A prominent high-temperature thermal event is noted during the slow cooling Step 2 and during the subsequent heating Step 3. An exothermic peak is observed in DSC results from each sample with a maximum temperature that shifts to lower values with increased cooling rates during cooling Step 2. The observed magnitude of the DSC signal increases with increasing cooling rate, as expected. A large endothermic peak is observed that begins as an increase in DSC baseline signal that persists over a large temperature range and culminates in a peak while the sample is subjected to heating as described in Step 3. The peak temperatures measured upon cooling and heating are provided in Table 10.
Figure 35: DSC results from three FePd samples initially in the quenched A1 state measured in four steps: 1) heated from room temperature to 900 °C at 20 K/min; 2) slowly cooled from 900 °C to room temperature at 2, 1, or 0.5 K/min; 3) re-heated from room temperature to 900 °C at 10 K/min; 4) cooled from 900 °C to room temperature at 40 K/min.
Table 10: Temperatures of events observed in DSC results on FePd.

<table>
<thead>
<tr>
<th>Step</th>
<th>heat/cool rate (K/min)</th>
<th>Mid-Temp Event (°C)</th>
<th>High-Temp Event (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. heating</td>
<td>20</td>
<td>439.7 ± 3</td>
<td>439.8 ± 3</td>
</tr>
<tr>
<td>2. cooling</td>
<td>0.5</td>
<td>450.8 ± 10</td>
<td>549.5 ± 3</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>452.9 ± 5</td>
<td>538.1 ± 3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>458.3 ± 5</td>
<td>525 ± 3</td>
</tr>
<tr>
<td>3. heating</td>
<td>10</td>
<td>458.9 ± 3</td>
<td>653.8 ± 3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>460.4 ± 3</td>
<td>653.6 ± 3</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>464.7 ± 3</td>
<td>654.2 ± 3</td>
</tr>
<tr>
<td>4. cooling</td>
<td>40</td>
<td>437.4 ± 3</td>
<td>437.5 ± 3</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>437.5 ± 3</td>
<td>437.7 ± 3</td>
</tr>
</tbody>
</table>

4.2.2 Discussion from the Effect of Cooling Rate on the A1→L1₀ Chemical Ordering Transformation in FePd

Analysis of the structure, magnetism, and calorimetry results is presented in Sections 4.2.2.1, 4.1.2.1, and 4.2.2.2, respectively. The progression of the chemical-ordering transformation with cooling rate is discussed in Section 4.2.2.3.

4.2.2.1 Analysis of the Microstructure and Crystal Structure

The evolution of the microstructure and crystal structure of FePd samples cooled through the reported chemical order-disorder temperature are analyzed in this section. The microstructure, particularly the presence of ridges in the optical micrograph results, is discussed first. Following, presentation and analysis of X-ray diffraction results indicates that a mixture of phases is present in the slowly-cooled FePd samples.

Features observed during examination of the samples using optical microscopy provide clues into the A1-L1₀ chemical ordering process by revealing changes in the
accompanying microstructure produced by cooling A1-structured samples through the order-disorder transition temperature. The ridges observed in the micrographs are characteristic of lattice twinning where the lattice forms a series of parallel coherent crystal interfaces across a mirror plane. Twinning has been previously reported in chemically ordered FePd as discussed in Section 2.3.1. Strain in this system is attributed to differences in lattice parameters and unit cell volumes between the A1 and L1₀ phases. The twins observed in S2 are ~5 μm in width, consistent with the macrotwins observed in previous works [42]. The observation that the presence of twins is greatest in the most quickly cooled sample suggests that twinning occurs early in the A1-L1₀ phase transformation and that more-slowly-cooled samples may have additional mechanisms of strain relaxation.

While XRD results obtained from the slowly-cooled samples (S2, S1, S0.5) have many attributes in common with the L1₀ XRD pattern, the very small (001) superlattice peak intensities and the different determined values of tetragonality (c/a) for samples subjected to different cooling rates indicate that the slowly-cooled FePd samples are only partially transformed to the L1₀ chemically ordered structure (Section 4.2.1.1). Evidence of a two-phase mixture in these samples is examined in the following paragraphs by analyzing changes in the degree of chemical ordering and in the lattice structure. The intensity of the (001) peak indicates the degree of chemical ordering while the 2θ angle of the (002) peak indicates the degree of tetragonality.

The degree of chemical ordering in the S2, S1, and S0.5 samples is less than expected given the measured intensity of the (002) fundamental Bragg reflection. While determination of the chemical long-range order parameter was not possible in these
samples due to the low intensities of the superlattice peaks, the degree of chemical ordering was determined by comparing measured and ideal superlattice intensities. The ideal superlattice intensities were calculated from the integrated intensities of the (002) fundamental peaks when assuming a long-range order parameter \( LRO = 1 \) and correcting for instrumental affects (see Appendix A) as shown in Eq. (4.1). The integrated intensities of the \( \text{L1}_0 \) (001) superlattice peaks are smaller than the ideal (001) peak intensities. The ratios of the measured:ideal (001) Bragg reflection intensities are 0.2 (S2), 0.5 (S1), and 0.7 (S0.5) as shown in Figure 36. The degree of chemical ordering in the S2, S1, and S0.5 samples increased with decreased cooling rate.

\[
I_{(001)}^{\text{ideal}} = LRO^2 \frac{I_{002}^*}{I_{002}^*} I_{001}^* 
\]  

(4.1)

where: \( I_{(001)}^{\text{ideal}} \) = ideal intensity for the (001) peak based on measured (002) intensity

\( I_{001}^* \) = calculated intensity of the (001) peak from structure factors

\( I_{002} \) = measured intensity of the (002) peak

\( I_{002}^* \) = calculated intensity of the (002) peak from structure factors

\( LRO \) = chemical long-range order parameter

A mixture of two phases is suggested by the different lattice parameters calculated in the S2 sample (see Section 4.2.1.1). The \( c \) lattice parameter calculated from the fundamental Bragg reflections is different than the \( c \) lattice parameter calculated from the superlattice Bragg reflections for the S2 sample. The only way that these two calculations
can result in different $c$ lattice parameters is if there are two different phases in the samples. The superlattice reflections correspond to the $L1_0$ phase while the fundamental reflections have contributions from both phases. The two phases in the samples are both tetragonal, evidenced by $(c/a)_{fund}$ and $(c/a)_{sup}$ are both less than one, and the phase corresponding to the superlattice peaks has lattice parameters similar to that of the $L1_0$ phase.

It is concluded from analysis of the relative peak intensities $I_{(001)}/I_{ideal}^{(001)}$ and the differences in lattice parameters calculated from fundamental versus superlattice reflections that the S2, S1, and S0.5 samples contain a mixture of the $L1_0$ phase and a tetragonal but chemically-disordered phase.

![Graph](image.png)

**Figure 36:** Ratio of the experimentally measured integrated intensity to the expected intensity of the (001) superlattice reflection as a function of cooling rate, measured using XRD on FePd. Line is drawn to guide the eye.

The full width at half maximum (FWHM) of XRD peak intensity provides information on how the lattice is changing with cooling rate. The FWHM data displayed as a function of cooling rate (Figure 34) indicate that the breadth of the (002) Bragg reflection is significantly greater than that of the (200) Bragg reflection, with a difference
that is greatest for the fastest cooling rate. The large breadth of the (002) Bragg reflection, especially for sample S2, indicates either that crystallites in these samples have varying values for the $c$ lattice parameter or that the lattice is experiencing a great amount of strain in the $c$-axis direction. The decrease in FWHM with slower cooling rates suggests that the lattice is able to relieve strain or approach an equilibrium value of the $c$-lattice parameter when given more time at elevated temperatures. The (002) peak FWHM trend with cooling rate is consistent with the optical microscopy results that show the presence of lattice twins, which are most prominent in the S2 sample. Both the (002) peak FWHM trend and the lattice twins trend with decreasing cooling rate indicate that there are high levels of strain in the S2 sample and the strain is relieved with slower cooling. Application of the Williamson-Hall analysis to XRD data, which attributes XRD peak broadening to a combination of size and strain effects, could not be carried out in this work due to the very low intensities of the other peaks in the XRD patterns. Therefore the lattice strain in slowly-cooled FePd samples is concluded to be present but unquantified.

The lattice long-range order parameter $LRO_{tet(fund)}$ increases as a function of increased cooling rate, Figure 37. $LRO_{tet(fund)}$ is indicative of the degree of tetragonality in the material determined from the ratio of lattice parameters from the fundamental Bragg reflections, $(c/a)_{fund}$. The values of the determined $LRO_{tet}$ increase from $0.73 \pm .01$ (S2) and to $0.98 \pm .01$ (S1) and settles at $1.00 \pm .01$ (S0.5). The $LRO_{tet}$ values determined for the as-quenched A1 and as-annealed L1$_0$ samples (Section 4.1.1.2) are included in Figure 37 for comparison and have values of zero and $0.988 \pm .01$, respectively. The $LRO_{tet}$ corresponding to the annealed L1$_0$ sample is not unity because the measured
lattice parameters were compared against the literature values[39]. The changes in the $LRO_{tet}$ parameter with respect to cooling rate show how the overall sample lattice approaches the $L1_0$ lattice and provide a measure of how far the $A1\rightarrow L1_0$ transformation has progressed.

![Graph showing $LRO_{tet}$ as a function of cooling rate.](image)

**Figure 37:** The lattice long range order parameter, $LRO_{tet}$, calculated from the ratio of lattice parameters determined from fundamental Bragg reflections as a function of cooling rate.

The following two possible scenarios are proposed to describe the progression of the $A1\rightarrow L1_0$ transformation in FePd based on structural results. In the first scenario, the $A1\rightarrow L1_0$ transformation in FePd occurs through nucleation of the $L1_0$ phase during cooling through the chemical order-disorder transformation temperature resulting in lattice strain. This strain causes the untransformed $A1$ phase to become tetragonally distorted and form twins to relieve the lattice strain. More-slowly-cooled samples also form twins but are also able to accommodate the strain through other mechanisms,
possibly through the formation of $c$-axis variants, recovery, or relaxation. In the second scenario, the A1→L$_{10}$ transformation proceeds via initial formation of the a chemically disordered tetragonal phase known as A6, then chemically ordering to form L$_{10}$ [7]. The structural results are in agreement with either of these interpretations and they will be discussed further in Section 4.2.3.

### 4.2.2.2 Calorimetric Analysis

Analysis of calorimetric data provides insight into the enthalpic changes that occur in FePd during the heating and cooling processes. Analysis of the calorimetric data will first tie the noted mid- and high-temperature thermal events to physical changes in the samples. Additional analysis will be conducted on the noted changes in the Curie transition temperatures as reported in Section 3.6.1.1.1 followed by changes in the order-disorder temperatures and enthalpies reported in Section 3.6.1.1.2, and finally address and interpret the presence of a pre-peak to chemical disordering in Section 3.6.1.1.3.

The mid-temperature thermal event recorded in the FePd DSC data corresponds to a Curie transition while the high-temperature event corresponds to the chemical order-disorder transformation, as discussed in Section 4.1.3. The salient temperature points of the calorimetry data that are analyzed are the $T_C$, the pre-peak onset temperature, the peak-onset temperature, and the peak temperature, as identified in Figure 38 for both cooling and heating processes. The pre-peak onset temperature marks the temperature at which the DSC trace deviates from the baseline prior to the main peak. The peak onset temperature marks the beginning of the main peak where a tangent of the peak intersects a tangent of the baseline. The peak temperature is the temperature at which the DSC signal is at a maximum or minimum.
XRD results have demonstrated that FePd samples S2, S1, and S0.5 consist of a partially L1₀-ordered phase as a result of heating A1-type FePd from room temperature to 900 °C and then slowly cooling back to room temperature; it follows that the chemical-ordering process occurred during DSC Steps 1 and 2. As the mid-temperature thermal event has already been explained as a Curie-type transition, the high-temperature exothermic peak noted in the DSC data when collected in Step 2 is attributed to the chemical-ordering transformation. The L1₀ chemical ordering process is known to be exothermic in the related FePt compound and the transformation temperature range corresponds well to those reported previously in FePd [38, 97]. The endothermic peak noted in data collected during the subsequent heating process (Step 3) is then ascribed to the chemical-disordering process of the S2, S1, and S0.5 samples.

Examination of the Curie temperature, peak-onset and peak temperatures and enthalpies, and the pre-peak feature is carried out in the following sub-sections.

Figure 38: DSC traces for cooling Step 2 and heating Step 3, as described in the main text. The $T_C$, pre-peak onset, peak onset, and peak temperatures are indicated.
3.6.1.1.1 Examination of the Curie transition Temperature of FePd

The Curie temperatures of the S2, S1, and S0.5 samples were first measured in Step 2, and in Step 3 during the subsequent heating process. There is a large error in determining $T_C$ in Step 2 due to the low signal-to-noise ratio therefore $T_C$ measured in Step 3 serves as a more reliable measurement for S2, S1, and S0.5. The Curie temperatures decrease from $465 \pm 3$ °C for the most-quickly-cooled (S2) sample to $459 \pm 3$ °C for the slowest-cooled (S0.5) sample (Figure 39). Sample S2 exhibits the highest $T_C$ measured in this sample series, 7.2 degrees higher than that measured for the $T_C$ of L1$_0$ FePd (Section 4.1.1.3).

![Figure 39: The Curie temperature with respect to cooling rate as observed in DSC results.](image)

109
3.6.1.1.2 Examination of the Temperatures and Enthalpies of the Chemical Order-Disorder Transformation of FePd

Thermal changes due to the chemical-ordering transformation of FePd were observed in DSC results measured during slow cooling in Step 2. It was seen that the peak onset and peak temperature of the ordering transformation shifted to higher temperature with slower cooling rate as shown in Figure 40. The fact that the peak temperature is below the equilibrium transformation temperature (~660 °C) and that the peak shifts with cooling rate indicates that chemical ordering is a kinetically-limited transformation. Therefore chemical-ordering is a kinetically-limited transformation, however chemical-disordering is not kinetically-limited (Section 4.1.2.2).

The subsequent heating curves of the S2, S1, and S0.5 samples showed thermal changes due to the chemical-disordering process in Step 3. All of the slowly-cooled samples have the same peak temperature in Step 3 as shown in Figure 40(b). The peak onset temperature measured in the heating Step 3 did increase slightly when the sample was more slowly cooled in the previous Step 2, although this change is within the measurement error. The peak onset and peak temperatures measured from L1₀-structured FePd heated at 10 K/min (results in Section 4.1.4 and repeated here for comparison) are higher than the corresponding features seen in data from samples S2, S1, and S0.5 (Figure 40(a)). All of the peak onset disordering temperatures are lower than the disordering temperature given in the equilibrium phase diagram for Fe₅₀Pd₅₀ [38]. The lower peak onset and peak temperatures of the S2, S1, and S0.5 samples indicate that they are more easily disordered than the annealed L1₀ samples, which may be due to grain coarsening with longer heat treatments that makes disordering more difficult. Comparison of the peak onset disordering temperatures to the order-disorder temperature
given in the phase diagram indicates that disordering begins at lower temperatures than the reported order-disorder temperature.

The total enthalpies of transformation of the FePd alloys are plotted as a function of cooling rate in Figure 41 for cooling Step 2 and heating Step 3. The enthalpies measured on cooling in Step 2 are significantly lower than those measured on subsequent heating in Step 3. The dependence of enthalpy on cooling rate is significant for the enthalpies measured on cooling in Step 2, but is small for the enthalpies measured on heating in Step 3. Results showing that the enthalpies on heating are greater than those on cooling are attributed to additional energetic changes due to changes in the microstructure. It is also possible that these processes are occurring during the cooling step but are not observed due to being spread across a wide temperature range and due to the small signal inherent to DSC measurements with very slow heating/cooling rates.

The activation energy for chemical ordering could not be calculated from the DSC results measured on cooling because the transformation does not go to completion. The Kissinger method to determine activation energies is only valid when the enthalpy change measured from the onset temperature to the peak temperature is equivalent across all heating/cooling rates and the results in Figure 41 do not meet this condition.
Figure 40: Temperatures from calorimetry results on FePd plotted as a function of sample state. The (a) peak-onset and exothermic peak temperatures from the DSC cooling branch, and (b) the peak-onset and peak temperatures from the heating branch are shown. Lines are drawn to guide the eye.
3.6.1.1.3 Examination of the DSC Pre-peak Signal that Precedes Chemical Disordering in FePd

The pre-peak noted in the DSC traces is identified by a deviation from the baseline in the heating steps beginning at ~500 °C and is followed by the exothermic peak at T ~ 655 °C. To show the relative magnitude of the pre-peak signal, DSC data collected at 20 K/min on FePd samples initially in the A1- and L10 states are plotted alongside each other in Figure 42. A slight bump appears in the baseline in the DSC data of the A1 sample but it is far smaller than that seen in the data for the as-annealed L10 sample thereby confirming that the pre-peak signal noted in the disordering steps does indeed constitute a measurable deviation from the baseline.

Changes in the pre-peak onset temperature, pre-peak breadth, and the enthalpy content encompassed in the pre-peak are examined between the S2, S1, S0.5 and L10
samples. Although the shape of the pre-peak signal is slightly different for all three samples, the pre-peak onset temperatures do not change significantly, Figure 43. The pre-peak onset was higher for the L1₀ samples than for S2, S1, and S0.5. The breadth of the pre-peak is defined as the temperature difference between the pre-peak onset and peak onset temperatures and is plotted in Figure 44, with finite changes that increase with decreasing cooling rate. The percent of the total enthalpy that is contained within the pre-peak was ~45% in all samples, nearly equal to the percent contained within the peak itself, as shown in Figure 45.

The existence of a pre-peak is consistent with DSC results on the chemical disordering of other L1₀ systems [98, 99]. In the literature many authors have attributed this pre-peak to a pre-disordering process wherein the long-range chemical order decreases slightly before the transition temperature resulting in an endothermic DSC signal [21]. Other authors suggest that short-range chemical order changes by a continuous second-order process so that the pre-peak is due to changes in short-range order while the peak is due to changes in long-range order [100].

Another theory that has been suggested is that the pre-peak emerges at the annealing temperature. The idea is that an equilibrium short-range-order state was obtained at the annealing temperature and quenched in. Then, subsequent heating in the DSC would show no changes until the temperature was above the annealing temperature, then the system would continue to lose short-range order resulting in the pre-peak [101]. The results presented here refute this idea. By using constant cooling rates, the samples were not allowed to equilibrate at any one annealing temperature, yet, the pre-peak is observed as a distinct increase in the DSC signal.
It is interesting that the heating steps exhibit this pre-peak but the cooling steps do not, suggesting that the chemical-disordering and ordering transformations proceed by different mechanisms or that the signal from the pre-peak is too small to be detected during slow cooling.

**Figure 42:** Comparison of DSC traces taken on heating to show the significance of the pre-peak above the baseline. FePd beginning in the quenched A1 state and in the annealed L1₀ state were both measured at 20 K/min on the same FePd sample.

**Figure 43:** Pre-peak onset temperature of FePd measured on heating in DSC. The x-axis indicates the rate at which the sample was cooled in previous step. Line drawn to guide the eye.
4.2.2.3 Progression of the Chemical-Ordering Transformation in FePd

The long-range order parameter calculated from the tetragonality $LRO_{tet}$ provided one measure of the progression of the $A1 \rightarrow L1_0$ transformation, but the relative enthalpies
of transformation can also be used to characterize the fraction transformed to L1\(_0\). The enthalpically determined fraction transformed to the L1\(_0\) phase increased with increasing heat treatment as seen in Figure 46. The fraction transformed to the L1\(_0\) phase of the S2, S2, and S0.5 samples was determined as the ratio of the transformation enthalpy measured on cooling to the transformation enthalpy of the L1\(_0\) sample measured on heating. The annealed L1\(_0\) sample from Section 4.1 is assumed to be fully transformed to the L1\(_0\) phase in this determination. The increase in fraction transformed with decreasing cooling rate is very significant in the cooling data.

![Figure 46: The fraction transformed to the L1\(_0\) phase determined from the relative enthalpy. Line drawn to guide the eye.](image)

Examination of the lattice parameters, unit cell volume, and tetragonality (as determined from the fundamental Bragg peaks) with respect to the enthalpically determined fraction transformed to L1\(_0\) on cooling reveals the correlations between the structural and energetic changes in the system. The parameters determined from the superlattice Bragg reflections are not plotted because they were more or less constant across all samples. The lattice of FePd, from the fundamental Bragg peaks, became more
tetragonal with increasing fraction transformed, due to a significant reduction of the $c$ lattice parameter and an increase in the $a$ lattice parameter. The lattice parameters and the tetragonality ($c/a$) appear to have a step-like change between 62% and 71% transformed.

Figure 47: Effect of fraction transformed (i.e., relative measured enthalpy) on (a) the lattice parameters, (b) unit cell volume, and (c) unit cell tetragonality in FePd determined from the fundamental Bragg reflections. Lines drawn to guide the eye.
The $LRO_{\text{tet}}$ of the unit cell and the fraction transformed determined from the relative enthalpies can both be used as indications of how far the $\text{A1} \rightarrow \text{L1}_0$ transformation has gone toward completion. One would expect these two parameters to be equivalent; however, that is not observed when these two parameters are plotted against the cooling rate, as in Figure 48. Instead, $LRO_{\text{tet}}$ gives a much higher indication of ordering that do the relative enthalpies. These results indicate that tetragonality develops earlier in the ordering transformation than other endothermic processes.

![Figure 48](image.png)

**Figure 48:** The relative enthalpy (enthalpies measured during cooling relative to the enthalpy of disordering $\text{L1}_0$) and $LRO_{\text{tet}}$ (the lattice long range order parameter calculated from the unit cell tetragonality) are plotted as functions of the cooling rate.
4.2.3 Significance of Work from the Effect of Cooling Rate on the A1→L1₀ Chemical Ordering Transformation in FePd

The results presented in this Dissertation on the microstructure, crystal structure, and thermal changes of FePd slowly cooled through the reported order-disorder transformation temperature are consistent with a chemical-ordering mechanism in which a tetragonal chemically disordered structure forms. The presence of the tetragonal chemically disordered phase is supported by different lattice parameters calculated based on the superlattice compared to the fundamental Bragg reflections observed in X-ray results. The presence of the tetragonal chemically disordered phase is also supported by the smaller than expected superlattice peaks in the slow-cooled samples that indicate the overall lattice of the sample is tetragonal but not well chemically ordered. The presence of this phase can be explained by the following two different proposed mechanisms. The results presented in this Dissertation are consistent with either mechanism.

1) Strain-distorted A1 phase becomes tetragonal: In this proposed mechanism, the L₁₀ phase nucleates in the initially A1 matrix and generates lattice strain due to the difference in lattice parameters between the L₁₀ and A1 phases. The A1 phase becomes tetragonally distorted because it is coherent with the L₁₀ nuclei and is therefore subjected to strain at the A1/L₁₀ interfaces. The distorted A1 phase is detected by XRD as a chemically disordered tetragonal phase. Twins form in the lattice to alleviate the strain. Vlasova et al. have observed that the L₁₀ phase formed plates in an initially A1-structured FePd sample during short isothermal annealing times, and that the A1 phase between the plates became tetragonally distorted, which is consistent with this first proposed mechanism [4].
2) *New metastable A6 FePd phase:* In this proposed mechanism, the A6 phase is an intermediate phase in the Fe-Pd system and the chemical-ordering transformation is really the sum of two processes wherein A1→A6→L1_0. The pre-peak observed in DSC results on heating may represent a chemical-disordering process prior to the main transformation; in other words, the DSC pre-peak may correspond to the L1_0→A6 process. Lattice twins form in order to relieve strain caused by the development of tetragonality in the A1→A6 transformation. Vlasova et al. [7] observed that selected area electron diffraction of an FePd sample subjected to severe plastic deformation showed unequivocal evidence of a tetragonal chemically disordered A6 phase (see Section 2.3.1) suggesting that the A6 structure may be a metastable intermediate phase.

More slowly cooled samples are able to alleviate strain in either chemical-ordering mechanism through the formation of c-axis variants, recovery, relaxation, recrystallization, further transformation to the L1_0 phase, or other means. Microstructural changes, resulting in deformation of the sample surfaces, occurred in the samples studied in this work and are likely responsible for the differences in enthalpies measured for the ordering process on cooling and for the disordering process on subsequent heating.

DSC results presented in this Dissertation indicated that the fastest cooled sample, which has the highest volume fraction of the tetragonal chemically disordered phase, has a Curie transition temperature higher than the $T_C$ of L1_0. This higher $T_C$ could be because the A1 phase has different magnetic exchange interactions when it becomes tetragonally distorted (mechanism #1). Alternatively, the higher $T_C$ could be because the A6 phase has a higher $T_C$ than the A1 or L1_0 phases (mechanism #2). The measured $T_C$ data of the
slowly cooled samples is in disagreement with Vlasova et al. who indicated that the A6 phase has a $T_C$ between that of the A1 and L1$_0$ phases in FePd [7].
5 FeNi Results and Discussion

The aim of this Dissertation work was to gain understanding of the L1\textsubscript{0} chemically ordered phase and of the chemical-disordering transformation in FeNi, with the goal of determining the magnetic properties correlated to the L1\textsubscript{0} structure and elucidating the barriers to the order-disorder transformation. To that end, the structural and magnetic characteristics of L1\textsubscript{0} FeNi (tetrataenite) extracted from meteoritic materials were characterized and correlations between the structure and magnetism are drawn in Section 5.1. The microstructure was found to consist of regions \(~50\ \mu\text{m}\) with an anisotropic crystal structure. The crystal structure was further determined to be L1\textsubscript{0}-structured FeNi. Magnetic results showed tetrataenite to have strong uniaxial magnetic anisotropy and a high observed Curie temperature \(\sim 560\ \text{°C}\). Calorimetry showed that tetrataenite chemically disorders at the same temperature as the observed \(T_C\), indicating that a simultaneous chemical and magnetic disordering transition occurs. In Section 5.2, Calorimetric changes were studied as functions of the heating rate to quantitatively determine the thermodynamic and kinetic parameters of the L1\textsubscript{0}\rightarrow\text{A1} chemical-disordering transformation and to add insight into the kinetic mechanisms of the transformation. The enthalpy of transformation between A1 and L1\textsubscript{0} phases was experimentally determined as was the activation energy for chemically disordering L1\textsubscript{0} FeNi. The kinetic mechanism of chemical disordering was found to be vacancy controlled.

5.1 Correlations of Structure and Magnetism of L1\textsubscript{0} FeNi

In this section, L1\textsubscript{0}-structured FeNi extracted from the NWA6259 meteorite was investigated to study the relationships between structure and magnetism. Structural
confirmation of the presence of L1$_0$ FeNi in the NWA6259 meteorite was achieved in collaborative work carried out in parallel to this Dissertation and is summarized in Section 2.3.2. The presence of L1$_0$ FeNi in the Estherville meteorite has been studied in prior [77]. The work presented in this section provides further information on the microstructure of the meteoritic samples and the degree of chemical ordering, and it correlates the structure to the observed magnetic results. Experimental results are shown in Section 5.1.1 followed by discussion in Section 5.1.2. The significance of this work for understanding the structure-magnetism relationships is presented in Section 5.1.3.

5.1.1 Results on the Correlations of Structure and Magnetism of L1$_0$ FeNi

Structural (microstructural and crystal structure), magnetic and calorimetric experimental results on tetrataenite from the NWA6259 meteorite are presented in this section. Structural results, comprised of observations and data collected from optical microscopy with polarized light and synchrotron X-ray diffraction (XRD) are presented in Section 5.1.1. Magnetic results from magnetic force microscopy (MFM) and vibrating sample magnetometry (VSM) are shown in Section 5.1.2. Lastly, calorimetric results from differential scanning calorimetry (DSC) measurements are displayed in Section 5.1.3.

5.1.1.1 Structural Results

The microstructure and the crystal structure of tetrataenite in the NWA6259 meteorites were examined with optical microscopy using polarized light. As presented in Section 5.1.1.2, MFM also contributed information concerning the microstructure of the
Estherville and NWA6259 meteorites. The crystal structure and arrangement of variants in the NWA6259 meteorite were examined with single-crystal XRD.

Polarized light micrographs of the NWA6259 meteorite showed interconnecting regions of contrast. In Figure 49(a) regions appear orange, green/yellow, and green/gray. In Figure 49(b) regions appear green, orange, and brown. These regions varied in size from a few microns to ~50 μm across as seen in Figure 49. There is no obvious pattern to the arrangement of the regions. When the direction of polarized light was rotated 180°, the color of each region changed.

Figure 49: Polarized light micrograph of two regions of the NWA6259 meteorite. (a) Image taken by the author of this Dissertation. (b) Image taken by collaborators[75].

The microstructure of tetrataenite was investigated with XRD pole figure measurements to confirm the presence of the L1₀ phase and to determine the crystallite orientations. Selected pole figures from NWA 6259 are shown in Figure 50, collected at d-spacings corresponding to the locations in k-space (inverse space) for expected L1₀ FeNi diffraction peaks based on reported lattice parameters [52]. Pole figure images with d-spacing corresponding to L1₀ (111) and (200) fundamental Bragg reflections are shown in Figure 50(a) and (b), respectively, while the pole figures with d-spacing corresponding
to the (110), (201) and (112) superlattice reflections are shown in Figure 50(c), (d), and (e), respectively. Figure 50(a) shows four large-sized diffraction spots arranged like the corners of a square, with four medium-sized spots forming a smaller square inside (square-like shaped are marked with superimposed black lines). An additional set of four medium-sized spots are located on the opposite side of the pole figure from the first set of medium spots. Lastly, there is a medium-sized spot at the top center and at the bottom center of Figure 50(a) denoted by black arrows. Figure 50(b) displays two large-sized spots on opposite sides of the pole figure (indicated by solid black circles) with a ring of medium spots around each one (marked with dashed black circles). Additionally, there are spots at the top and bottom center in the same positions as the previous image (arrows). Figure 50(c), (d), and (e) exhibit arrays of small-sized spots arranged in a matrix-like fashion (each spot is marked with a black circle). All of the images appear to have mirror symmetry across a near-horizontal line and across a near-vertical line.
Figure 50: Pole figure results of NWA6259 meteorite with \(d\)-spacings corresponding to \(\text{L}1_0\) reflections: a. (111) fundamental, b. (002) fundamental, c. (110) superlattice, d. (201) superlattice, and e. (112) superlattice.

The crystal structure of tetrataenite was investigated with XRD \(\theta\)-2\(\theta\) measurements to determine the lattice parameters and to measure the intensities of the superlattice reflections for estimation of the long-range order parameter and distribution of \(c\)-axis variants (calculations in Section 5.1.21). Results from \(\theta\)-2\(\theta\) XRD measurement performed on NWA6259, with the sample oriented such that the intensity of the (002) reflection was maximized in the pole figure results, show the presence of the (001) and (003) superlattice peaks, as seen in Figure 51(a). The (110) superlattice peak was detected by orienting the sample to maximize the (220) fundamental reflection, as seen in Figure 51(b). In addition to the \(\text{L}1_0\) FeNi Bragg peaks, there are additional unidentified peaks observed in the XRD results. Specifically these peaks are observed in the \(2\theta\) range 66.0°-
67.2° and at 82° in both the pole figures and in θ-2θ data. The NWA 6259 L₁₀ FeNi lattice parameters are calculated as \( a = 3.578 \pm 0.001 \) Å, \( c = 3.585 \pm 0.001 \) Å, \( c/a = 1.0019 \pm 0.0004 \), with a unit cell volume = 45.90 ± 0.02 Å³. The full width at half maximum of the fundamental peaks was 0.35 ± 0.01 degrees (See Section 3.4).

![Figure 51](image)

**Figure 51**: L₁₀ superlattice Bragg peaks of (001), (110), and (003) reflections are clearly observed in NWA 6259 tetrataenite during single-crystal XRD carried at NSLS beamline X20A. The sample was oriented along (a) the (002) direction, and (b) the (220) direction.

The change in intensity and angle of the (001) superlattice and (200) fundamental reflections with changing incident X-ray energy was measured to confirm that these XRD peaks belong to the L₁₀ FeNi phase and to aid in future synthesis efforts. The superlattice peaks of L₁₀ FeNi are expected to have a maximum intensity at the Fe absorption edge (7.11 keV) based on the phenomenon of anomalous diffraction (see Appendix A). The L₁₀ FeNi Bragg reflections from the (001) and (200) reflections systematically shifted to lower angles with increased X-ray energy (Figure 52), but the peak intensities changed non-monotonically. The (001) peak intensity increased rapidly as energy increased from 6.7 to 6.86 keV, then increased gradually for energies 6.86 to 7.04 keV, increased rapidly
again to a peak at 7.1 keV, then dropped off sharply as shown in Figure 53(a). The intensity of the peak corresponding to the (200) increased greatly as energies increased from 6.7 to 6.9 keV, decreased gradually in the range 6.9 to 7.1 keV, then dropped off sharply (Figure 53 (a)). The ratio of the integrated intensities of $I_{(001)}/I_{(002)}$ gradually increases with increased energy to a sharp peak at 7.1 eV as seen in Figure 53(b). Future efforts to confirm L1$_0$-structure FeNi in synthesized laboratory samples will require anomalous diffraction and results from meteoritic studies presented in this Dissertation provide guidance for those future studies.

![Figure 52: XRD peaks from NWA6259 meteorite measured in the 2θ range corresponding to (a) the (001) superlattice and (b) the (200) fundamental peaks of L1$_0$ FeNi. Diffraction was measured at varying incident X-ray energies in the vicinity of the iron absorption edge.](image)
Figure 53: Integrated intensities of XRD peaks from NWA6259 meteorite in the 2θ range corresponding to (a) the (001) superlattice and (200) fundamental peaks for L1₀ FeNi, and (b) the ratio of the (001) and (200) integrated intensities.

5.1.1.2 Magnetic Results

The magnetic domain structure, room temperature field-dependent behavior, magnetocrystalline anisotropy, and thermomagnetic behavior of tetrataenite were probed using MFM and VSM.

The magnetic domains of tetrataenite were measured in two meteoritic samples: Estherville and NWA6259. The magnetic domains of tetrataenite in the Estherville meteorite exhibit a mostly featureless cream-colored area with a large island showing a flower-like pattern in the MFM results shown in Figure 54(a). The Kamacite phase (bcc α-Fe with < 7 wt% Ni) occupies the lower right corner of Figure 54(a) marked with a dashed line. The magnetic domain structure of tetrataenite in the NWA6259 meteorite is
observed as a very complicated array of features across a 100 x 100 μm field of view, as seen in Figure 54(b).

Figure 54. Magnetic domains of tetrataenite from (a) the Estherville meteorite demonstrate flower-like domains, and (b) the NWA6259 meteorite reveal a complex magnetic structure, as measured by MFM.

Room-temperature hysteresis curves carried out on the NWA 6259 sample in its as-received state show a virgin magnetization curve that increases gradually with increased applied magnetic field. As seen in Figure 55, the saturation magnetization is 140 emu/g and the coercivity is 1000 Oe. After the same sample was heated to 700 °C (red curve), the saturation magnetization did not change but the remanence and coercivity decreased to negligible values. After a second heating to 700 °C (green curve), the room temperature magnetization increased by 14% to 159 emu/g; the coercivity and remanence remained at negligible values.

NWA6259 has an experimental apparent Curie temperature ($T_C$) of 557 °C when measured on heating from its as-received state shown in black in Figure 55. On cooling, the Curie transition is observed at 467 °C. A second $M$ vs. $T$ curve measured on the same sample indicates a small decrease in magnetization at $T = 387$ °C, followed by a Curie
transition at 467 °C. On the second cooling, a sharp magnetic transition is observed at $T_C = 387$ °C shown in red in Figure 55.

The anisotropy constant was determined in this work for NWA6259 in its as-received state as $K_1 = 1.4 \times 10^6$ erg/g ($1.1 \times 10^7$ erg/cc assuming density of 8.3 g/cc) as shown in Figure 56. The room-temperature anisotropy constant of the NWA6259 meteorite after being heated twice to 700 °C was found to be two orders of magnitude lower, with $K_1 = 3.6 \times 10^4$ erg/g ($3.1 \times 10^5$ erg/cc) (Figure 56).

Figure 55: Magnetization of FeNi from the NWA6259 meteorite (a) as a function of applied field, and (b) as a function of temperature. The NWA6259 in the as-received state has higher $H_C$, $M_R$, and $H_K$ than after the 1st and 2nd $M$ vs. $T$ measurements. The $M$ vs. $T$ measured on the as-received state shows a Curie temperature at 557 °C, with $T_C = 467$ °C during the first cooling branch, and $T_C = 387$ °C on second heating/cooling $M$ vs. $T$ measurements.
5.1.1.3 Calorimetric Results

Enthalpic changes in the NWA6259 meteorite were measured using differential scanning calorimetry (DSC) to study the temperatures of the chemical order-disorder transformation and magnetic transition in tetrataenite. DSC results show two enthalpic changes in the heat flow when the as-received sample is heated from room temperature to 900 °C at 5 K/min. The first change in heat flow occurs as a small endothermic peak at 147 °C followed by a larger asymmetric endothermic peak at 555 °C. A second measurement on the same sample under the same conditions shows a small endothermic peak at 145 °C and a kink in the baseline at 387 °C. The results are plotted in comparison with the initial magnetization curves of the meteorite as-received and after being heated to 700 °C.
to the magnetothermal results (magnetic data is also shown in Section 5.1.1.2) in Figure 57. The large endothermic peak observed on heating the as-received meteoritic sample using DSC occurs at the same temperature as the tetrataenite Curie transition observed using VSM, indicated by the black dashed line through the DSC and VSM results in Figure 57. The kink in the DSC baseline of the 2\textsuperscript{nd} heating data corresponds to the same temperature as the Curie transition observed during the 2\textsuperscript{nd} cooling in VSM results, indicated in Figure 57 by the red dashed line.

![Figure 57: Comparison of the heat flow and magnetization as functions of temperature for two samples extracted from adjacent sites on the NWA6259 meteorite. Both samples in the as-received state exhibit a transformation at ~555 °C. In subsequent heating/cooling steps, both samples show a transition at ~387 °C.](image)

5.1.2 Discussion on the Correlations of Structure and Magnetism of L1₀ FeNi

Discussions of the results obtained from tetrataenite derived from the NWA 6259 meteorite are divided into structural analysis in Section 5.1.2.1, magnetic analysis in Section 5.1.2.2, and calorimetric analysis in Section 5.1.2.3.

5.1.2.1 Structure Analysis

The microstructures and crystal structures of the phases present in the NWA6259 meteorite are analyzed in this section. Discussion in this section first addresses the unexpected peaks observed in θ-2θ measurements then delve into an analysis of the microstructure and crystal structure of the L1₀ FeNi phase present in the meteoritic sample. The microstructural data indicates that the L1₀ crystal structure exists in the meteoritic sample in three mutually perpendicular orientations. The crystallographic data is analyzed to determine the long-range order parameter and estimate the relative abundance of c-axis variants.

The unexpected peaks in the θ-2θ measurements are attributed to a mineral inclusion, common in meteorite samples. Kamacite (bcc Fe with up to 7 wt% Ni) is a common phase in many meteorites and matches well with the observed unexpected peaks. The strongest lines of bcc Fe are the (110) at 44.6, (200) at 65.0, and (211) at 82.3° 2θ. The (110) peak of bcc Fe is close to the (111) peak of tetrataenite so it is not surprising that they may overlap in the experimental data. The unexpected peaks in the θ-2θ measurements do not match well with reference XRD patterns for sulphide and phosphide inclusions, which also are known to populate the NWA6259 meteorite;
indicating that sulphide and phosphide are not present in detectable quantities in the
diffracting region of the specific sample used for XRD measurement.

The pole figure results measured from NWA6259 are consistent with the existence
of a face-centered crystal oriented with the [110] direction normal to the sample surface
[83]. Tetrataenite is expected to be nearly cubic (results showed $c/a = 1.0019 \pm 0.0004$ in
Section 5.1.1.1) therefore the initial analysis can be done with respect to an fcc unit cell,
which has the expected pole figure shown in (Figure 58) when measured along the [110]
direction [83]. The pole figure results that correspond to the (111) Bragg reflections of
$L1_0$ FeNi (Figure 59) show the four largest spots match with the positions of the (111)
Bragg reflections in Figure 58. Furthermore, the pole result with $2\theta$ corresponding to the
(200) of $L1_0$ FeNi (Figure 59) show the two largest diffraction spots at the positions of
the expected (100) reflections for the fcc unit cell.

In addition, diffraction spots at the $d$-spacing corresponding to the $L1_0$ FeNi (111)
and (200) were modeled to an fct crystal using *Fitequipoint* software [102] with results
shown in Figure 59. The diffraction spot marked “a”, in the upper center portion of
Figure 59(a), was chosen as the zone axis. Diffraction spots marked “b”, “c”, and “d”
were identified as (111) reflections corresponding to a face-centered tetragonal-type
crystal in the same orientation as “a”, while (200) reflections for the same crystal
orientation are identified by dashed black circles in Figure 59(b). The other diffraction
spots in the (111) and (200) pole figures corresponded to expected peak positions for a
crystal rotated 90°. The correspondence of the pole figure results to these models
indicates that the $L1_0$ crystallites in the meteorite are oriented mutually perpendicularly to
each other and the lattice is oriented such that the $<110>$ is 3.57° from the sample normal direction.

Figure 58: Expected reflection positions in a pole figure of a fcc crystal measured along the (110) direction (after Ref. [83]). Yellow triangles mark {111} Bragg reflections and pink squares mark {100} Bragg reflections. Image rotated so as to roughly match the orientation of the pole figures collected from the NWA6259 meteorite.

Figure 59: Pole figure results modeled as an fct structure with Fitequipoint software [102]. (a) (111) peaks corresponding to fcc crystal with orientation “a”. (b) (200) peaks corresponding to fcc crystal with orientation “a”.
Further information on the orientation of the L1$_0$ structure in the meteoritic sample is accomplished by examining the \{110\} superlattice reflections observed in the pole figure data (Figure 60). For a single crystallite of L1$_0$, superlattice peaks only result from the (110) and (1\overline{1}0) crystal planes [these planes are equivalent to the (\overline{1}10) and (1\overline{1}0) crystal planes so that the \{110\} Bragg reflection has a multiplicity of four] due to the reduced symmetry adopted by the chemically ordered system. It follows that the six \{110\} diffraction spots observed in the pole figure results are attributed to L1$_0$ crystallites oriented in three orthogonal directions. The \{110\} pole figure diffraction spots are related to the (110) crystal planes in three perpendicular unit cell variants shown in Figure 60. The strong orientation relationship between the (110) diffraction spots indicates that the three crystal orientations are mutually perpendicular and are likely coherent.

These pole figure results are consistent with reports of the mechanism of L1$_0$ phase formation from the parent fcc phase in the related L1$_0$-type FePd and FePt systems. During the A1$\rightarrow$L1$_0$ phase transition the tetragonal L1$_0$ phase may form with the individual c-axes of the constituent crystallites arranged in a manner that is coherent with the [100], [010], or [001] directions of the parent phase so that three crystal lattice variants are possible [6, 22-24].
Figure 60: XRD pole figures showing the (110) superlattice reflections resulting from the three orthogonal L1$_0$ variants.

The long-range order parameter and the distribution of the crystallographic variants of tetrataenite in NWA 6259 may be found from $\theta$-2$\theta$ measurements of the superstructure and fundamental Bragg reflection pairs. A summary of the Bragg reflections measured and the angles of the diffractometer for each reflection are summarized in Table 11 ($\lambda = 1.54062$ Å). The long-range order parameter ($LRO$) was calculated from the $\theta$-2$\theta$ data using the method and specific instrument parameters defined in Appendix A. To calculate LRO, the integrated intensities of the superlattice reflections were compared to their corresponding fundamental reflections of the same orientation (i.e., $\chi$, $\varphi$, $\omega$ held constant) such that the (001) was compared to the (002), and the (110) to the (220). The long-range order parameters of tetrataenite variants in NWA 6259 were found to be 1.18, 0.93, and 0.89 for Variants A, B, and C, respectively. The determination of $LRO$ for Variant A is
non-physical; however, the reason for this result is not clear at the present time. The average of the LROs of the three variants yields \( LRO(\text{average}) = 1.0 \pm 0.1 \). The distribution of variants indicates that 51% of the meteorite in the probed region has one \( c \)-axis direction (Variant A) while Variants B and C account for 19% and 30% of the sample by volume, respectively.

Table 11: The angles of Bragg reflections measured for the three variants in the NWA6259 meteorite at beamline X20A of the NSLS using a point detector with analyzer \((\lambda = 1.54062 \, \text{Å})\).

<table>
<thead>
<tr>
<th></th>
<th>(hkl)</th>
<th>( \theta )</th>
<th>2( \theta )</th>
<th>( \chi )</th>
<th>( \varphi )</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variant A</td>
<td>(001)</td>
<td>15.968</td>
<td>24.787</td>
<td>53.155</td>
<td>174.46</td>
<td>3.5745</td>
</tr>
<tr>
<td></td>
<td>(200)</td>
<td>29.0755</td>
<td>51.002</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(110)</td>
<td>21.2595</td>
<td>35.37</td>
<td>54.375</td>
<td>53.75</td>
<td>3.5745</td>
</tr>
<tr>
<td></td>
<td>(220)</td>
<td>41.0785</td>
<td>75.008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Variant B</td>
<td>(110)</td>
<td>21.2595</td>
<td>35.37</td>
<td>64.2</td>
<td>122</td>
<td>3.5745</td>
</tr>
<tr>
<td></td>
<td>(220)</td>
<td>41.0785</td>
<td>75.008</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Variant C</td>
<td>(001)</td>
<td>15.968</td>
<td>24.787</td>
<td>36.79</td>
<td>355.85</td>
<td>3.5745</td>
</tr>
<tr>
<td></td>
<td>(002)</td>
<td>29.0755</td>
<td>51.002</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.1.2.2 Magnetic Analysis

Analysis of the magnetic results examines the characteristics of the magnetic domains in MFM results and the changes in bulk magnetic properties with heating seen in VSM results. The magnetic domain structure indicates high uniaxial anisotropy that is confirmed in bulk measurement. Progressive changes in the hysteresis and \( M \) vs. \( T \) behavior, as the sample is subjected to heating and cooling cycles, suggests a multi-stage disordering transformation.

The magnetic domain structure measured in the Estherville meteorite is comparable to the flower-like domain patterns exhibited by NdFeB (Figure 61) and is characteristic of materials with high uniaxial magnetocrystalline anisotropy. The flower-like pattern
occurs when a crystal of high anisotropy is oriented with the easy axis of magnetization (the c-axis for $\text{L}_1\text{FeNi}$) out of plane. The magnetic flux must form closed loops and it is generally energetically favorable to form those loops inside the sample material. However, if the material possesses sufficiently high uniaxial anisotropy then the flux forms closed loops outside of the sample rather than assume an orientation other than the easy-axis of magnetization inside the sample. A schematic drawing of the magnetic domains and flux loops resulting in the flower-like domain pattern is shown in Figure 61(b).

The domain structure of the NWA6259 meteorite is complicated and presents no clear pattern. This indicates that there are many orientations of the c-axis in the measured NWA6259 sample and that they are magnetically interacting.

Figure 61: Magnetic domain structure of materials with high uniaxial magnetocrystalline anisotropy. (a) NdFeB crystal showing a twin boundary with flower-like magnetic domains in the upper portion of the image and a branching pattern in the lower portion of the image (reproduced from Ref. [92]). (b) Schematic representation of magnetic flux in a high-anisotropy material drawn in side-view showing stray field above the surface (reproduced from Ref. [103]).
The progression of room temperature hysteresis loop behavior of tetrataenite in NWA6259 with heat treatment indicates the presence of multiple magnetic phases. The properties of the three observed magnetic phases are shown in Table 12. The as-received meteoritic sample displayed high anisotropy ($H_K = 20$ kOe), $M_S = 140$ emu/g, and a Curie transition at $557 \, ^\circ C$ coincident with the chemical disordering temperature. The second magnetic phase shows soft ferromagnetic behavior ($H_K \sim 0$), the same $M_S$ as the as-received phase, and a Curie temperature at $467 \, ^\circ C$ observed in the 1st cooling and 2nd heating $M$ vs. $T$ data. The third magnetic phase shows soft ferromagnetic behavior, a distinct increase in saturation magnetization ($M_S = 159$ emu/g), and a Curie transition at $387 \, ^\circ C$ observed as a small step, or a change in slope, in the 2nd heating and as the only step in the 2nd cooling $M$ vs. $T$ data. The as-received meteoritic sample is known to be L10-structured from the structural results presented in Section 5.1.1. The magnetocrystalline anisotropy constant calculated in this Dissertation for NWA6259 is $K_1 = 1.4 \times 10^6$ erg/g ($1.1 \times 10^7$ erg/cc assuming density of 8.3 g/cc), which is very comparable to Néel and Paulevé’s values of 1.0-1.3 $\times 10^7$ emu/cc for L10 FeNi [11, 71].

The magnetic properties of the third phase are consistent with known properties of chemically disordered fcc (A1) FeNi [1, 25]. The Curie temperature of A1 FeNi with 43 - 44 at.% Ni composition is reported as $T_C \approx 390 - 415 \, ^\circ C$[104].

The structure and identity of the second magnetic phase is unknown. Three possible explanations for “Magnetic Phase 2” are presented here.

1) *A1 and L10 mixture:* It may be that regions of L10 order persist in the sample after being heated to $700 \, ^\circ C$ so that the observed magnetic behavior is a result of a mixture of A1 and L10 phases. A mixture of A1 and L10 is expected to
have low anisotropy but the $M_S$ should be a value between that of the A1 and L1$_0$. However, the measured $M_S$ of Magnetic Phase 2 is equal to that of L1$_0$. A mixture of A1 and L1$_0$ also does not explain the Curie transition at 467 °C. The intrinsic $T_C$ of L1$_0$ FeNi is expected to be 727 ± 200 °C [12] (see Section 5.1.2.3) and that of A1 Fe$_{57}$Ni$_{43}$ is ~390 °C [1]. A mixture of phases would not produce an average $T_C$, but rather show both transitions in turn. Thus, the Curie transition at 467 °C observed on the first cooling step of the $M$ vs. $T$ measurement cannot be explain by a mixture of A1 and L1$_0$ phases.

2) *Spinodal decomposition:* The sample may be undergoing a spinodal decomposition transformation into a high-Ni ferromagnetic phase and a low-Ni ferromagnetic phase as predicted by the Fe-Ni low temperature phase diagram [1]. In this scenario, the Curie transition at 467 °C is attributed to the new high-Ni ferromagnetic phase. However, a lower temperature Curie transition attributed to the low-Ni ferromagnetic phase is not observed in the results.

3) *Metastable phase formation:* The “Magnetic Phase 2” may correspond to an intermediate structural phase formed during the L1$_0$$\rightarrow$A1 transformation. It was proposed in Chapter 4 that FePd forms an intermediate chemically disordered tetragonal phase (A6) during the chemical-disordering transformation. It is possible that FeNi also exhibits an intermediate disordered structural phase with the magnetic properties observed in these results.
Table 12: The progression of magnetic properties in a NWA6259 sample indicates the presence of three magnetic phases.

<table>
<thead>
<tr>
<th>Magnetic Phase</th>
<th>Saturation magnetization $M_S$ (emu/g)</th>
<th>Anisotropy field $H_K$ (kOe)</th>
<th>Curie temperature $T_C$ (°C)</th>
<th>Crystal structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received (Phase 1)</td>
<td>140</td>
<td>20</td>
<td>557</td>
<td>$L_{10}$</td>
</tr>
<tr>
<td>Magnetic Phase 2</td>
<td>140</td>
<td>~0</td>
<td>467</td>
<td>?</td>
</tr>
<tr>
<td>Magnetic Phase 3</td>
<td>159</td>
<td>~0</td>
<td>387</td>
<td>$A_1$</td>
</tr>
</tbody>
</table>

5.1.2.3 Calorimetric Analysis

$L_{10}$ FeNi samples exhibited a small endothermic peak at $T \sim 145$ °C followed by a prominent, broad and asymmetric endothermic peak (555 °C). The large endothermic peak is attributed to the chemical-disordering process induced by heating at a constant rate in the DSC (Figure 62). The small endothermic peak is consistent with a phase change in FeS, a common meteoritic mineral, which is reported to undergo a solid/solid $\alpha$-$\beta$ phase transformation at 138 °C with an enthalpy of 2.4 kJ/mol (54.6 J/g) [96]. Based on the measured enthalpy compared to the enthalpy of transformation of FeS reported in the literature, the fraction of FeS in the NWA 6259 meteorite is estimated as 6 ± 2 percent by mass, where the largest source of error is sample-to-sample variability. The fraction of tetrataenite in the sample was estimated as the sample mass minus the calculated FeS mass for each sample. The large endothermic peak at 555 °C is consistent with a first-order chemical-disordering process from the $L_{10}$ structure to the $A_1$ structure [21]. The $L_{10} \rightarrow A_1$ chemical-disordering process is endothermic because energy is required to transform the structure from the lower-energy chemically ordered state to the higher-energy disordered state.
The chemical-disordering transformation observed in DSC occurs at the same
temperature as the Curie transition measured during VSM study (or magnetometry). The measured simultaneous thermal and magnetic transformations occurring at 557 °C are interpreted as a first-order magnetostructural transformation wherein the L1₀ phase is retained far above the literature chemical order-disorder transition temperature of 320 °C. Retention of the L1₀ phase above the reported order-disorder temperature indicates that the chemical-disordering transformation is kinetically limited (see Section 5.2 for further details on the chemical-disordering kinetics). When tetrataenite does chemically disorder at 557 °C, it is already above the magnetic Curie temperature of A1 (disordered) FeNi; therefore tetrataenite undergoes a magnetic transition from the ferromagnetic state to the paramagnetic state as the A1 phase is formed. In other words, the observed Curie temperature is dependent upon the kinetic chemical disordering transformation temperature. The intrinsic Curie temperature, where the energy of spontaneous magnetization is equal to the thermal energy, may be much higher than the observed kinetic-dependent \( T_C \) for L1₀ FeNi. If the L1₀ structure could be retained at higher temperature, it is estimated that the intrinsic \( T_C \) is 727 ± 200 °C based on models of the magnetic exchange interactions [12].

It must be noted that no sign of the “Magnetic Phase 2” was noted in DSC results. The meteoritic sample was heated to 900 °C in DSC but only to 700 °C in VSM, due to the temperature limitations of the respective instruments. The results suggest that heating to 700 °C, as in the VSM, was only sufficient to partially transform to the A1 phase whereas heating to 900 °C, as in the DSC, allowed for a complete transformation to the
A1 phase. However, no enthalpic changes were detected in DSC results between 700 and 900 °C. This discrepancy between VSM and DSC results warrants further investigation.

5.1.3 **Significance of work on the Correlations of Structure and Magnetism of L1\textsubscript{0} FeNi**

In this section, the microstructure, crystal structure, magnetic domain structure, and bulk magnetic behavior of tetrataenite extracted from the NWA6259 meteorite were characterized and thermal signatures from the chemical disordering transformation were measured. Tetrataenite from the NWA6259 meteorite was confirmed to have the L1\textsubscript{0} structure as shown by the presence of (001), (110), and (003) superlattice peaks in single-crystal X-ray results and the L1\textsubscript{0} crystallites exist in three mutually perpendicular crystallographic variants. It was discovered that L1\textsubscript{0} FeNi undergoes a magnetostructural phase transition in which magnetic disordering and chemical disordering occur simultaneously at 557 °C. Additionally, there is magnetic evidence that an intermediate phase may form during the chemical-disordering transformation.

The results presented in Section 4.2.1 have contributed to two publications [12, 75] and mark the first time that the magnetocrystalline anisotropy constant ($K_u = 1.1 \times 10^7$ erg/cc.) has been evaluated for the L1\textsubscript{0} form of FeNi since the 1960s [11]. Based on these results, the theoretical maximum energy product ($BH_{max}$), which describes the usable magnetic energy stored in a magnet, of L1\textsubscript{0} FeNi has been estimated as 42 MGOe [75]. In comparison with the magnetic properties of other permanent magnets (Table 13) it is clear that L1\textsubscript{0} FeNi has a competitive ($BH_{max}$) with current industrially relevant magnets and could potentially replace the weaker ferrite and Alnico magnets as well as the
stronger but much more expensive Pt-based and rare-earth magnets. From an applications perspective, it is noteworthy that the L1₀ phase is retained in the 30-250 °C temperature regime where permanent magnets in many motors need to operate. Furthermore, tetrataenite’s $M_S$ decreases slowly with increasing temperature and has a higher maximum energy product $(BH)_{max}$ at 200 °C than today’s Dy-content NdFeB permanent magnets [12].

Table 13: Magnetic properties of permanent magnet materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Structure</th>
<th>$M_S$ (emu/cc)</th>
<th>$K_1 \times 10^7$ (erg/cc)</th>
<th>Theoretical $(BH)_{max}$</th>
<th>$T_C$ (°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alnico</td>
<td>composite</td>
<td>1120</td>
<td>0.68 (shape)</td>
<td>10</td>
<td>[105]</td>
<td></td>
</tr>
<tr>
<td>FeNi</td>
<td>L1₀</td>
<td>1220 ± 20</td>
<td>1.1</td>
<td>42</td>
<td>557</td>
<td>This work</td>
</tr>
<tr>
<td>FeNi</td>
<td>A1</td>
<td>1280 ± 10</td>
<td>0.0036</td>
<td>~ 0</td>
<td>387</td>
<td>This work</td>
</tr>
<tr>
<td>FePd</td>
<td>L1₀</td>
<td>1080±20</td>
<td>1.9±0.3</td>
<td>48 [3]</td>
<td>455</td>
<td>This work</td>
</tr>
<tr>
<td>FePt</td>
<td>L1₀</td>
<td>1140</td>
<td>6.6</td>
<td>51</td>
<td>477</td>
<td>[3]</td>
</tr>
<tr>
<td>Nd₂Fe₁₄B</td>
<td>$D_{4h}^{14}$</td>
<td>1270</td>
<td>4.6</td>
<td>64</td>
<td>312</td>
<td>[3]</td>
</tr>
</tbody>
</table>

5.2 Thermal Stability and Kinetic Mechanism of Order-Disorder of L1₀ FeNi

In this section, the aim of the Dissertation work is to quantify and understand the chemical-disordering thermodynamics and kinetics in nominally equiatomic FeNi to inform L1₀ FeNi synthesis efforts. Results in this section build the L1₀→A1 magnetostructural phase transformation (Section 5.1) with the goal to elucidate the kinetic transition mechanism(s) and thermodynamic driving force. Quantitative determinations of the enthalpy of transformation and the activation energy barrier are presented along with evidence that the process of chemical disordering in the L1₀-type FeNi phase proceeds by a one-dimensional growth process. It is deduced that this growth process is limited by a low concentration of available atomic vacancies at the interface of
the ordered and disordered phases to facilitate the atomic arrangement needed for transformation to the A1 phase. Based on the results presented in this section, it is expected that vacancy formation is critical for L1₀ formation in synthesis efforts.

5.2.1 Results on the Thermal Stability and Kinetic Mechanism of Order-Disorder of L1₀ FeNi

The prominent asymmetric peaks in the DSC traces are characterized by resultant heat-flow rates that increase gradually with increasing temperature. The peak onsets are located at approximately $T = 427 \, ^\circ\text{C}$, with peak maximums found at temperatures ranging from $T = 525 \, ^\circ\text{C}$ (obtained at a heating rate of 1 K/min) to $T = 584 \, ^\circ\text{C}$ (obtained at a heating rate of 25 K/min). All observed peaks are followed by sharp drop-offs. The peak temperature obtained as a function of the heating rate is provided in Table 14. The apparent magnitude of the DSC signal increases with increased heating rate, as anticipated. No enthalpic changes in this temperature range were detected when samples were subjected to a second heating in the DSC apparatus (not shown). This result is consistent with the occurrence of a kinetically irreversible phase transformation process. The enthalpy measured at each heating rate is summarized in Table 14 with average determined enthalpy of transformation $\Delta H_{L1_0 \rightarrow A1} = 4.0 \pm 0.2 \, \text{kJ/g-atom}$. 
Figure 62: DSC results obtained from meteorite NWA6259 measured at constant heating rates of 1, 5, 10, 20, and 25 K/min. All traces exhibit an asymmetric endothermic peak corresponding to a first-order endothermic chemical-disordering process.

Table 14: Summary of DSC measurement results on the chemical-disordering process of tetrataenite in the NWA6259 meteorite.

<table>
<thead>
<tr>
<th>Heating Rate (K/min)</th>
<th>Sample mass (mg)</th>
<th>Tetrataenite mass (mg)</th>
<th>T_{peak} (°C)</th>
<th>Enthalpy (kJ/g-atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>65.5 ± 0.2</td>
<td>61.1 ± 0.2</td>
<td>525 ± 3</td>
<td>4.0 ± 0.2</td>
</tr>
<tr>
<td>5</td>
<td>69.8 ± 0.2</td>
<td>64.5 ± 0.2</td>
<td>553 ± 3</td>
<td>4.2 ± 0.2</td>
</tr>
<tr>
<td>10</td>
<td>54.4 ± 0.2</td>
<td>52.5 ± 0.2</td>
<td>566 ± 3</td>
<td>4.1 ± 0.2</td>
</tr>
<tr>
<td>20</td>
<td>52.9 ± 0.2</td>
<td>52.9 ± 0.2</td>
<td>578 ± 3</td>
<td>3.9 ± 0.2</td>
</tr>
<tr>
<td>25</td>
<td>84.7 ± 0.2</td>
<td>82.3 ± 0.2</td>
<td>584 ± 3</td>
<td>4.0 ± 0.2</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>84.7 ± 0.2</strong></td>
<td><strong>82.3 ± 0.2</strong></td>
<td><strong>584 ± 3</strong></td>
<td><strong>4.0 ± 0.2</strong></td>
</tr>
</tbody>
</table>
5.2.2 Discussion on the Thermal Stability and Kinetic Mechanism of Order-Disorder of L1₀ FeNi

Analysis of the DSC results obtained from tetrataenite (43 ± 1 at% Ni) in the NWA6259 meteorite provides quantitative values of the enthalpy of formation of the L1₀ phase $\Delta H_{form}^{L1₀}$ as discussed in Section 5.2.2.1.1 and the activation energy of chemical disordering $Q_t$ as discussed in Section 5.2.2.1.2. These results also confirm that the chemical disordering of tetrataenite is a thermally activated process. It is also shown that chemical disordering is a kinetically limited process that proceeds via one-dimensional growth.

5.2.2.1.1 Examination of the Thermal Stability of L1₀-Structured FeNi

The experimentally determined enthalpy of formation of L1₀-type FeNi (43 ± 1 at% Ni) is $\Delta H_{form}^{L1₀} = -7.6 \pm 0.6 \text{ kJ/g·atom}$. This is calculated by taking the sum of the experimental enthalpy of transformation measured in this work ($\Delta H_{L1₀→A1} = 4.0 \pm 0.2 \text{ kJ/g·atom}$) and the enthalpy of formation of the disordered A1 phase (43 at% Ni) reported by Swartzendruber ($\Delta H_{form}^{A1} = -3.6 \pm 0.6 \text{ kJ/g·atom}$) using Eq. (2.12) [104]. The known equilibrium phases in the Fe-Ni system are the A2 (bcc) phase, which has its lowest enthalpy of formation at 0 at% Ni ($\Delta H_{form}^{A2} = 0 \text{ kJ/g·atom}$), and the L1₂ phase, which has its lowest enthalpy of formation at ~70 at% Ni ($\Delta H_{form}^{L1₂} = -7.3 \pm 1.5 \text{ kJ/g·atom}$) [62, 106]. The value of $\Delta H_{form}^{L1₀}$ (FeNi) reported in this Dissertation would fall below a convex hull line drawn between the enthalpies of formation of the A2 and L1₂ phases suggesting that L1₀ FeNi is enthalpically stable. The enthalpy of formation of the FeNi
L$_{10}$ phase $\Delta H_{\text{form}}^{L_{10}}$ reported here is larger and more negative than the values provided by previous computational efforts of Cacciamani et al. [62]. This discrepancy might be due to an underestimation of the magnetic contribution to the thermodynamic stability of the phase. Cacciamani et al. reported the Curie temperature $T_C$ of L$_{10}$ FeNi as 427 °C; this is equivalent to that of the A1 FeNi phase, but much smaller than the experimental and computational Curie temperature of L$_{10}$ FeNi of $T_C = 727 \pm 200$ °C [12]. Even with this proposed underestimation of the magnetic contribution, Cacciamani et al. predicted that L$_{10}$ FeNi is the stable phase at absolute zero temperature. The results reported here suggest that L$_{10}$ FeNi is enthalpically stable; however, it is not yet known whether the entropy associated with formation of the L$_{10}$ FeNi phase stabilizes or destabilizes this phase. In some systems, such as the L$_{12}$-structured Fe$_3$Pt, the ordered phase is not enthalpically stable but the entropy is known to stabilize the chemically ordered structure [107]. Further work to determine the entropy contribution to the free energy of L$_{10}$ FeNi is needed to determine its thermodynamic stability.

For comparison, Table 15 provides the enthalpies of formation for a selection of L$_{10}$-type phases; all values were either taken directly from the literature (FePt, CoPt) [107, 108], or were calculated utilizing Eq. (2.12) (FePd, AuCu) [40, 96, 109, 110] and were assumed to be temperature-independent. While the $\Delta H_{\text{form}}^{L_{10}}$ value for tetrataenite is the smallest of all of the listed values, it is close to that of AuCu at $\Delta H_{\text{form}}^{L_{10}} = -8.7$ kJ/g-atom. Further, the FeNi and AuCu phases have similar chemical order-disorder transition temperatures ($T_{OD}(\text{FeNi}) = 320$ °C, $T_{OD}(\text{AuCu}) = 385$ °C). These two similarities result in driving forces for the formation these two L$_{10}$-structured phases that
are similar at 300 °C (0.25 kJ/g·atom for FeNi, 0.4 kJ/g·atom for AuCu). However, L₁₀ AuCu crystallizes in observable laboratory time-scales despite possessing a driving force for phase formation that is much smaller than that of FePt. On the other hand, L₁₀ FeNi does not form readily at all. These observations concerning the thermodynamic driving forces for L₁₀ phase formation in the FeNi system warrant an analysis of the kinetic barriers to the formation of this phase.

Table 15: Comparison of thermodynamic parameters of material systems with L₁₀↔A₁ transformations: thermodynamic chemical order-disorder temperature \(T_{OD}\); enthalpy of transformation \(\Delta H_{L₁₀→A₁}\); driving force \(\Delta G\) at 300 °C; and enthalpy of formation of L₁₀ phase \(\Delta H_{form}^{L₁₀}\) determined experimentally and from calculations in the literature using the generalized gradient approximation (GGA)[111].

<table>
<thead>
<tr>
<th></th>
<th>FeNi</th>
<th>AuCu</th>
<th>FePd</th>
<th>CoPt</th>
<th>FePt</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(43 ± 1 at% Ni)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(T_{OD}) (°C)</td>
<td>320</td>
<td>385</td>
<td>605</td>
<td>825</td>
<td>1300</td>
</tr>
<tr>
<td>(\Delta H_{L₁₀→A₁}) (kJ/g·atom)</td>
<td>4.0 ± 0.2</td>
<td>1.8 ± 0.2</td>
<td>2.4 ± 0.2</td>
<td>3.1 ± 0.2</td>
<td>10.2 ± 2.1</td>
</tr>
<tr>
<td>(\Delta G) at 300 °C (kJ/g·atom)</td>
<td>0.25</td>
<td>0.40</td>
<td>1.00</td>
<td>1.97</td>
<td>7.85</td>
</tr>
<tr>
<td>Experimental (\Delta H_{form}^{L₁₀}) (kJ/g·atom)</td>
<td>-7.6 ± 0.6</td>
<td>-8.7</td>
<td>-11.8</td>
<td>-9.8</td>
<td>-27.2</td>
</tr>
<tr>
<td>GGA-calculated [111] (\Delta H_{form}^{L₁₀}) (kJ/g·atom)</td>
<td>-5.8</td>
<td>-4.6</td>
<td>-6.2</td>
<td>-10.9</td>
<td>-25.7</td>
</tr>
<tr>
<td>Ref.</td>
<td>This work, [96, 104]</td>
<td>[109, 110, 112]</td>
<td>This work, [40, 96, 113]</td>
<td>[108, 114, 115]</td>
<td>[107, 114, 116, 117]</td>
</tr>
</tbody>
</table>

5.2.2.1.2 Examination of the Kinetic Barriers and Mechanisms of Transformation in Tetrataenite

The measured endothermic peak temperatures occur approximately 200 degrees above the established chemical order-disorder temperature (320 °C) of L₁₀-type FeNi
[11], which confirms that the chemical-disordering transformation is highly kinetically limited. The onset and peak temperatures of the endothermic signals move to higher temperatures with increasing heating rate, which is consistent with a thermally activated nucleation and growth process[15]. The activation energy characterizing the chemical-disordering process in NWA6259 tetrataenite is calculated from the Kissinger Method (Section 2.1.2.2) in which \( \ln \left( \frac{\beta}{T_{\text{peak}}^2} \right) \) is plotted versus \( \frac{1}{k_B T_{\text{peak}}} \), and \( T_{\text{peak}} \) is the peak temperature in DSC results; such a plot results in a slope that may be linearly fit to find the negative activation energy of transformation, \( Q_t \). The activation energy of chemically disordering tetrataenite is \( 3.08 \pm 0.07 \) eV (Figure 63).

![Kissinger plot of DSC results measured at heating rates of 1, 5, 10, 20 and 25 K/min. The clear linear trend has the slope with a linear fit equal to the negative activation energy \( Q_t = 3.08 \pm 0.07 \) eV.](image)

**Figure 63:** Kissinger plot of DSC results measured at heating rates of 1, 5, 10, 20 and 25 K/min. The clear linear trend has the slope with a linear fit equal to the negative activation energy \( Q_t = 3.08 \pm 0.07 \) eV.

The activation energy to chemically disorder tetrataenite \( (Q_t = 3.08 \pm 0.07 \) eV/atom) determined in this work is comparable to the activation energy for lattice diffusion \( (Q_d) \) in the fcc Fe\(_{50}\)Ni\(_{50}\) system, which is reported to be 3.08-3.39 eV/atom [16]. In addition, \( Q_t \) is far larger than the activation energy for grain boundary diffusion \( (Q_{GB}) \)
for the same composition, which is reported to be 1.06 eV/atom (see Table 16) [2, 16, 118]. The agreement between the measured activation energy for L1₀ chemical disordering and for lattice diffusion in fcc FeNi, implies that the rate of chemical disordering in tetrataenite is dependent upon the rate of vacancy creation and migration. This is occurring despite the fact that the transformation is expected to be polymorphic, which implies that the transformation should only require atomic migration across the interface with an activation energy close to the grain boundary diffusion activation energy. Lattice diffusion requires both the formation and the migration of vacancies, which permits the lattice diffusion activation energy $Q_L$ to be approximated as the sum of the activation energies of both processes. On the other hand, vacancies are easily created and annihilated at grain boundaries. Thus, the activation energy for grain boundary diffusion $Q_{GB}$ is dependent only on the energy barrier to vacancy migration [16]. A vacancy-controlled mechanism to facilitate the order-disorder transformation in the FeNi system has been proposed by previous authors [77, 118, 119]. Penisson and Bourret [119] found good agreement between their data and a model of the rate of long-range chemical ordering that is proportional to the vacancy concentration produced by electron irradiation of FeNi. The conclusion that the L1₀↔A1 transformation rate in the FeNi system is controlled by the requirement to create and move vacancies to the L1₀/A1 phase boundary is consistent with the results reported here. Additionally, this deduction highlights the conclusion that highly defective microstructures, such as those with very fine-grained matrices containing many grain boundaries, will facilitate L1₀ phase formation in the FeNi system [16].
The very slow formation of the L1₀ phase in FeNi compared to its formation in other material systems is attributed to the combination of a low driving force and slow diffusivity below $T_{OD}$ (see Table 16). For context, the grain boundary diffusivities of fcc FePt and fcc FeNi at $T = 300$ °C are very similar; thus, the relative sluggishness of the A1↔L1₀ transformation in FeNi is explained by slow lattice diffusion due to a lack of vacancies in the FeNi matrix, and the low driving force to form L1₀ FeNi compared to L1₀ FePt. The driving force to form L1₀ FeNi is comparable to that of L1₀ AuCu, as previously mentioned; however, the lattice diffusivity of fcc FeNi is many orders of magnitude smaller than that of fcc AuCu, which explains the much slower chemical order-disorder transformation observed in FeNi.

**Table 16: Comparison of kinetic parameters of material systems with L1₀→A1 transformations: thermodynamic chemical order-disorder temperature $T_{OD}$; activation energy $Q_t$ of the chemical order-disorder L1₀/A1 transformation; activation energies of lattice diffusion $Q_L$ and of grain boundary diffusion $Q_{GB}$ in the disordered phase; lattice and grain boundary diffusivities $D$ at 300 °C in the disordered phase.**

<table>
<thead>
<tr>
<th></th>
<th>FeNi (43 ± 1 at% Ni)</th>
<th>AuCu</th>
<th>FePd</th>
<th>CoPt</th>
<th>FePt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{OD}$ (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L1₀→A1 $Q_t$ (eV/atom)</td>
<td>L1₀→A1 3.08 ± 0.07</td>
<td>A1→L1₀ 1.2 ± 0.1</td>
<td>A1→L1₀ 2.8 ± 0.2</td>
<td>A1→L1₀ 1.7 ± 0.1</td>
<td></td>
</tr>
<tr>
<td>$Q_L$ (eV/atom)</td>
<td>3.08-3.39</td>
<td>1.0-1.2</td>
<td>2.41-2.72</td>
<td>2.84 ± 0.02</td>
<td>1.32 ± .03</td>
</tr>
<tr>
<td>$Q_{GB}$ (eV/atom)</td>
<td>1.06 ± 0.07</td>
<td>0.5-0.6</td>
<td></td>
<td></td>
<td>0.80 ± .04</td>
</tr>
<tr>
<td>$D_L$ at 300 °C (cm²/s)</td>
<td>~1E-27</td>
<td>~1E-14</td>
<td>~1E-22 to ~1E-24</td>
<td>6.7E-26</td>
<td>8E-23</td>
</tr>
<tr>
<td>$D_{GB}$ at 300 °C (cm²/s)</td>
<td>2.1E-19</td>
<td>~1E-12</td>
<td></td>
<td></td>
<td>~1E-18 to ~1E-19</td>
</tr>
<tr>
<td>Ref.</td>
<td>This work, [2, 16]</td>
<td>[112, 120]</td>
<td>This work, [40, 113, 121]</td>
<td>[114, 115]</td>
<td>[107, 114, 116, 117]</td>
</tr>
</tbody>
</table>
The kinetic mechanism of the chemical disordering of L1₀ FeNi is characterized by one-dimensional (1D) growth of the A1 phase evidenced by the asymmetric shape of the peak in the DSC results [122]. This peak shape is similar to DSC results observed for multilayers where the asymmetry is attributed to a 1D growth process [18, 20]. It is reported that the reaction of multilayers of Ni and Al exhibit an asymmetric DSC exotherm upon formation of NiAl₃ [122]. This peak character is attributed to a growth mechanism where grains of the chemically ordered NiAl₃ phase nucleate on layer interfaces, coalesce, and then progress as a 1D front until the disordered phase is consumed [122]. Likewise, the disordering of tetrataenite occurs by nucleation and impingement of A1 nuclei along interfaces in the meteorite followed by 1D growth. This mechanism of coalescence at the grain boundaries followed by 1D growth is more likely for large grains [123]. Previous work [75] has characterized the microstructure of the NWA6259 meteorite as consisting of large orthogonal c-axis variants ranging in size from ~10 μm to 100 μm, and it is likely that variant interfaces serve as preferential nucleation sites of the A1 disordered phase. Given the large size of the c-axis variants (microns rather than nanometers) in the NWA6259 meteorite, it is reasonable that A1 nuclei first grow and impinge along the variant interfaces then proceed to consume the ordered phase. Based on the mechanism of 1D phase growth beginning at interfaces, it is concluded that enhancement of interfaces, boundaries and free surfaces may increase the rate of phase transformation in FeNi.
Figure 64: DSC data fit using the Michaelsen-Dahms model [19]: (a) model fit to 5 K/min data ($n = 1.27 \pm .01$, $v_{\text{Kiss}} = 2.99 \pm .01 \times 10^{16}$ s$^{-1}$), and (b) results for $n$ and $v$ as a function of heating rate.

Further information on the kinetic mechanism of chemical disordering is gained by determining the Avrami exponent representing the transformation order (see Section 2.1.2.2). An Avrami exponent of $n \approx 1$ was determined from fits of the Michaelsen-Dahms equation (see Section 2.1.2.2 [19]) to the DSC data curves, which are all similar to the example shown in Figure 64(a) for the 5 K/min heating rate. The Michaelsen-Dahms model fit the peak and high-temperature side of the peak well, but failed to
correctly model the gradual increase of the DSC trace before the peak. The values of $n$ and $\theta_{Kiss}$ were constant across the lower heating rates as shown in Figure 64(b). The slight change in values for the highest heating rates is most likely due to the thermal lag of the calorimeter. The Avrami exponent suggests that the growth mechanism is interface controlled. Typically, interface-controlled growth only requires vacancy migration because vacancies are easily created at interfaces. However, in this system it is seen that growth has an activation energy similar to lattice diffusion, suggesting that vacancy formation is difficult even at interfaces. The variant interfaces in the meteorite are coherent, which may make vacancy creation at variant interfaces more difficult.

5.2.3 Significance of Work on the Thermal Stability and Kinetic Mechanism of Order-Disorder of L1$_0$ FeNi

The conclusions on the thermal stability and kinetic mechanism of formation of L1$_0$ FeNi based on results presented in this section are summarized as follow. The chemical order-disorder enthalpy of transformation is $\Delta H_{L1_0 \rightarrow A1}$ (43 ± 1 at% Ni) = 4.0 ± 0.2 kJ/g·atom. The enthalpy of formation of the L1$_0$ phase (43 ± 1 at% Ni) is experimentally determined to be -7.6 ± 0.6 kJ/g·atom, which is larger and more negative than previous estimates. Chemical disordering is a thermally activated and kinetically limited process. The activation energy of chemical disordering is 3.08 ± 0.07 eV/atom and the results are consistent with a vacancy-controlled mechanism of transformation.

This work sheds light on the kinetic barriers to L1$_0$ FeNi formation and highlights the importance of generating vacancies in the FeNi lattice to enable atomic rearrangement. It is recommended that future synthesis efforts focus on vacancy formation to enable atomic
rearrangement. Increasing L\textsubscript{1\textsubscript{0}} phase stability in order to enhance the driving force for transformation, which may be possible through nanostructuring and the addition of ternary dopants, is also suggested.
6 Conclusions

The overarching goal of this Ph.D. Dissertation is to understand the relationship between structure and magnetism in L1₀-structured ferrous materials and to determine the mechanisms governing the L1₀→A1 chemical order-disorder transformation. Two material systems, FePd and FeNi, that exhibit the L1₀→A1 chemical order-disorder transformation were studied in this work. Correlations between microstructure, crystal structure, magnetic domain structure, and bulk magnetic properties were investigated to enhance fundamental scientific knowledge of these materials. The thermal stabilities of the L1₀ structure in both FePd and FeNi were established to understand the driving forces for chemical ordering and disordering. The kinetic mechanisms of chemical disordering and ordering were investigated using calorimetry and studying structural and magnetic property changes as functions of heating and cooling rates in the FePd system. In tetrataenite, the kinetic mechanism of chemically disordering was elucidated by calorimetric measurements with varying heating rates. Specific conclusions from experimental results on FePd (6.1) and FeNi (6.2) are summarized in this section.

6.1 Conclusions Regarding the FePd System

Conclusions from experimental work conducted on the FePd material system are presented in two parts. First, knowledge gained from comparison of the A1- and L1₀-structured samples (4.1) is summarized. Secondly, conclusions are presented on the mechanisms of chemical ordering in FePd that are revealed by examining the effect(s) of the cooling rate on the structure and heat evolved when samples are slowly cooled at different rates through the reported chemical order-disorder temperature (4.2).
In Section 4.1, the magnetic behaviors of A1- and L1₀-structured FePd were investigated and the enthalpy difference between the two phases was measured to expand the basic scientific understanding of the properties of L1₀ FePd. The magnetic domain structure imaged in L1₀-structured FePd is correlated with that of a material with high magnetocrystalline anisotropy and a twinned microstructure. The magnetic behavior of L1₀-structured FePd in the vicinity of the Curie temperature, \( T_C \), is consistent with that described by tricritical mean-field theory, indicating that the magnetic phase transformation is in a thermodynamic state that lies in-between first- and second-order character. The existence of a thermodynamic tricritical point, as indicated by the results presented in this Dissertation, may underlie the inconsistencies in \( T_C \) reported in the literature as the nature of the Curie transition can change when the material exhibits small variations in composition or other attributes due to different processing techniques used by different authors. The enthalpy of transformation from the L1₀ phase to the A1 phase in FePd was experimentally determined to be \( 2.4 \pm 0.2 \) kJ/g·atom and the enthalpy of formation for L1₀ FePd is \( \Delta H_{\text{form}}^{L1_0} = -11.8 \) kJ/g·atom. The L1₀→A1 chemical-disordering transformation is not kinetically limited in FePd under the conditions tested.

The experimental evidence presented in Section 4.2 indicates that a tetragonal chemically-disordered phase is formed in FePd during the process of chemical ordering upon cooled through the order-disorder temperature. Lattice twinning was evident in such samples and was most prominent in the most quickly cooled sample, which indicates high levels of strain in that sample. Two possible mechanisms are proposed for the way in which chemical ordering proceeds. The first possible mechanism proceeds through nucleation of the L1₀ phase in the A1 matrix, which causes strain due to lattice mismatch.
In this scenario, the A1 phase becomes tetragonally-distorted as a result of this strain. The second proposed mechanism for chemical ordering in the FePd system identifies the disordered tetragonal structure as a metastable A6 phase which is a member of the Fe-Pd phase diagram. In this scenario, the A1 phase first becomes tetragonally distorted to form the A6 phase, and then chemically orders to form L1₀ in a two-step process. Both potential mechanisms are consistent with the observed structural and calorimetric results. These structural changes indicated that the chemical-ordering transformation in FePd occurs through a combination of first-order processes. Enthalpy changes occurring during chemical ordering are due to the combination of changes in chemical order, crystal structure, and microstructure.

6.2 Conclusions Regarding the FeNi System

Tetrataenite extracted from meteoritic samples was examined to establish the structural and magnetic character of the L1₀-structured FeNi (Section 5.1), and to study the thermodynamic and kinetic barriers to the chemical order-disorder transformation (Section 5.2).

Results obtained in Section 5.1 demonstrate that tetrataenite extracted from the NWA6259 meteorite consists of the L1₀-structured FeNi phase that is characterized by hard ferromagnetic behavior and exhibits a simultaneous chemical- and magnetic-disordering (magnetostructural) transformation at T~560 °C. Tetrataenite extracted from the NWA6259 meteorite is confirmed to have the L1₀ structure as shown by the presence of (001), (110), and (003) superlattice peaks in single-crystal X-ray diffraction results; the L1₀ crystallites exist in three mutually perpendicular crystallographic variants. The average chemical long-range order parameter \( LRO \) is confirmed to be equal to one. The
relative abundances of the three L1\textsubscript{0} variants are estimated to be 51%, 30%, and 19%.

The magnetocrystalline anisotropy of tetrataenite was found to be $K_u = 1.1 \times 10^7$ erg/cc in confirmation of the $K_1$ value reported for L1\textsubscript{0} FeNi formed by neutron irradiation in the 1960s [71]. L1\textsubscript{0} FeNi undergoes an endothermic transformation that is consistent with a chemical-disordering process at the same temperature at which it is observed to undergo a Curie transition. Characterization of this simultaneous chemical- and magnetic-disordering transformation indicates that the $T_C$ of L1\textsubscript{0}-structured FeNi is far higher than that of A1-structured FeNi and further the observed L1\textsubscript{0} $T_C$ is dependent upon the kinetic chemical order-disorder temperature.

In Section 5.2, the thermodynamic and kinetic parameters associated with the chemical disordering of tetrataenite were experimentally determined by examining the heat evolved with varying heating rates. The chemical order-disorder enthalpy of transformation is $\Delta H_{L1_0 \rightarrow A1} = 4.0 \pm 0.2$ kJ/g·atom and the enthalpy of formation of the L1\textsubscript{0} phase (43 ± 1 at% Ni) is experimentally determined as -7.6 ± 0.6 kJ/g·atom, which is larger and more negative than previous estimates indicating that the L1\textsubscript{0} phase is enthalpically stable in FeNi of composition 43 ± 1 at% Ni. The chemical disordering transformation is a kinetically-limited and thermally activated process. The activation energy of chemical disordering is 3.08 ± 0.07 eV/atom and the results are consistent with a vacancy-controlled mechanism of transformation that proceeds with one-dimensional growth. Results presented in Section 5.2 shed light on the kinetic barriers to L1\textsubscript{0} FeNi formation and highlight the importance of generating vacancies in the FeNi lattice to enable atomic rearrangement.


7 Recommendations for Future Work

Results of this Dissertation provide fundamental knowledge on the correlations of structural and magnetic properties of \( \text{L}_1_0 \)-structured FePd and FeNi. Further, insight is gained into the mechanisms of chemical order-disorder transformations in ferrous binary alloys and fundamental thermodynamic and kinetic factors influencing the transformation. Specific routes are recommended to enhance formation of the \( \text{L}_1_0 \) structure in FeNi during synthesis efforts. However, there are still many open questions to be addressed, specifically:

1) Under what conditions is the Curie transition thermodynamically first-order or second-order in FePd?

2) Does the entropy contribution to the free energy stabilize or de-stabilize the \( \text{L}_1_0 \) structure in FeNi?

3) Are there intermediate structural or magnetic phases occurring during the \( \text{A}_1 \rightarrow \text{L}_1_0 \) and \( \text{L}_1_0 \rightarrow \text{A}_1 \) transformations and what role might these phases play in transformation rate?

Recommendations and guidance for future research directions to address the above questions is provided here. It is anticipated that results obtained from experiments recommended in this Section will provide insight into the \( \text{A}_1 \leftrightarrow \text{L}_1_0 \) chemical order-disorder transformation in ferrous intermetallics.
Recommendation I: Pursue synthesis of L1\textsubscript{0} FeNi by manipulating the thermodynamic and kinetic parameters that influence the chemical ordering transformation

Future work on L1\textsubscript{0} FeNi is expected to focus on synthesis; towards that objective, recommendations are made based on the results of this Dissertation work. Results in this Dissertation showed that the rate of the chemical order-disorder transformation of L1\textsubscript{0} FeNi is limited by two kinetic factors: a low driving force for chemical ordering (\(\Delta G\)) and a high activation energy for transformation (\(Q_t\)) (see Section 5.2 for details). These limitations are briefly explained below by comparing \(\Delta G\) and \(Q_t\) for the FeNi system to that of other related systems which readily form the L1\textsubscript{0} structure. Particular attention is given to the intermetallic compounds – FePt and AuCu (see specific values in Table 17, and Section 5.2 for more details).

(a) Limitations due to low driving force: The driving force for chemical ordering transformation \(\Delta G\) is approximated as a function of the enthalpy of transformation \(\Delta H_{L1_0 \leftrightarrow A1}\), the thermodynamic chemical order-disorder temperature \(T_{OD}\), and the undercooling \((T_{OD} - T)\) given by[14]:

\[
\Delta G \approx \frac{\Delta H_{L1_0 \leftrightarrow A1} \cdot |T_{OD} - T|}{T_{OD}} \quad (7.1)
\]

The enthalpy of transformation between the L1\textsubscript{0} and A1 FeNi phases with 43 ± 1 at.% Ni was determined in this work to be \(\Delta H_{L1_0 \leftrightarrow A1} = 4.0 \pm 0.2\) kJ/g-atom. The order-disorder temperature is known to be 320 °C [11]. Therefore, at a reasonable annealing temperature such as 300 °C, the driving force for forming
L1₀-structured FeNi from the A1 phase is $\Delta G = 0.25 \text{ kJ/ g·atom}$. The driving force to form the L1₀ structure in FeNi is comparable to that of AuCu, but an order of magnitude smaller than that of FePt (see Table 17).

(b) *Limitations due to high activation energy:* The activation energy for chemically disordering L1₀ FeNi was determined in this Dissertation work to be $Q_t = 3.08 \pm 0.07 \text{ eV/atom}$, which is equal to the activation energy of lattice diffusion $Q_L$ in FeNi [16]. Lattice diffusion requires both vacancy creation and vacancy migration and the equivalency between $Q_t$ and $Q_L$ indicates that chemical disordering is limited by the need to create and move vacancies. Both the disordering and ordering processes require rearrangement of the atoms, which is facilitated by the presence of vacancies, therefore it is informative to compare activation energies for lattice diffusion across material systems. The activation energy for lattice diffusion in FeNi is much larger than that of both AuCu and that of FePt (see Table 17).

To summarize the findings: the L1₀ structure forms readily in AuCu despite having a low driving force because it has fast lattice diffusion; the L1₀ structure forms readily in FePt because it has a large driving force and fast lattice diffusion; the L1₀ structure does not form readily in FeNi because it has a small driving force and slow diffusion.
Table 17: Comparison of thermodynamic and kinetic parameters of a selection of material systems with L1₀↔A1 transformations: thermodynamic chemical order-disorder temperature $T_{OD}$; driving force $\Delta G$ at 300 °C; activation energy $Q_t$ of the chemical order-disorder L1₀/A1 transformation; activation energies of lattice diffusion $Q_L$ and of grain boundary diffusion $Q_{GB}$ in the disordered phase.

<table>
<thead>
<tr>
<th></th>
<th>FeNi (43 ± 1 at% Ni)</th>
<th>AuCu</th>
<th>FePt</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{OD}$ (°C)</td>
<td>320</td>
<td>385</td>
<td>1300</td>
</tr>
<tr>
<td>$\Delta G$ at 300 °C (kJ/ g·atom)</td>
<td>0.25</td>
<td>0.40</td>
<td>7.85</td>
</tr>
<tr>
<td>L₁₀/A₁ $Q_t$ (eV/atom)</td>
<td>L₁₀→A₁ 3.08 ± 0.07</td>
<td>A₁→L₁₀ 1.2 ± 0.1</td>
<td>A₁→L₁₀ 1.7 ± 0.1</td>
</tr>
<tr>
<td>$Q_L$ (eV/atom)</td>
<td>1.06 ± 0.07</td>
<td>0.5-0.6</td>
<td>0.80 ± .04</td>
</tr>
<tr>
<td>$Q_{GB}$ (eV/atom)</td>
<td>3.08-3.39</td>
<td>1.0-1.2</td>
<td>1.32 ± .03</td>
</tr>
<tr>
<td>Ref.</td>
<td>This work, [2, 16, 96]</td>
<td>[109, 110, 112, 120]</td>
<td>[107, 114, 116, 117]</td>
</tr>
</tbody>
</table>

It is recommended that future synthesis efforts focus on enhancing both the driving force for the chemical ordering transformation and the diffusivity in the FeNi system. The following routes are suggested.

a) **Enhance driving force for transformation:** The addition of ternary dopants, such as metals that form the L₁₀ structure with either Fe or Ni, may increase the stability of FeNi-based L₁₀ resulting in an increased $T_{OD}$. The driving force for transformation is increased if the annealing temperature is kept constant when $T_{OD}$ is increased. Alternatively, the annealing temperature can be increased to keep the driving force unchanged but increase the diffusion rate when $T_{OD}$ is increased.

b) **Enhance diffusivity:** Local atomic re-arrangement, necessary for chemical ordering, is limited in Fe-Ni by slow diffusion, thought to be due to a low concentration of vacancies[16, 119]. The activation energy for diffusion at grain boundaries and free surfaces is half the activation energy for diffusion in the
lattice \[16\] (see Table 17). Therefore, increasing vacancies, defects, and free surfaces is expected to enhance diffusion. To enhance the rate of the chemical ordering transformation, it is recommended to use severe plastic deformation, nanostructuring, or other methods to increase vacancies, defects, grain boundaries, and free surfaces.

The lattice diffusivity is directly related to the vacancy concentration as shown in Eq. (2.16) therefore the necessary vacancy concentration can be found from the desired diffusivity using Eq. (7.2). Here, the desired diffusivity for synthesis of \(L_1\) \(FeNi\) is set equal to that of \(AuCu\) because \(FeNi\) and \(AuCu\) have similar \(T_{OD}\) and \(\Delta G\) at 300 °C. At 300 - 350°C, \(AuCu\) transforms to \(L_1\) over the course 8-14 days \[110\]. Thus, formation of \(L_1\) \(FeNi\) in laboratory timescales at 300 °C requires increasing the vacancy concentration by a factor of \(10^{13}\) from the equilibrium concentration \(C_v^{FeNi, equilibrium}\). It has been hypothesized that severe plastic deformation methods can increase the vacancy concentration at a particular temperature to be equal to the vacancy concentration below the melting temperature \[124\]. This means that severe plastic deformation could theoretically increase the vacancy concentration in \(FeNi\) at 300 °C by a factor of \(10^{17}\) \[16, 104\], which should be sufficient to synthesize \(L_1\) \(FeNi\) in laboratory timescales.

\[
\frac{D_{AuCu}^L}{D_{FeNi}^L} = \frac{C_v^{FeNi, needed}}{C_v^{FeNi, equilibrium}}
\]  

(7.2)
Recommendation II: Investigate the nature of the Curie transition in FePd to determine under what conditions the transition is thermodynamically 1\textsuperscript{st}-order or 2\textsuperscript{nd}-order

Previous limited publications on the Curie transition in L1\textsubscript{0} FePd have reported disagreeing Curie temperatures as well as evidence of an unexplored “anomalous” behavior of the AC susceptibility in the vicinity of the Curie transition in this compound [5, 7]. Analyses of L1\textsubscript{0} FePd magnetization data measured as a function of temperature in this Dissertation demonstrated that the critical exponents ($\beta_{MT}$, $\gamma_{MT}$, $\delta_{MT}$) in the vicinity of the Curie transition were consistent with those derived from the tricritical mean-field theory, indicating that the annealed FePd sample with the L1\textsubscript{0} structure resides at a thermodynamic tricritical point (Section 4.1.2.1). The tricritical point occurs at the crossover between conditions (i.e. intensive parameters such as temperature, pressure, composition, magnetization) resulting in a first-order transformation and conditions causing a second-order transformation [94]. It is worthwhile to note that the change from 2\textsuperscript{nd}-order-type magnetic transition to 1\textsuperscript{st}-order-type magnetic transition has been observed experimentally in other functional magnetic materials [28]. Furthermore, a tricritical point is known to exist in the FeNi system near the 50/50 composition[1]. A thermodynamically 1\textsuperscript{st}-order transformation has not been previously observed in FePd. It is recommended to vary the composition, possibly through the addition of ternary species, to study the effect on the thermodynamic order of the Curie transition and under what conditions a 1\textsuperscript{st}-order transition may be induced.
**Recommendation III: Investigate the entropy contribution to the stability of the L1$_0$ phase in FeNi**

It has been a much debated topic whether L1$_0$ FeNi is an equilibrium phase or not \[1, 62, 104\] (Section 2.3.2). Stability is dependent upon the Gibbs free energy, $\Delta G$, of the phase relative to other phases in the material system. The Gibbs free energy is a function of enthalpy $\Delta H$ and entropy $\Delta S$: $\Delta G = \Delta H - T\Delta S$. Results from this Dissertation demonstrate that L1$_0$-structured FeNi with 43 ± 1 at% Ni is enthalpically stable relative to other Fe-Ni phases (Section 5.2). However confirmation of whether L1$_0$ FeNi is an equilibrium phase requires information regarding the entropy contribution to the free energy of the phase relative to other Fe-Ni phases. In some systems, such as L1$_2$-structured Fe$_3$Pt, the entropy contribution significantly lowers the free energy of the chemically ordered phase relative to other phases in the material system thereby stabilizing the chemically ordered phase \[107\]. It is recommended that the entropy difference between the L1$_0$ and A1 phases be quantified by measuring the change in heat capacity of the system when the L1$_0$ phase is heated through the chemical disordering temperature. The magnetic entropy between the ferromagnetic L1$_0$ phase and paramagnetic A1 phase of FeNi may be determined by examining the dependence of the magnetostructural transition temperature (L1$_0$$\rightarrow$A1) of tetrataenite on applied magnetic field under constant heating rate conditions.

**Recommendation IV: Investigate the existence of intermediate phases during the A1$\leftrightarrow$L1$_0$ transformations in FePd and FeNi systems**
Evidence of an intermediate phase in the A1$\leftrightarrow$L1$_0$ transformation was seen in structural results on FePd (Section 4.2) and in magnetic results on FeNi (Section 5.1). Confirmation and characterization of the intermediated phases is of great importance to understanding the mechanism by which the chemical ordering and disordering A1$\leftrightarrow$L1$_0$ transformations proceed. Recommendations for future work concerning the intermediate phase are given in this section for FePd (a) and for FeNi (b).

(a) Evidence of the presence of a tetragonal chemically disordered phase in FePd is presented in sections of this Dissertation that address structural results obtained on FePd (Section 4.2). It remains to be proven whether this tetragonal chemically disordered phase is an intermediate step in a A1$\rightarrow$A6$\rightarrow$L1$_0$ phase transformation or whether this phase is an unstable distortion of the A1 phase resulting from severe lattice strain due to nucleation of the L1$_0$ phase.

1. Whether the A6 phase is an intermediate step or not may be investigated by subjecting the sample to a series of heat treatments to isolate the A6 phase. In this Dissertation, the fastest cooling rate used on FePd was 2 K/min and that sample showed the greatest signs of the A6 phase (S2 defined in Section 4.2, structural analysis in Section 4.2.2.1). It is recommended to study the effect of cooling rates $\sim$5 – 20 K/min on the lattice parameters to determine the conditions that promote the A6 phase. Additionally, it is recommended to use X-ray diffraction with in-situ heating to study the development of tetragonality and of chemical order while slowly cooling through $T_{OD}$.

2. If the A6 phase is an intermediate metastable phase, then it can be isolated and its magnetic properties can be studied. The S2 sample in this work ($T_C$ in
4.2.2.2.1) has a $T_C$ that is 7.2 °C higher than $T_C$ of the L1$_0$ FePd phase measured in this work. In contrast, Vlasova et al. [7] reported a tetragonal chemically-disordered phase formed in FePd subjected to high pressure torsion that exhibited a Curie transition below that of the L1$_0$ phase [7]. Verification of the Curie temperature and establishment of other magnetic properties of the intermediate phase in FePd requires further investigation using a variety of magnetic probes. It is recommended to conduct magnetothermal cycles similar to those conducted on meteoritic tetrataenite (Sections 5.1.1.2, 5.1.2.2) to observe changes in the magnetic properties.

(b) Magnetic evidence of the existence of an intermediate phase in FeNi was presented in this Dissertation work (Section 5.1). It was observed that L1$_0$ FeNi goes through a multi-stage magnetic transformation when subjected to multiple heatings to 700 °C in the VSM (Section 5.1.1.2, 5.1.2.2). This progression of magnetic behavior realized upon heating and cooling repeatedly through the L1$_0$ FeNi transition temperatures was indicated by the appreciable changes in $T_C$ with each heating and cooling step. It is speculated that the $T_c$ and $M_s$ reached a steady state during thermal testing based on the consistency of the final $T_C$ and $M_S$ with previously reported values for the A1 FeNi phase [25, 57]. Evidence of the possible presence of an intermediate FeNi phase was also observed in the $M(H)$ hysteresis behavior that showed a loss of anisotropy after the first magneto thermal cycle $M(T)$ and an increase in $M_S$ after the second magneto thermal cycle $M(T)$ (Sections 5.1.1.2, 5.1.2.2). Future work focused on monitoring the crystal structure as L1$_0$-type FeNi undergoes the chemical disordering transformation is needed to determine if a tetragonal chemically
disordered transitional phase exists in FeNi, similar to that observed in FePd. In particular, neutron diffraction (or scattering) measurements could allow correlations between magnetic changes and structural changes during *in-situ* heating.
## 8 Nomenclature

### Letters

- $a, b, c$  
  lattice parameters, Å
- $a_{LAS}$  
  term in Law of Approach to Saturation due to voids and impurities
- $a_{XRD}$  
  volume fraction of sample oriented for diffraction
- $A$  
  Area, m$^2$
- $A1$  
  fcc chemically disordered phase
- $A6$  
  fct chemically disordered phase
- $A_{XRD}$  
  absorption correction factor
- AFM  
  atomic force microscopy
- bcc  
  body-centered cubic unit cell
- bct  
  body-centered tetragonal unit cell
- $b_{LAS}$  
  term in Law of Approach to Saturation: 8/105 for cubic, 4/15 for uniaxial
- $b_{XRD}$  
  fraction of incident X-ray beam that is diffracted
- $B$  
  magnetic flux or induction, G
- BNL  
  Brookhaven National Laboratory
- $C$  
  concentration
- $C_P$  
  specific heat capacity, J/K
- $C_V$  
  concentration of vacancies
- $d$  
  interplanar spacing in a lattice, Å
- $D$  
  diffusivity, cm$^2$/s
- $D_0$  
  temperature independent diffusion constant, cm$^2$/s
- DSC  
  differential scanning calorimetry
- $DW$  
  Debye-Waller factor
<table>
<thead>
<tr>
<th>Term</th>
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<tr>
<td>EBSD</td>
<td>electron backscattered diffraction</td>
</tr>
<tr>
<td>EDS</td>
<td>energy-dispersive X-ray spectroscopy</td>
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<tr>
<td>(E_K)</td>
<td>anisotropy energy, erg/cc</td>
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<tr>
<td>(f)</td>
<td>atomic scattering factor</td>
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<tr>
<td>(F)</td>
<td>structure factor</td>
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<tr>
<td>fcc</td>
<td>face-centered cubic unit cell</td>
</tr>
<tr>
<td>fct</td>
<td>face-centered tetragonal unit cell</td>
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<tr>
<td>FWHM</td>
<td>full width at half maximum, °</td>
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<tr>
<td>(G)</td>
<td>Gibbs free energy, J</td>
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<tr>
<td>(\Delta G_d)</td>
<td>free energy due to destruction of defects, J</td>
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<tr>
<td>(\Delta G_V)</td>
<td>driving force for transformation at a certain temperature, J/m³</td>
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<tr>
<td>(\Delta G_N)</td>
<td>activation free energy barrier to nucleation, J</td>
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<td>misfit strain energy per volume, J/m³</td>
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<td>h₀</td>
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<td>(H_K)</td>
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<td>(\Delta H_{1+2})</td>
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<tr>
<td>(\Delta H_{\text{form}}^1)</td>
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<td>integrated intensity</td>
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\( I_{\text{sup}} \) Integrated intensity of a superlattice peak

\( I^*_{\text{sup}} \) Calculated integrated intensity of a superlattice peak

\( I_{\text{fund}} \) Integrated intensity of a fundamental peak

\( I^*_{\text{fund}} \) Calculated integrated intensity of a fundamental peak

\( k_B \) Boltzmann’s constant, J/K

\( K \) anisotropy constant, erg/cc

\( L1_0 \) fct chemically ordered phase

\( L1_2 \) fcc chemically ordered phase

\( L_{\text{XRD}} \) Lorentz factor

\( LRO \) chemical long range order parameter

\( LRO_{\text{tet}} \) long range order parameter calculated from unit cell tetragonality

\( m \) magnetic moment, emu

\( M \) magnetization, emu/g or emu/cc

\( M_0 \) magnetization at 0 K, emu/g or emu/cc

MFM magnetic force microscopy

\( M_R \) magnetic remanence, emu/g or emu/cc

\( M_S \) saturation magnetization, emu/g or emu/cc

\( M_{\text{start}} \) Martensitic start temperature

\( n \) Avrami exponent

NSLS National Synchrotron Light Source

\( P_{\text{XRD}} \) polarization factor

\( p \) multiplicity factor

\( P \) pressure, atm
Q  activation energy, J/mol

r  radius, m

r_α, r_β  fraction of the α-sites (β-sites) rightly occupied by A atoms (B atoms)

R  ideal gas constant

S  entropy, J/K

SEM  scanning electron microscopy

t  time, s

l_{infinite}  infinite thickness, m

T  temperature, K

T_C  Curie temperature, K

T_{OD}  chemical order-disorder temperature, K

(u, v, w)  atom position in the unit cell

U  internal energy of the system, J

V  volume, L

VSM  vibrating sample magnetometry

X_A  mole fraction of species A

X_V  transformed volume fraction

XRD  X-ray diffraction

\frac{dX_V}{dT}  growth rate of the product phase

z  number of nearest neighbors

(BH)_{max}  magnetic energy product
Greek and Symbols

$\alpha_{mon}$  monochrometer angle, °

$\alpha, \beta$-site denotes a particular lattice site in a unit cell

$\beta$  heating rate, K/s

$\beta_{MT}$  critical exponent in the Landau equation

$\gamma$  interfacial strain, J/m²

$\gamma_{MT}$  critical exponent in the Landau equation

$\Gamma$  atomic jump frequency, #/s

$\delta$  average jump distance, m

$\delta_{MT}$  critical exponent in the Landau equation

$\theta$  angle, °

$\lambda$  wavelength of radiation, Å

$\mu$  linear absorption coefficient

$\mu_0$  permeability of free space, H/m

$\mu_B$  Bohr magneton, J/T

$\rho$  density, g/cm³

$\nu_{Kiss}$  frequency factor found by Kissinger method, 1/s

$\Xi$  magnetic contribution to the free energy, J

$\phi$  heat flow, W/g

$\varphi$  angle, °

$\chi$  angle, °

$\chi_0$  paramagnetic contribution

$\omega$  angle, °
Subscripts and Superscripts

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<tr>
<th>Subscript</th>
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<tr>
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<td>f</td>
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<td>growth process</td>
</tr>
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10 Appendices
Appendix A: Calculation of Intensities and the Long-Range-Order Parameter from XRD Results

X-ray diffraction can be used to detect the L1₀ phase because there are two notable changes that occur in a XRD pattern when an equiatomic AB alloy transforms from the A1 structure to the L1₀ structure. The first change is a splitting of peaks due to reduction of the crystal symmetry from cubic to tetragonal and the second change is the addition of superstructure peaks due to chemical-ordering[21].

The chemically-disordered state has a cubic crystal structure but upon chemical ordering it transforms to a tetragonal unit cell. In the tetragonal unit cell the lattice parameters are \( a = b \neq c \) while the angles between sides of the unit cell are all 90°. Since the \( c \) lattice parameter in a tetragonal unit cell is unique from the \( a \)- and \( b \)-parameters, the \( d \)-spacing of the L1₀-type structure is different from that of the cubic structure. Fundamental Bragg peaks separate into two peaks upon symmetry reduction. This peak splitting is an excellent indicator of tetragonality and can be used to detect the L1₀ phase and calculate the \( a \) and \( c \) lattice parameters[21, 83]. A long range order parameter \( LRO_{tet} \) indicative of the cubic to tetragonal change, is given by

\[
LRO_{tet}^2 = \frac{1 - \frac{c}{a}}{1 - (\frac{c}{a})^*}
\]

(10.1)

where \((c/a)^*\) is the reported tetragonality in literature. \( LRO_{tet} = 1 \) represents tetragonality equal to the literature L1₀ phase and \( LRO_{tet} = 0 \) perfectly cubic.

Additional Bragg peaks appear in the XRD patterns that are attributed to chemical ordering. In the chemically-disordered A1 structure, each plane has an average atomic scattering factor \( F_{av} \) that is the same for \{001\}-planes and \{002\}-planes. The x-ray beams
diffraeted from the \{001\}-planes is in phase with each other and out of phase with beams diffracted from the \{002\}-planes so that the diffracted beams interfere destructively. However, in the L1\textsubscript{0} structure, the \{001\}-planes and \{002\}-planes have different scattering factor $F_A$ and $F_B$ so the diffracted beams interfere constructively. This results in additional peaks in the XRD pattern called superstructure peaks[21]. The chemical long range order parameter $LRO$ is a measure of how completely the $\alpha$-sites are occupied by $A$ atoms [21]. $LRO = 1$ represents perfect chemical order and $LRO = 0$ chemical disorder. This parameter answers the question: are the right atoms in the correct lattice positions?

The order parameter can be determined from measurable quantities by comparing the relative integrated intensities of superstructure and fundamental peaks in an XRD pattern[83].

$$LRO^2 = \frac{I_{sup}/I_{fund}}{I_{sup}^*/I_{fund}^*}$$  \hspace{1cm} (10.2)

$$I^* = A_{XRD} \cdot p \cdot |F|^2 \cdot L_{XRD} \cdot P_{XRD} \cdot e^{-2DW}$$  \hspace{1cm} (10.3)

where: $I_{sup}$ and $I_{fund}$ = measured integrated intensity values

$I_{sup}^*$ and $I_{fund}^*$ = expected intensity values

$A_{XRD}$ = absorption correction factor

$p$ = multiplicity factor

$F$ = structure factor
\[ L_{XRD} = \text{Lorentz factor} \]

\[ P_{XRD} = \text{polarization factor} \]

\[ \exp(-2DW) = \text{temperature factor} \]

\[ DW = \text{Debye-Waller factor} \]

The many factors involved in calculation of the Bragg peak intensity values are briefly summarized as follows. The absorption correction factor, \( A_{XRD} \), is the absorption coefficient of the material accounting for x-rays absorbed by the sample and is constant for thick, flat samples that fully fill the X-ray beam (expression given below). The multiplicity factor, \( p \), takes into consideration the additive effect of multiple planes having the same \( d \)-spacing. The structure factor \( F \) is a mathematical description of how a material scatters incident radiation (details follow). The Lorentz factor, \( L_{XRD} \), corrects for variations in the integrated intensity due to geometry as the \( 2\theta \) scan progresses. These variations occur because the beam covers a larger surface area at lower \( \theta \), but penetrates deeper into the sample at higher \( \theta \). The Lorentz factor describes the peak height and peak broadening due to appreciable off-Bragg-angle diffraction. The polarization factor, \( P_{XRD} \), stems from scattering that occurs because the incident beam is not polarized, although some polarizing does occur when using synchrotron X-ray with a monochromator. Lastly, the temperature factor, \( \exp(-2DW) \), accounts for thermal vibrations in the crystal lattice. The temperature factor is expressed in terms of the wavelength, \( \lambda \), and Bragg angle as \( \exp(-2DW) = \exp \left( -2 \left( \sin \theta / \lambda \right)^2 \right) \). By combining experimental XRD data with Equations (2) and (3), the chemical long-range-order parameter \( LRO \) can be calculated \[83\].
The absorption correction factor [83] is expressed as:

\[ A_{XRD} = a_{XRD} b_{XRD} \int e^{-2\mu x \sin \theta} dx \]  

(10.4)

where \( a_{XRD} \) is the percent of the volume with the correct orientation for diffraction, \( b_{XRD} \) is the fraction of the incident beam that is diffracted by the sample, \( \mu \) is the linear absorption coefficient, and \( x \) is depth of diffracting planes below the sample surface.

When the sample is infinitely thick, the absorption correction factor simplifies to:

\[ A_{XRD} = \frac{a_{XRD} b_{XRD}}{2\mu} \]  

(10.5)

The criterion for “infinite thickness” is chosen such that the intensity diffracted from a plane on the back side of the sample is \( 1/1000^{th} \) of the intensity diffracted by a plane on the front side of the sample. Therefore,

\[ t_{\text{infinite}} = \frac{3.45 \sin \theta}{\mu}. \]  

(10.6)

The linear absorption coefficient for the alloy is calculated from the linear absorption coefficients of the constituent elements (available by NIST [125]), elemental densities \( \rho \), and compositions as

\[ \mu_{\text{AB}} = \rho_{\text{AB}} \left( X_A \left( \frac{\mu_A}{\rho_A} \right) + X_B \left( \frac{\mu_B}{\rho_B} \right) \right). \]  

(10.7)

The structure factor [13, 83] can be calculated for the L1₀ structure and related to the order parameter by
\[ F = \sum f e^{2\pi i (h u + k v + l w)} \]

\[ = \begin{cases} 
4(X_A f_A - X_B f_B) & \text{for (hkl) mixed odd and even} \\
4(X_A f_A + X_B f_B) & \text{for (hkl) all odd or all even}
\end{cases} \]  

(10.8)

\[ F_{\text{sup}} = 2LRO(f_A - f_B) \]
\[ F_{\text{fund}} = 2(f_A + f_B) \]  

(10.9)

where: \( f \) = atomic scattering factor (tabulated in the Appendix of Cullity[83])

\( (h, k, l) = \) Miller indices

\( (u, v, w) = \) atom locations in the unit cell

\( X_A, X_B = \) atomic fractions of A, and of B

\( f_A, f_B = \) atomic scattering factor of A atoms, and of B atoms

\( F_{\text{sup}} = \) the structure factor for superlattice reflections

\( F_{\text{fund}} = \) the structure factor for fundamental reflections

The distribution of the variants is found by comparing the integrated intensities [83] of the superlattice peaks normalized by the calculated intensities as:

\[ \% \text{Variant A} = \frac{\left( \frac{I_{\text{sup}}}{I_{\text{sup}}^*} \right)_{/A}}{\left( \frac{I_{\text{sup}}}{I_{\text{sup}}^*} \right)_{/A} + \left( \frac{I_{\text{sup}}}{I_{\text{sup}}^*} \right)_{/B} + \left( \frac{I_{\text{sup}}}{I_{\text{sup}}^*} \right)_{/C}} \times 100 \]  

(10.10)

**Anomalous Diffraction**

Anomalous diffraction was used in this Dissertation to enhance the intensity of superlattice Bragg peaks from the L1_0 FeNi phase. The superlattice peaks in L1_0 FeNi
have an expected intensity under Cu-Kα radiation that is ~0.3 % of the intensity of the fundamental (111) Bragg reflection. This very low superlattice intensity arises from the small difference between scattering factors of the Fe and Ni elements. Anomalous diffraction is a method used to enhance the intensity of superlattice peaks. In this method the energy of the incident X-rays are tuned to the absorption edge of one of the elements, in this case Fe. Near the absorption edge, the magnitude of the scattering factor of Fe is significantly reduced while the scattering factor of Ni is less changed. In this manner, the contrast between the Fe and Ni scattering factors is amplified and therefore the intensity of the superlattice peaks, which depends on this difference, is amplified [83]. The corresponding theoretical superlattice and fundamental peak intensities were calculated as follows:

\[
I^*_{S} = |(f_0 + f')_Fe - (f_0 + f')_Ni|^2 \cdot m \cdot L \cdot P
\]

\[
I^*_{F} = |(f_0 + f')_Fe + (f_0 + f')_Ni|^2 \cdot m \cdot L \cdot P
\]

where \(f_0\) is the Thompson elastic scattering of the element at each \(\sin \theta/\lambda\) considered, \(f'\) is the real part of the anomalous scattering factor determined from interpolation of the tables presented by Sasaki [126].

**Ideal Peak Intensities of FePd from Laboratory XRD Measurements**

The expected peak intensities of the superstructure peaks, based on the measured intensities of the fundamental peaks, were calculated using Eq. (9.2). The specific correction factors involved in finding the calculated expected intensities for the superlattice and fundamental Bragg reflections are given here.
The combined Lorentz and Polarization factor for power diffraction is expressed as

\[ L_{\text{XRD}} P_{\text{XRD}} = \frac{1 + \cos^2(2\theta)}{\sin^2 \theta \cos \theta} \].

The absorption correction factor was calculated to account for effects of finite sample size as the samples tested were smaller than the incident x-ray illuminated area. The absorption correction factor as a function of the x-ray incident angle was determined by comparison of the experimental integrated intensities of the Bragg reflections of two polycrystalline randomly oriented Si powder disk references, with diameters ~6 mm (equal to diameter of the FePd samples) and ~22 mm (larger than x-ray illuminated area) [127].

**LRO of Tetrataenite from XRD Measurements at Beamline X20A of the National Synchrotron Light Source (NSLS)**

The LRO and distribution of variants of L10 FeNi in the NWA6259 meteorite were calculated using Eq. (9.2) and Eq. (9.10), respectively. The specific correction factors involved in finding the calculated expected intensities for the superlattice and fundamental Bragg reflections are given here.

The absorption correction factor for tetrataenite measured using beamline X20A at the NSLS was calculated as infinitely thick but not infinitely wide. In FeNi, the infinite thickness was found to be 4.7 μm for the lowest Bragg angle corresponding to the (001) and 13.5 μm for the highest Bragg angle of interest (220), under synchrotron radiation with wavelength 1.54062 Å. Superlattice peaks of tetrataenite were compared to fundamental peaks of the same orientation (e.g. (001) to (002), (110) to (220)) therefore the \( a_{\text{XRD}} \) parameter in Equation (9.4), representing the volume fraction of the sample oriented for diffraction (see Appendix A), remained constant between the superlattice and fundamental measurements. The factor \( b_{\text{XRD}} \) was calculated as the fraction of the beam
that was filled with the sample at each angle. For the specific experimental setup, the beam extended past the sample at low angles but was smaller than the sample at higher angles as illustrated in Figure 65. The factor $b_{XRD}$ was found for the specific geometry of the sample and the beamline as:

$$b_{XRD} = \begin{cases} \left( \frac{\pi}{3} + \sqrt{3} \right) \sin(\theta + \omega) & \text{for } 2\theta < 52.85^\circ \\ 1 & \text{for } 2\theta > 63.38^\circ \end{cases} \quad (10.13)$$

![Figure 65: Illustration of the incident beam area in the plane of the sample surface for experiments at the NSLS beamline X20A.](image)

The Lorentz factor for single crystal diffractometers is calculated as $L = 1/\sin(2\theta)$ while the polarization factor is given by $P_{XRD} = \left(1 + \cos(2\alpha_{mon})\cos^2(2\theta)\right)/2$ where $2\alpha_{mon}$ is the diffraction angle in the monochromator [128]. The observed (200) Bragg peak appeared as a single peak (no splitting due to tetragonality observed) and therefore the intensity of the measured (200) peak is assumed to be due to a sum of the intensities of
the (200), (020), and (002) Bragg reflections. Likewise, the observed (220) is attributed to a sum of the (220), (202) and (022) Bragg reflections.

The experimental integrated intensities, factors for determining the calculated intensity, the long-range-order parameter, and the distribution of variants are summarized in Table 18. It should be noted that the LRO for Variant A was calculated as being greater than one, which is physically impossible; the reason for this result is not clear at the present time.

Table 18: Long-range-order parameter and distribution of variants calculated for the meteorite NWA6259.

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