APPLICATION OF HIGH-RESOLUTION DILATOMETRY TO THE STUDY OF
CRITICAL PHENOMENA IN ANTIFERROMAGNETIC SYSTEMS

by

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of the requirements for the degree

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This dissertation has been read by each member of the dissertation committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the Division of Graduate Education.

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November 2010
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Thermal expansion is an under-utilized physical property with enormous potential in its application to the study of classical critical phenomena. The Pippard relation scales the coefficient of volume thermal expansion multiplied by temperature with heat capacity in the vicinity of a continuous phase transition. This justifies the study of critical behavior, characterized by critical-exponent $\alpha$, with the coefficient of volume thermal expansion instead of heat capacity. We evaluate potential advantages and disadvantages and develop strategies uniquely suited to the analysis of critical behavior exhibited by the coefficient of thermal expansion. The most notable disadvantages arise as a result of numerically differentiating thermal-expansion data to obtain its coefficient. In the course of assessing the detrimental effects of this procedure, we developed a critical expression for thermal expansion, with which we quantitatively evaluate the effect numerical differentiation has on the study of critical phenomena. Antiferromagnets are less susceptible than ferromagnets to long-range dipole contributions, which adjust critical behavior away from theoretical predictions. Therefore, three antiferromagnetic materials were selected to test the suitability of studying critical behavior with thermal expansion. Single crystals of CaMn$_2$O$_4$ and Bi$_2$CuO$_4$ were grown and characterized by methods described in careful detail. The coefficient of thermal expansion is studied along the principal crystallographic axes of each material demonstrating that the critical behavior exhibited along each axis is the same as that exhibited by the volume. Both transitions belong to the three-dimensional Ising universality class which settles a long-standing question by suggesting that Bi$_2$CuO$_4$ exhibits easy-axis anisotropy rather than easy-plane anisotropy. The thermal expansion of each material (as opposed to the coefficient of thermal expansion) is studied with our critical expression in order to increase the critical temperature range close to the Néel temperature. The limitations of studying the critical behavior of a polycrystalline sample are demonstrated when we investigate the antiferromagnetic transition of $\alpha$-Mn. This element has a surprisingly complicated magnetic structure and our results constrain its transition to be in either the three-dimensional Heisenberg or $n = 4$ universality class.
INTRODUCTION TO CRITICAL PHENOMENA

Thermodynamic Phase Transitions

Characteristic Elements

A phase transition is the transformation of an interactive system from one thermodynamic phase $S_1$ into a distinct phase $S_2$. These states are conventionally described by their thermodynamic free energy $F_i(T, P, H) \ (i = 1, 2)$ which, for the thermodynamic states of interest in this work, are mainly functions of temperature $T$, pressure $P$, and applied magnetic field $H$. Consider a system consisting of phases 1 and 2, which is in thermodynamic equilibrium with $T$, $P$, and $H$. The system selects the phase $S_i$ in which $F_i(T, P, H)$ is a minimum as shown in Figure 1. Given a system with two or more possible unique thermodynamic states, there generally exist well-defined boundaries between them. We say generally exist because sometimes the boundary terminates at a position in phase space referred to as the critical point. Assuming we are far from any critical point, the boundary between $S_1$ and $S_2$ in the $(T, P)$ plane is defined by satisfying a continuity relationship: $F_1(T, P, H) = F_2(T, P, H)$. Along the smooth, well-behaved curve where the continuity relation is satisfied, coexistence between $S_1$ and $S_2$ is allowed (the system need not pick one) and both $F_1(T, P, H)$ and $F_2(T, P, H)$ are non-analytic in the sense that they are not infinitely differentiable. The boundary, known more technically as the phase-transition curve, is generally a
function of all relevant thermodynamic parameters, making it possible for small shifts of any relevant parameter $\zeta + \delta \zeta$ to facilitate a phase transition between two states. In Figure 1, we exhibit how a temperature shift ($P$ and $H$ are held constant) is responsible for a phase transition between points $A$ and $B$. When this occurs, the phase transition is driven by the growth of thermal fluctuations in the system. This kind of a transition is referred to as a thermodynamic phase transition. We contrast this with quantum phase transitions, which occur at $T \sim 0$ K where shifts in $P$, $H$, doping level $x$, or other parameters allow the system to cross a phase-transition curve. The phase transition in this case is driven by zero-point quantum fluctuations, which are a direct result of Heisenberg’s uncertainty principle. Figure 2 depicts a quantum critical point.
at $H \sim 4.5$ T in heavy-fermion system CeCoIn$_5$.[1] Even at zero temperature, the system is able to transition between superconductivity and conventional Fermi-liquid behavior if $H$ is sufficiently near 4.5 T. Though quantum phase transitions are quite interesting, we focus solely on thermodynamic phase transitions in this work and no additional attention is devoted to their quantum counterparts. When a phase-transition curve exists between two states $S_1$ and $S_2$, we can solve its functional form for $T$ and define a critical temperature $T_C(P, H)$. The first characteristic element of a thermodynamic phase transition is therefore a well-defined critical temperature $T_C(P, H)$. As a corollary, it is sometimes possible to adjust the state of a system by a non-adiabatic process in which the system crosses a phase-transition curve without undergoing a phase transition. This procedure results in a fragile, meta-stable state.

Figure 2. Phase diagram for CeCoIn$_5$ displaying a quantum critical point.
Common examples of this include superheating, supercooling, and supersaturation. We return to the concept of supersaturation later when we discuss crystal growth.

Next, we consider the functional form of the thermodynamic free energy $F(T, P, H)$. To be consistent with thermodynamics, we require that it be analytic except in the vicinity of a phase boundary or critical point. Furthermore, if $F(T, P, H)$ is to be consistent with analogous energy representations such as the Hamiltonian $\mathcal{H}$, it must contain the same intrinsic symmetry as $\mathcal{H}$. These two requirements (analyticity and symmetry) are at the heart of Landau’s phenomenological theory of phase transitions.\cite{2, 3} To satisfy these two requirements, we introduce the concept of the order parameter $\sigma$, which is the second element common to thermodynamic phase transitions.

The order parameter $\sigma$ is a thermodynamic parameter which is zero for temperatures greater than the critical temperature $T_C$, but is non-zero below it (in the “ordered” state). Each distinct class of thermodynamic phase transition has its own characteristic order parameter, though some are more abstract than others. Table 1 displays several common thermodynamic phase transitions and their respective order parameters $\sigma$. As an example, consider a ferromagnetic phase transition where the order parameter, as read from Table 1, is the magnetization $M$. We plot $M$ in Figure 3, emphasizing its distinct behavior above and below $T_C$. Above $T_C$, $M(T) = 0$ because thermal energy $k_B T$ is larger than the magnetic-exchange energy $J$. However, below $T_C$, $M(T) \neq 0$ because the exchange energy is able to override the randomizing
Table 1. Common phase transitions and their characteristic order parameters.

<table>
<thead>
<tr>
<th>Phase Transition</th>
<th>Order Parameter $\sigma$</th>
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<tbody>
<tr>
<td>liquid-gas</td>
<td>critical density $\rho - \rho_C$</td>
</tr>
<tr>
<td>ferromagnetic</td>
<td>magnetization $M$</td>
</tr>
<tr>
<td>antiferromagnetic</td>
<td>sublattice magnetization $M_i$</td>
</tr>
<tr>
<td>superconductivity</td>
<td>complex gap parameter $\Delta$</td>
</tr>
<tr>
<td>superfluidity</td>
<td>condensate wave function $\langle \psi \rangle$</td>
</tr>
<tr>
<td>ferroelectricity</td>
<td>polarization $P$</td>
</tr>
<tr>
<td>structural</td>
<td>critical elastic strain $(a - b)/b$</td>
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</tbody>
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effect of thermal energy. From Figure 3, we can see that if we construct $F$ from a series expansion in powers of $M$, the non-analyticity required of $F$ at $T_C$ is built in. This is exactly what is done in any calculation employing Landau’s phenomenological theory of phase transitions. This being the case, we are able to drop the individual expressions for $F_i$ in thermodynamic states $S_i$. A single expression for $F$ can be constructed in such a way that it is valid for two states and the boundary between them.

Order parameters have their own intrinsic dimensionality (number of unique components) and symmetry. For example, in the case of a magnetic transition, we know the order parameter commonly assumes a dimensionality of one (scalar), two (vector with two components), or three (vector with three components), representing the Ising, XY, and Heisenberg models, respectively.[2] Or if we consider superconductivity, the complex order parameter $\Delta$ always has two components: a magnitude and a phase. We are able to construct the symmetry of $F(T, P, H)$ so that it is consistent with the analogous Hamiltonian, by exploiting the intrinsic symmetry of $\sigma$. This is
Figure 3. Magnetization $M(T)$, normalized by its value at $T = 0$ K, is plotted as a function of temperature for a generic ferromagnet. $M(T)$ is identified as the order parameter of the transition because it is zero above $T_C$ and non-zero below as indicated in the cartoons representing magnetic moments in the system.

how we arrive at the third characteristic element of thermodynamic phase transitions: symmetry breaking.

A phase transition from phase $S_1$ to $S_2$, where $S_2$ is the low-temperature phase, typically breaks one or more symmetries intrinsic to $S_1$. Consider again the example displayed in Figure 3, where we assume the cartoon system represents a single magnetic domain with $10^{23}$ magnetic moments. For $T > T_C$, the randomizing effect of dominant thermal energy allows the system to exhibit rotational symmetry. Rotational invariance is broken below $T_C$, however, where magnetic-exchange interactions are strong enough to facilitate the ordering of magnetic moments along an energetically-favorable crystallographic orientation. Most phase transitions lead to
broken symmetries as a system goes from a disordered to ordered state. One may ask: where does the symmetry go? These symmetries are transferred to Goldstone-excitation modes, which retain them in the low-symmetry phase.[4] For example, the Goldstone excitation for the ferromagnetic case is the spin wave or magnon, which preserves rotational invariance.[4] There are a few notable cases where no spontaneous symmetry breaking occurs. For example, topological order in both the theoretical Kosterlitz-Thouless[5] and experimental quantum Hall[6] states requires no broken symmetries. These exotic quantum states, and indeed, any phase transition without broken symmetry, are outside the scope of this work.

**Classification Systems**

*Ehrenfest Scheme*. When presented with a set of seemingly unrelated elements, one goal of science is to catalogue or categorize them and thereby understand their respective relationships. Whether it is the Linnaean taxonomy system,[7] Mendeleev’s periodic table of the elements,[8] or Murray Gell-Mann and his eight-fold way categorization of Baryons and Mesons,[9] well-informed classification systems lead to further scientific understanding. Interestingly, despite rapid advances in classical thermodynamics following its first reliable experiments in the seventeenth century, it was not until 1933, after the foundations of even quantum mechanics were solidified, that Paul Ehrenfest described a classification scheme for phase transitions.[10] Ehrenfest proposed a system whereby phase transitions would be organized by the degree of
non-analyticity of their underlying thermodynamic free energy. Since, all thermodynamic parameters are derived from partial derivatives of the free energy with respect to other thermodynamic parameters, the order of the transition is defined by the lowest derivative which exhibits a discontinuity. Thus, a first-order phase transition is expected to exhibit a jump discontinuity in the volume $V$, entropy $S$, and magnetization $M$, while a second-order transition has a discontinuity in heat capacity $C_P$, compressibility $K_T$, coefficient of volume thermal expansion $\Omega_P$, and magnetic susceptibility $\chi_T$ to name a few examples. Table 2 lists common first and second derivatives of the Gibbs free energy $G$. While normally only first- and second-order transitions are discussed, Ehrenfest’s classification system allows for the possibility of phase transitions of third, fourth, two-hundred seventy-sixth, and on up to infinite order. Indeed, it was at one time believed that the condensation of an ideal Bose-Einstein gas provided a tangible example of a third-order phase transition.[11]
However, the classification system of Ehrenfest is of limited utility. While there is little problem with his description of a first-order phase transition, second-order transitions are rarely observed in nature as he defined them. In fact, only superconductivity in zero magnetic field exhibits the hallmark discontinuity in $C_P$ at $T_C$ required of second-order transitions. Most transitions that cannot be classified as first order do not seem to belong among any higher order phase-transition classification either. Instead, these transitions tend to exhibit power-law behavior in thermodynamic parameters.

**Modern Scheme.** The modern classification scheme of phase transitions, attributed to Fisher,[2] generalizes Ehrenfest’s infinite number of phase-transition categories by reducing them to three orders: first (discontinuous), second (continuous), and infinite. Note that the terms “first order” and “discontinuous” as well as “second order” and “continuous” are interchangeable and both forms are used in contemporary literature. Nearly every phase transition is classified as first or second order. Infinite-order transitions are those which break no symmetry such as the previously identified Kosterlitz-Thouless transition. A first-order transition, in the modern sense, is characterized by the same conditions Ehrenfest’s system required, while a continuous transition is simply a transition that is not first (or infinite) order.

Given the simple definitions of the modern classification scheme, it is beneficial to briefly discuss the central characteristics of a first-order transition. Just as Ehrenfest
required, they exhibit jump discontinuities at $T_C$ in both their volume and entropy. The jump in entropy ($\Delta S$) can be associated with an energy by multiplying by $T_C$: 

$$Q = T_C \Delta S,$$

with $Q$ being the latent heat of the transition. When a system with a first-order transition approaches $T_C$ from above (below), a characteristic thermal energy $Q$ must be released (absorbed) before the system may continue to cool (warm).

The origin of the latent heat is found in the fact that two distinct phases coexist at $T_C$ in a first-order phase transition. Each phase has the same thermodynamic free energy but different entropies, thus the latent heat is the entropy cost required to convert from one phase to the other. As a direct consequence of phase coexistence, the length scale which characterizes the degree of order in the “ordered phase” (the correlation length $\xi$) remains finite at $T_C$.

A continuous or second-order phase transition exhibits characteristics which contrast it with those of a first-order transition such as continuous entropy and volume across $T_C$ and $\xi \to \infty$ at $T_C$. As a consequence of these properties, there is no phase coexistence or latent heat in a second-order transition. If these requirements are met, and spontaneous breaking of one or more symmetries occurs, the transition is second order. As a corollary, we note that the symmetry of the low-symmetry state must be an irreducible subgroup of the symmetry of the high-symmetry state for the transition to be considered continuous.[12] This class of phase transition has absorbed Ehrenfest’s transitions of order second through infinity minus one so that the behavior of
thermodynamic response functions like $C_P$ may exhibit simple jump discontinuities or more complicated power-law behavior.

**Critical Phenomena**

**Historical Perspective**

The existence of phase transitions has been known since man first observed water freeze in winter. But the first experimental observation of critical phenomena was published relatively recently in 1869 by Thomas Andrews. Andrews discovered the phenomenon of critical opalescence in the liquid-gas phase transition of CO$_2$ wherein density fluctuations grow to sizes comparable to the wavelength of light as $T_C$ is approached, and the normally transparent liquid becomes “cloudy” due to Rayleigh scattering of light. It was the indirect observations of the growth of fluctuations in the density (the order parameter for this phase transition) that made this a new and revolutionary discovery. A hallmark of critical phenomena is the buildup of fluctuations in the order parameter near $T_C$ and their subsequent divergence at $T_C$. Since Andrew’s discovery, knowledge regarding critical phenomena has been advanced by some of the world’s top theorists and experimentalists and is conventionally applied to fluid and magnetic systems.

To gain some perspective regarding the volume of modern literature concerned with the study of critical behavior, we searched the ISI Web of Science® database for the phrases “critical behavior”, “critical phenomena”, “critical exponent”, and
Figure 4. The number of publications for which the phrases “critical behavior” (black curve), “critical phenomena” (red curve), “critical exponent” (green curve), and “critical exponents” (blue curve) appear in the title or abstract (post-1990 publications only) as a function of year. Lines are a guide to the eye. The inset displays the number of publications for which the phrase “critical behavior” appears in the title. “critical exponents”. The number of publications which include these phrases in their titles or abstracts are displayed in Figure 4 as a function of year. The large increase around 1990 does not reflect a massive increase in publications, but rather, is simply an artifact of the database’s capabilities. For publications predating 1990, the search results required that the phrase be in its title, but those published after 1990 might just have the phrase as a keyword or in its abstract. The inset shows the number of publications for which the phrase “critical behavior” is present in the title for pre- and post-1990 publications, which removes the artifact at 1990, and provides a more realistic perspective. In general, it appears work concerning critical
behavior has saturated in recent years, but is holding steady at a high volume of publications. There is no reason to anticipate this trend will not continue indefinitely into the future.

**Characteristic Elements**

A system exhibiting critical phenomena experiences fluctuations of its order parameter as its temperature nears $T_C$. The length scale of these fluctuations is characterized by the correlation length $\xi$. As $T_C$ is approached, the size of fluctuations rapidly increase and $\xi$ diverges to infinity at $T_C$. Therefore, the system ceases to have a finite characteristic length, and it is invariant under scaling transforms.[4] This seemingly innocuous statement has some profound consequences. In fact, we are able to identify many of the characteristic elements of critical phenomena purely as a result of scale invariance.

The property of scale invariance in a system near $T_C$ implies that all thermodynamic parameters are homogeneous functions under scaling transforms in which the length scale is adjusted. When a homogenous function $f(q)$ has its unit of characteristic length $q$ scaled by a factor of $\lambda$, it transforms as

$$f(\lambda q) = g(\lambda) f(q),$$

(1.1)

where $g(\lambda) = \lambda^p$ and $p$ is the degree of homogeneity,[2, 4] When such a scaling transform is applied to the thermodynamic free energy, the static scaling hypothesis
asserts that[2]
\[ F_S(T, h) = |g_t|^{2-\alpha}Y \pm \left( g_h/|g_t|^\Delta \right), \]  
(1.2)
where \(2 - \alpha\) and \(\Delta\) are the degrees of homogeneity and \(g_h\) and \(g_t\) are the “length scales” of the system which have been transformed.[4, 14] The scaling form of the free energy in Equation (1.2) is the origin of diverging behavior in many thermodynamic parameters such as heat capacity in the vicinity of \(T_C\) \((g_t \sim t \equiv (T - T_C)/T_C\) where \(t\) is the reduced temperature). Thermodynamic parameters are derived from derivatives of the free energy and go as power laws of the degrees of homogeneity, which we call critical exponents. Power-law behavior of most thermodynamic parameters with characteristic critical exponents is one of the hallmark elements of critical phenomena and is a consequence of the scale-invariant nature of systems in the vicinity of \(T_C\).

After measuring the critical exponents experimentally for many systems, it was observed that the critical exponent values for seemingly distinct phase transitions were identical.[2] Theoretical support for the existence of so-called “universality classes”, characterized by specific critical-exponent values, followed some decades after this initial observation. As it turns out, the only relevant characteristics of a system, which contribute to the values of its critical exponents, are the number of degrees of freedom of its order parameter and the spatial dimensionality of the system. This short list of characteristics allows such diverse transitions as the superfluid transition in \(^4\text{He}\) and the superconducting fluctuations in \(\text{YBa}_2\text{Cu}_3\text{O}_7\) to exhibit the same critical exponents and, therefore, belong to the same universality class.[15]
Anomalies in thermodynamic parameters in the vicinity of $T_C$, characterized by power-law behavior with critical exponents which are classified into a finite number of categories called universality classes, comprise the cardinal elements of critical phenomena. Each of these is considered in detail in the following sections of this chapter. As a final clarifying point, the preceding discussion focused on static critical phenomena, but critical phenomena can also be dynamic. We refer those interested in dynamic critical phenomena to an authoritative review in Reference [16], as the subject is outside the scope of this work.

**Beyond Magnetic and Fluid Systems**

Before we continue our description of critical phenomena, it is important to emphasize its profound relevance to more than just the archetypical fluid and magnetic systems with which it is typically associated. There exist a wide range of other seemingly unrelated systems which benefit from a treatment inherited from the concepts of critical phenomena. These examples include experiments and models demonstrating how the fragmentation of spherical polymer plastics upon impact with a hard surface is asymptotically described by a mass distribution which goes as a power law with universal exponents.[17] Modern cosmology theories invoke a series of symmetry-breaking phase transitions during the expansion and cooling of the early universe which result in scale-invariant distributions of initial mass fluctuations. This is a necessary condition to explain the large-scale structure of astronomical bodies and the formation of galaxies.[18] Interestingly, topological defects in pressure-quenched superfluid helium
and liquid crystals have been used to study the behavior of the cosmological phase transition \((T_C = 10^{27} \text{ K})\) by analogy.\([19, 20, 21]\) And the evolution of predator-prey dynamics in theoretical ecosystems displays a scaling indicative of a non-equilibrium critical point.\([22]\) It is possible to list many more applications of critical phenomena to varied physical systems. Instead, we offer one final example, illustrated in greater detail: the study of stock markets.

H. Eugene Stanley was the first to refer to the application of statistical physics to study stocks, currency markets, and other problems of interest in economics as “econophysics”. Rapid advances are currently being made in this field by physicists familiar with the concepts of critical phenomena. Much effort is devoted to the study of stocks where data are readily available and sufficiently voluminous. The focus of these studies is on the probability density function (PDF) of the log returns of stock prices, the behavior of which, has many fascinating analogies with systems exhibiting critical phenomena. For example, the PDF of log returns of the U. S. S&P 500 index presents scale-invariant behavior in the vicinity of large-scale fluctuations such as the October 1987 stock market crash.\([23]\) The authors of that study claimed this was the first published evidence of a phase transition and critical behavior in the dynamics of a financial index. Stock-price fluctuations themselves have been adequately described by an Ising model.\([24]\) Furthermore, asymptotic power-law behavior has been identified in the cumulative distribution of stock-price returns and a study by Plerou and
Stanley demonstrated the universality of its exponent by showing they are statistically equivalent for data from three distinct stock exchanges: New York, London, and Paris. Universality of the exponents has also been demonstrated through different periods of time dating back to the 1929 stock market crash. What is perhaps most impressive is that Stanley claims the power-law behavior persists over ten decades! In stark contrast to this impressive result, nature limits power-law behavior to about three decades for magnetic phase transitions.

**Critical Exponents**

**Definition of Exponents**

Any study of critical behavior, whether experimental or theoretical, tends to focus on dimensionless numbers called the critical exponents. In the vicinity of a phase transition exhibiting critical behavior, a thermodynamic quantity \( f(|t|) \), expressed as a function of reduced temperature \( t = (T - T_C)/T_C \), obeys the limit

\[
\lambda \equiv \lim_{|t| \to 0} \frac{\ln f(|t|)}{\ln |t|},
\]

where \( \lambda \) is the critical exponent. This implies that the functional form of \( f(|t|) \) is dominated by a term \(|t|^{\lambda}\) in the limit \(|t| \to 0\). However, the complete functional form is fairly complicated in general with analytic terms and non-analytic corrections to the dominant singularity. This complexity highlights one of the most useful properties of the critical exponent: while it is generally impossible to study the complete functional form of \( f(|t|) \) experimentally, the critical exponent may be measured.
Of course, measuring the critical exponent is not trivial by any means and there are several experimental obstacles that arise due to $\lambda$ being defined in the limit $|t| \to 0$. Still, the critical exponents are more-or-less experimentally accessible. The other important virtue of the critical exponents is that their values are indicative of the universality class to which the phase transition belongs.

The most concise way to define four of the more common critical exponents ($\alpha$, $\beta$, $\gamma$, and $\delta$), is to consider the singular term of the free energy $F_S$. Ignoring, for now, irrelevant variables and other corrections, it has the scaling form of Equation (1.2)[14]

$$F_S(T, h) = |g_t|^{2-\alpha} Y_{\pm} \left( g_h / |g_t|^\Delta \right),$$

where $\Delta = \beta + \gamma$, $g_t$ and $g_h$ are non-linear scaling fields, and $Y_{\pm}$ is the scaling function. To first order, the fields are $g_t = t + \ldots$ and $g_h = h + \ldots$ where $h$ is the ordering field. As previously mentioned, the scaling form of Equation (1.4) is a consequence of scale invariance near $T_C$.[4] The heat capacity $C_H$, magnetization $M$, and magnetic susceptibility $\chi_T$ are calculated from derivatives of the free energy. To lowest order and in the limit $h \to 0$, we obtain[14]

$$C_H \propto \frac{\partial^2 F_S}{\partial t^2} \approx Y''_{\pm} (0) |t|^{-\alpha} + \ldots$$

$$M = \frac{\partial F_S}{\partial h} \approx Y'_{\pm} (0) |t|^\beta + \ldots$$

$$\chi_T = \frac{\partial^2 F_S}{\partial h^2} \approx Y''_{\pm} (0) |t|^{-\gamma} + \ldots,$$
where it is clear that $\alpha$, $\beta$, and $\gamma$ are the critical exponents associated with heat capacity, magnetization, and magnetic susceptibility, respectively. In truth, these distinctions are only accurate in the case of a magnetic system. For example, the exponent $\beta$ always characterizes the behavior of the order parameter of the transition (magnetization for a magnetic transition but critical density for a liquid-gas transition). If we set $T = T_C$, we can derive a fourth exponent. In the limit $|g_t|^{\Delta} / g_h \to 0$, the free energy $F_S$ may be written

$$F_S(T, h) = |g_h|^{(2-\alpha) / \Delta} Y_0 \left( g_t / |g_h|^{1 / \Delta} \right). \tag{1.6}$$

Using the notation of Reference [14], we calculate $M$ (this time for $h \neq 0$ and $T = T_C$) by a derivative with respect to $h$. To lowest order, $M$ is

$$|M| = B_c |h|^{1/\delta} + \ldots, \tag{1.7}$$

where we have defined $1/\delta \equiv -1 + (2-\alpha) / \Delta$ and $B_C$ is related to $Y_0$ in the expression for $F_S$. Therefore, the critical exponent $\delta$ corresponds to the magnetization along the critical isotherm. The defining relation for $\delta$ is more commonly expressed in a form similar to $H \sim |M|^\delta \text{sgn}(M).[2]$

Two other common critical exponents, $\nu$ and $\eta$, are less simple to define in a concise manner, but they come from statistical calculations of the correlation between spins (again, for a magnetic system). To be more general, these exponents are related to correlated fluctuations of the order parameter of the phase transition. In the case of a magnetic transition, we express[27] the fluctuations of the order parameter
(magnetization) from its average at position \(\vec{r}\) with \([M_z(\vec{r}) - \langle M_z(\vec{r}) \rangle] \). It is of interest to see how this fluctuation at \(\vec{r}\) is correlated to similar fluctuations at \(\vec{r}'\). This is mathematically described by the correlation function\(^{[2, 27]}\) \(G(\vec{r}, \vec{r}')\) defined by

\[
G(\vec{r}, \vec{r}') = \langle [M_z(\vec{r}) - \langle M_z(\vec{r}) \rangle] [M_z(\vec{r}') - \langle M_z(\vec{r}') \rangle] \rangle. \tag{1.8}
\]

The structure factor \(S(\vec{Q}, \omega)\), which is experimentally measured by neutrons in elastic or inelastic magnetic scattering, is a Fourier transform of the correlation function.\(^{[28]}\) Therefore, \(G(\vec{r}, \vec{r}')\) may be extracted experimentally from \(S(\vec{Q}, \omega)\). Calculation of \(G(\vec{r}, \vec{r}')\) depends on the specific system (its dimensionality and the nature of the spins), but it is generally the Green’s function of a partial differential equation characteristic of the system.\(^{[27]}\) One thing the solutions always have in common is that they include a term with units of length called the correlation length \(\xi\) which goes as \(\xi \sim |t|^{-\nu}\). Furthermore, if we set \(T = T_C\), the correlation function falls off with increasing separation between spins as \(G(\vec{r}) \sim |\vec{r}|^{-(d-2+\eta)}\) where \(d\) is the dimensionality of the lattice.\(^{[2, 29]}\)

Table 3. Common critical exponents associated with magnetic phase transitions and their definitions.

<table>
<thead>
<tr>
<th>Exponent</th>
<th>Therm. Parameter</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\alpha)</td>
<td>Heat Capacity</td>
<td>(C_H \sim</td>
</tr>
<tr>
<td>(\beta)</td>
<td>Magnetization</td>
<td>(M \sim</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>Susceptibility</td>
<td>(\chi_T \sim</td>
</tr>
<tr>
<td>(\delta)</td>
<td>Crit. Isotherm</td>
<td>(H \sim</td>
</tr>
<tr>
<td>(\nu)</td>
<td>Correlation Length</td>
<td>(\xi \sim</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Pair Correlation</td>
<td>(G(\vec{r}) \sim</td>
</tr>
</tbody>
</table>
There are many other critical exponents which may be defined, but the six aforementioned exponents are the most commonly studied, and are summarized in Table 3.

**Relations Between Exponents**

Given the definitions of the critical exponents as power laws of thermodynamic parameters, it is not surprising that relations between those same parameters result in relations between the exponents themselves. However, thermodynamics generally does not allow for exact, equality-containing relations between exponents. Rather, the relations tend to be inequalities. Though, some special cases usually exist for which use of the equality is appropriate. For example, the Rushbrooke inequality is known to be an equality for the mean-field theory and two-dimensional Ising model.[2] To get a feeling for how the relations are usually derived, we first state the following lemma[2]:

Let \( f(x) \sim x^\lambda \) and \( g(x) \sim x^\psi \) for sufficiently small positive \( x \). If \( f(x) \leq g(x) \), then \( \lambda \geq \psi \). Using the lemma, which is proved in Reference [2], we proceed to derive the Rushbrooke inequality.[30] The relationship between \( C_H \) and \( C_M \) (heat capacities in constant magnetic field and at constant magnetization) may be expressed by

\[
\chi_T (C_H - C_M) = T \left( \frac{\partial M}{\partial T} \right)_H^2, \tag{1.9}
\]

and because \( C_M \geq 0 \) for all temperatures, we arrive at the following general condition for \( C_H \)

\[
C_H \geq \frac{T}{\chi_T} \left[ \left( \frac{\partial M}{\partial T} \right)_H \right]^2. \tag{1.10}
\]
If we substitute in the definitions from Table 3 \( (C_H \sim |t|^{-\alpha}, \chi_T \sim |t|^{-\gamma}, \text{and} \ (\partial M/\partial T)_H \sim |t|^{\beta-1}) \) and apply the previously mentioned lemma, we conclude that 
\[-\alpha \leq 2(\beta - 1) + \gamma.\]
Upon rearrangement, the inequality becomes
\[
\alpha + 2\beta + \gamma \geq 2. \tag{1.11}
\]

The Rushbrooke inequality is but one of a large number of exponent relations, however, there are only a handful of relations\,[2] listed below, which are relevant to \( \alpha \).

\[
\begin{align*}
\alpha + 2\beta + \gamma &\geq 2 \quad \tag{1.12a} \\
\alpha + \beta(1 + \delta) &\geq 2 \quad \tag{1.12b} \\
\gamma(\delta + 1) &\geq (2 - \alpha)(\delta - 1) \quad \tag{1.12c} \\
\frac{2 - \alpha + \gamma}{2 - \alpha - \gamma} &\geq \delta \quad \tag{1.12d} \\
\frac{d\gamma}{2 - \alpha} &\geq 2 - \eta \quad \tag{1.12e} \\
d\nu &\geq 2 - \alpha \quad \tag{1.12f}
\end{align*}
\]

Two of the relations include \( d \), which is the lattice dimensionality.

In truth, the origin of exponent relations is deeper and more fundamental than can be inferred from short, two-line derivations. The exponent relations are sometimes referred to as scaling laws, because they are a direct consequence of the scaling hypothesis\,[31] wherein the singular part of the thermodynamic free energy \( F_S \) obeys
\[
F_S (\lambda^\alpha H, \lambda^{\alpha_T}t) = \lambda F_S (H, t). \quad \tag{1.13}
\]
Since Equation (1.13) is valid, we require only two independent critical exponents to fix $a_H$ and $a_T$ (degrees of homogeneity), and all other exponents may be obtained from, or at least constrained by, these original two.\[31\]

The Critical Exponent $\alpha$

We have already discussed some pertinent properties of common critical exponents, however, we must consider a few additional details regarding $\alpha$. First, we explore the range of values appropriate for $\alpha$ by considering thermodynamic constraints on entropy. But before entropy can be calculated, we require a suitable expression for $C_P$. The generic form of $C_P$, adopted from theory, is

$$C_P \simeq (A_\pm/\alpha)|t|^{-\alpha} + B + Dt,$$  \hspace{1cm} (1.14)

where $\pm$ subscripts indicate values above (+) and below (-) $T_C$ and $B + Dt$ provides an analytic background to model electronic and phonon contributions to $C_P$. Equation (1.14) is asymptotic with increasing validity as $T \to T_C$ ($t \to 0$). We perform a rough calculation of entropy by dividing $C_P$ by $T$ and integrating

$$\Delta S = \int \frac{C_P}{T} dT \simeq \frac{1}{T_C} \int C_P dT.$$ \hspace{1cm} (1.15)

Since the integral is performed over a narrow temperature range about $T_C$ it is reasonable to make the approximation $T \simeq T_C$. We calculate the differential entropy change above and below $T_C$ by integrating from $T_1$ to $T_C$ for $\delta S_-$ and from $T_C$ to $T_2$
for \( \delta S_+ (T_1 \leq T_C \leq T_2) \)

\[
\delta S_+ = \frac{A_+}{\alpha T_C^{1-\alpha}} \int_{T_1}^{T_C} (T_C - T)^{-\alpha} = \frac{A_+}{\alpha T_C^{1-\alpha}} \frac{(T_C - T_1)^{1-\alpha}}{1 - \alpha} \quad (1.16a)
\]

\[
\delta S_- = \frac{A_-}{\alpha T_C^{1-\alpha}} \int_{T_C}^{T_1} (T - T_C)^{-\alpha} = \frac{A_-}{\alpha T_C^{1-\alpha}} \frac{(T_2 - T_C)^{1-\alpha}}{1 - \alpha}. \quad (1.16b)
\]

The entropy difference \( \Delta S \) across \( T_C \), is obtained by

\[
\Delta S = \delta S_+ - \delta S_- = \frac{1}{\alpha T_C^{1-\alpha}} \frac{1}{1 - \alpha} \left[ A_+ (T_2 - T_C)^{1-\alpha} - A_- (T_C - T_1)^{1-\alpha} \right]. \quad (1.17)
\]

In the limits \( T_1 \to T_C^{-} \) and \( T_2 \to T_C^{+} \), \( \Delta S \to 0 \) for \( \alpha < 1.0 \). When \( \alpha = 1.0 \), \( \Delta S \) diverges for all temperatures, and \( \Delta S \) diverges at \( T_C \) when \( \alpha > 1.0 \). Entropic divergence at \( T_C \) is incompatible with the expectation that entropy be continuous across \( T_C \) for a continuous phase transition. Therefore, we conclude that \( \alpha < 1.0 \) is required to maintain the phase transition’s classification as continuous.

The requirement that \( \alpha < 1.0 \) is rather broad and implies the existence of three distinct cases, each with its own consequences. When \( 0.0 < \alpha < 1.0 \), \( C_P \), as defined in Equation (1.14), diverges to infinity at \( T_C \). However, when \( -\infty \leq \alpha < 0.0 \), \( C_P \) is finite at \( T_C \) (\( C_P = B \)). In either case, simple power-law behavior is exhibited, but the character of \( C_P \) at \( T_C \) is very different. When \( \alpha = 0.0 \), there are two possible behaviors, neither of which can be obtained by simply substituting \( \alpha = 0.0 \) into Equation (1.14). Either there is a discontinuous jump in \( C_P \) at \( T_C \) (standard second-order Ehrenfest phase transition) or \( C_P \) diverges logarithmically in the vicinity of \( T_C \).

To obtain the latter form of \( C_P \) for \( \alpha = 0.0 \), we invoke a different expression for the
free energy than is found in Equation (1.4). In this case, $F_S$ is[14]

$$F_S(T, h) \approx g_t^2 \left( \ln |g_t|^{-1} \right) Y_\pm \left( g_h/|g_t|^\Delta \right) + g_t^2 Y_\pm \left( g_h/|g_t|^\Delta \right),$$  \hspace{1cm} (1.18)

and $C_P$, as calculated from Equation (1.18), is

$$C_P \simeq -A_\pm \log |t| + B + Dt,$$  \hspace{1cm} (1.19)

where $B + Dt$ provides an analytic background representing degrees of freedom decoupled from critical behavior.

**Universality Classes**

**Why Universality?**

Heretofore, our description of critical exponents has suggested that they are bounded by certain values, but are otherwise unconstrained. If there are constraints, which physical parameters might be relevant in selecting critical exponent values for a given system? And if there are a finite number of relevant parameters, does that lead to a finite number of possible exponent values for all systems rather than a continuum of values between bounds? These questions are at the heart of a concept termed universality.

Critical-exponent values have been published for a sufficiently large number of systems for an obvious pattern to emerge. A few specific exponent values are obtained for a wide variety of different magnetic materials.[2] More surprisingly, some materials that undergo completely distinct types of phase transitions share equivalent critical
exponent values. This is the case, for example, for the superfluid transition in liquid $^4$He and magnetic ordering in an easy-plane magnetic system.\textsuperscript{[31]} The emergence of these special exponent values heralded yet another scientific classification system. In 1970, it was L. P. Kadanoff who first proposed\textsuperscript{[31]} that systems exhibiting critical behavior could be classified into a finite number of “universality classes”. Regardless of the specific details of the system or its physics, all members of a universality class share a fundamentally similar nature, the consequences of which are identical critical exponents.

The next logical question is: Which physical parameters are relevant when distinguishing between universality classes? In considering this question, we restrict our attention to magnetic systems, both because they are the focus of this work, and because they make clear, illustrative examples. The basis for the theoretical description of magnetism is the Hamiltonian $\mathcal{H}$, which models spin-exchange interactions

$$\mathcal{H} = -J \sum_{\langle ij \rangle} \vec{S}_i \cdot \vec{S}_j.$$  \hfill (1.20)

The structure and details of a generic magnetic Hamiltonian include explicit or intrinsic dependence on the dimensionality of the crystal lattice $d$, the dimensionality of the spins $n$, the strength of magnetic exchange $J$, and the magnitude of the spin $S$. With the exception of $J$, the parameters are all quantized. Therefore, we should expect that critical exponents do not depend strongly on $J$. Of course, $J$ itself depends on spin and lattice dimensionality among other things, but it does not influence the critical exponents. Two systems with similar magnetic Hamiltonians except $J_1 \neq J_2$
can still have \( \alpha_1 = \alpha_2 \). Additionally, critical exponents are, at worst, very weakly-dependent on \( S \), and some studies even suggest that they are completely independent of \( S \).[2, 32] There are high-temperature series-expansion calculations[33] which suggest \( \alpha \), in particular, is sensitive to \( S \); however, it is likely that too few terms were included in the expansion to formulate a reasonable conclusion.[32] Therefore, critical exponent \( \alpha \) might have a weak \( S \)-dependence, but like \( J \), it is not substantial enough to use as a degree of freedom in the definitions of universality classes.

The remaining parameters on which universality classes may depend are the dimensionality of the crystalline lattice \( d \) and spins \( n \).[2] The lattice dimensionality is most commonly one, two, or three, however, renormalization-group calculations sometimes study non-integer lattice dimensionality between \( d = 3 - 3.99 \), for which results are obtainable.[34] One may wonder about the relevance of a one or two-dimensional lattice, but we really mean quasi-low dimensional in those cases. For example, the parent compounds of the high-temperature superconducting cuprates are quasi-two-dimensional Heisenberg antiferromagnets.[35] The two-dimensional nature of \( d \) is guaranteed by their layered crystal structure and the large disparity between intraplane \( J_\parallel \) and interplane \( J_\perp \) magnetic-exchange strengths (spin ordering is facilitated via dominant intraplane interactions \( J_\parallel/J_\perp \sim 10^4 - 10^5 \)).[35] Spin-dimensionality \( n \) actually refers to the number of degrees of freedom of the order parameter (magnetization for ferromagnetism and sub-lattice magnetization for antiferromagnetism). Therefore \( n = 1, 2, 3 \) are nothing but the Ising, XY, and Heisenberg
models, respectively. But there are a wealth of other possible values \( n \) could take in theory. The \( n \)-vector model, introduced by Stanley,[36] allows for numerous other possibilities, and there are published calculations and descriptions for \( n = -2, 0, 1, 2, 3, 4, 6, 8, 12, 16, 24, 48, \) and \( \infty.\)[34]

**Concerning Antiferromagnetism**

Before we consider the properties of various universality classes, we address the fundamental question of whether the predictions for a given universality class, which are usually calculated assuming a ferromagnetic model, are equally justifiable for an antiferromagnetic system. More to the point, should we have considered the type of magnetic order as a distinct characteristic which defines the universality class along with \( d \) and \( n \)? Superficially, it appears there is an enormous difference between ferromagnetism (spontaneous alignment of spins below \( T_C \)) and antiferromagnetism (spontaneous anti-alignment of spins below \( T_N \)). For example, there is only one way to align spins in a ferromagnet, while there are five distinct ways in which anti-alignment occurs in antiferromagnetic systems[37] (see Figure 5). Despite this seemingly insurmountable difference, there is a lot of evidence suggesting that this and other differences are insufficient to result in distinct critical behavior. For example, to convert between a ferromagnet and antiferromagnet in the Ising model \( (n = 1) \), one need merely change the sign of the magnetic interaction strength and, in the limit of zero field, there is an exact equality of the partition function for each case.[27] Therefore, predictions for critical behavior are the same. For the Heisenberg model
Figure 5. Distinct types of magnetic order assuming spins reside at the corners of a generic cubic unit cell. Type B is ferromagnetic ordering, while the other five types are antiferromagnetic.

\[ n = 3 \], a similar equality of partition functions occurs in the limit of infinite spin. However, if the specific value of the spin has no influence on the universality class, as we have already suggested, then there is a correspondence between ferromagnetic and antiferromagnetic ordering for the Heisenberg model as well.\[27\] Furthermore, there is ample experimental evidence demonstrating that critical exponents measured for antiferromagnetic systems correspond to critical behavior predicted for analogous ferromagnetic systems.\[38\]

There are two relevant distinctions between ferromagnetic and antiferromagnetic critical behavior. Long-range dipole contributions cause a magnetic system to deviate from ideal critical behavior, which is defined in terms of short-range interactions only.\[39\] Fortunately, dipolar forces are negligible in most antiferromagnetic systems,
but they can be large in ferromagnets (especially if $T_C$ is relatively low).[38] It is probably this discrepancy between the effect of dipole contributions on each system that originally led many to believe separate universality classes were necessary for ferromagnets and antiferromagnets.[39] Ahlers and Kornblit studied the critical behavior of Heisenberg ferromagnets EuO, Ni, and Fe (in order of decreasing dipole contribution, respectively), and Heisenberg antiferromagnet RbMnF$_3$.[40] They demonstrated that all four systems belong to the same universality class though each exhibits a slightly different $\alpha$. When $\alpha$ is plotted as a function of material, it converges smoothly to the result expected for the three-dimensional Heisenberg universality class as dipole contribution decreases. In this sense, antiferromagnetic systems are ideal to study.

The second relevant difference between ferromagnetism and antiferromagnetism is that there are some universality classes which are defined only for antiferromagnetic systems. For example, Mukamel et al. pioneered the idea of $n = 4, 6, 8, 12, 16, 24,$ and 48 universality classes for systems where the magnetic and chemical unit cells do not coincide.[41, 42, 43] For ferromagnets, the chemical and magnetic unit cells are always equivalent, so it is impossible for a ferromagnet to belong to these universality classes. Furthermore, the possibility of geometric magnetic frustration, leading to non-collinear magnetic order in antiferromagnets, creates the opportunity for additional universality classes. Such systems may belong to a special chirality universality class which exists for $n = 2$ and $n = 3$.[44] Unlike the $n \geq 4$ universality classes, there
are many experimentally-confirmed examples of the chiral universality class.[44] We
describe these and other universality classes in greater detail in the next section.

Description of Universality Classes

Most universality classes are named for their $n$-value and there is a $d = 1$, 2, and 3
version of each. Unfortunately, the critical behavior of almost none of the universality
classes are exactly solvable. The simple $n = 1$ Ising model has an analytic solution
for the $d = 1$ case, solved by Ising,[45] and for $d = 2$ (only when $H = 0$), solved
by Onsager.[46] Otherwise, the other universality classes typically present hopelessly
intractable problems when one attempts to determine a fully analytic solution of their
critical behavior. In those cases, there are numerous approximation techniques which
are employed to obtain estimates for critical exponents. Unhappy with the state of
things, theorists proposed new universality classes that could be solved analytically,
but are often not representative of any physical system. One of these was proposed
by Stanley,[47] for $n \to \infty$. This universality class is equivalent to the spherical
model of Kac, which was the first model for which an analytic solution for $d = 3$
was possible.[48] Later, Balian and Toulouse extended the order-parameter dimen-
sionality into the negative region with their $n = -2$ universality class.[49] Bizarrely,
this universality class, which is sometimes referred to as the Gaussian universality
class,[34] provides exact results for arbitrary $d$ and corresponds to a random walk-
type model.[31] There is also the strange universality class of $n = 0$, studied by de
Gennes,[50] which corresponds to the $d$-dimensional self-avoiding random walk, and models a system of dilute polymer molecules well.[31]

When our focus narrows to antiferromagnetic systems, universality classes with $n \geq 4$, proposed by Mukamel et al., are possible.[41, 42, 43] Depending on the specific type of magnetic anti-alignment in an antiferromagnetic system, the magnetic unit cell may be larger than the chemical unit cell. In such cases, the magnetic ordering vector $\vec{k} \neq (0,0,0)$ and the symmetry group with which $\vec{k}$ transforms is an irreducible representation of the space group of the paramagnetic phase at $T > T_N$.[41] The dimensionality of the irreducible representation of the group with which $\vec{k}$ transforms is equivalent to $n$, and can be 1, 2, or 3, or more interestingly, 4, 6, 8, 12, 16, 24, or 48.[41] As with most universality classes, approximation methods are employed to the study their critical behavior. Brezin et al. discovered that universality was weaker for $n \geq 4$ than for $n \leq 3$, meaning anisotropy or other details potentially create a wider range of possible exponent values within a given universality class when $n \geq 4$.[51] At present, we are unaware of experimental confirmation of a system being classified in one of the $n \geq 4$ universality classes. Mukamel proposed a substantial list of possible systems such as $n = 4$: TbAs, TbP, TbSb, DyC$_2$, TbAu$_2$, and NbO$_2$, $n = 6$: UO$_2$, K$_2$IrCl$_6$, TbD$_2$, and Nd, $n = 8$: MnO, MnSe, NiO, and ErSB, and $n = 12$: DySb and HoSb.[41] Most of these materials were later found to exhibit first-order transitions or did not exhibit the expected behavior for a member of a $n \geq 4$ universality class. While all $n < 3$ systems have stable fixed points in their $\epsilon$ expansions, systems
with \( n \geq 4 \) commonly have only unstable fixed points in theirs.\cite{12} In these cases, critical fluctuations may drive what Landau theory would predict to be a classic continuous phase transition to become first order.\cite{52} This occurs only very near \( T_C \), so it may appear that critical behavior exists in these weak first-order systems, which has lead to some confusion and conflicting conclusions in the past.\cite{52} Still, the idea of \( n \geq 4 \) universality classes is theoretically sound, and there may well yet be a tangible example exhibiting observable critical behavior.

To characterize and organize the universality classes as a function of \( n \) and \( d \), it is particularly illustrative to consider some wonderful contour plots of critical exponents \( \alpha, \beta, \gamma, \) and \( \eta \), originally published by Fisher.\cite{34} They are reprinted here in adapted form in Figure 6 with written permission from the American Physical Society and Dr. Michael Fisher. The contours, which were calculated with renormalization-group theory, provide an excellent overview of how the critical exponents behave as continuous functions of \( n \) and \( d \). Focusing on the upper left-hand plot for \( \alpha \), we make a few observations. The \( \alpha = 0 \) line that separates negative and positive \( \alpha \) values is the logarithmic divergence form of \( \alpha = 0 \). While, for \( d \geq 4 \), \( \alpha \) is also zero, but here it is in the mean-field theory discontinuous-jump form. Interestingly, the vast majority of universality classes exhibit negative \( \alpha \), with the two- and three-dimensional Ising models being the only common exceptions. The latter is positive while the former exhibits a logarithmic divergence (\( \alpha = 0 \)). Finally, we observe that some contours
Figure 6. Contour plots of critical exponents $\alpha$, $\beta$, $\gamma$, and $\eta$ as a function of order-parameter dimensionality $n$ and crystal dimensionality $d$. The dots and squares indicate the position of universality classes as a function of coordinates $(d, n)$. Reprinted in adapted form with permission from M. E. Fisher, Rev. Mod. Phys. 46, 597-616 (1974). Copyright 1974 by the American Physical Society.
in Figure 6 have $\alpha \geq 1.0$. These are included for completeness, but as previously discussed, a phase transition must be classified as first order when $\alpha \geq 1.0$.

The universality classes represented in Figure 6 (those organized mainly by $n$ and $d$) are referred to as Wilson-Fisher universality classes. Looking beyond them, we can find the chiral universality classes, which are not represented in Figure 6. These exist purely because of the potential for geometric frustration of antiferromagnetically ordered spins in various triangular topologies. The non-collinear order which results in such cases contains an intrinsic degree of freedom called chirality. Chirality may be left- or right-handed and this extra degree of freedom results in a distinct chiral universality class for $n = 2$ (XY spins) and $n = 3$ (Heisenberg spins), which is characterized by a sharp discontinuity in $C_P$ with $\alpha$ in the neighborhood of 0.3-0.4.\[44] There are many tangible examples of chiral systems such as $n = 2$: CsMnBr$_3$, CsVBr$_3$ and $n = 3$: VBr$_2$, VCl$_2$, CsVCl$_3$, and RbNiCl$_3$.\[44]

**Experimental Determination of $\alpha$**

**Common Measurements to Determine $\alpha$**

As might be expected, the most direct way to measure the heat-capacity critical-exponent $\alpha$ is by measuring heat capacity. However, physicists are far more imaginative than to stop there. We call $\alpha$ the “heat-capacity” exponent, but any thermodynamic parameter that is proportional to heat capacity, should exhibit critical behavior characterized by exponent $\alpha$. This allows several experimentally accessible physical
properties to serve as suitable substitutions for heat capacity when measuring $\alpha$, including the temperature derivative of electrical resistivity $d\rho/dT$, thermal diffusivity $D$, thermal conductivity $\kappa$, and the temperature derivatives of optical birefringence $d(\Delta n)/dT$ and thermal expansion multiplied by temperature $\Omega T$. We discuss each of these measurements in turn, except thermal expansion, which is covered in great detail later.

A power-law anomaly in the derivative of electrical resistivity $d\rho/dT$ was observed in the vicinity of $T_C$ of ferromagnetic Ni.[53] This behavior is consistent with $|t|^{-\alpha}$-type critical behavior. From an elementary perspective, we know that collisions between conduction electrons and other conduction electrons or phonons influence the behavior of $\rho(T)$, so it makes sense that magnons should influence $\rho(T)$ as well. Work by de Gennes and Friedel[54] emphasized the role of long-range correlated spin fluctuations in scattering conduction electrons, which results in singular behavior of $\rho$ around $T_C$,

$$\rho(T) \simeq \rho_C - b|t| \ln \frac{1}{|t|},$$

(1.21)

where $b > 0$. However, this result is incompatible with experimental observations.[53] Fisher and Langer[55] later provided theoretical support for the observations of Craig et al. in Ni by arguing for the dominance of short-range interactions. Their calculations of relaxation rates $\tau$ assumed spin fluctuations are slow enough that inelasticity effects are negligible and they found that $d\rho/dT \sim |t|^{-\alpha}$.[55] Recent use of this technique has been successfully applied[56, 57] to ferromagnetic systems CrO$_2$ and Sr$_2$FeMoO$_6$. However, it is of limited utility. While there are many excellent
examples of ferromagnetic metals, antiferromagnetic metals are rare comparatively. To our knowledge, only one study of $d\rho/dT$ has been conducted on a metallic antiferromagnet. Malmström and Geldart studied elemental Dy in the vicinity of $T_N \simeq 180.5$ K.[58] However, this transition was later determined to be first order.[52]

Measurements of thermal diffusivity $D(T)$, which is proportional to heat capacity, are generally made with a photopyroelectric calorimeter.[59, 60] This measurement has been successfully applied[59, 60] to the critical behavior of antiferromagnetic systems such as NiO, CoO, and KMnF$_3$. Furthermore, when thermal effusivity $e(T)$ and $D(T)$ are measured simultaneously, thermal conductivity $\kappa$, which is a function of $e(T)$ and $D(T)$, can be calculated.[59, 60] Heat capacity and thermal conductivity are inversely proportional so $1/\kappa(T) \sim |t|^{-\alpha}$. However, for many magnetic systems, no anomaly is observed in direct[61] or indirect[60] measurements of $\kappa$. This is generally attributed to the lattice (or electronic) contributions to thermal conductivity dominating any smaller contributions from magnetic order.[61]

One final measurement, commonly used to measure $\alpha$, is the linear optical birefringence $\Delta n$. Its temperature derivative $d(\Delta n)/dT$ is proportional to the singular part of $C_P$ in the vicinity of antiferromagnetic phase transitions for many systems.[62, 63] There are two pertinent advantages to using this technique. The most important is that $\Delta n$ is relatively insensitive to phonons, so there is a small background contribution.[62, 63] The second advantage is that the effect of concentration gradients, which have been quenched into a doped system, may be minimized by a
particular orientation of the LASER with respect to the concentration gradient.[62] This is why the optical birefringence method is most commonly associated with the study of magnetic systems diluted with non-magnetic impurities. It has also been successfully applied[64] to antiferromagnetic di-Fluoride compounds such as FeF$_2$, MnF$_2$, CoF$_2$, and NiF$_2$. The technique does have severe limitations, however, and is applicable to only a small subset of antiferromagnetic systems. The phenomenon of birefringence occurs in materials with anisotropic optical properties, and so the system must not only be anisotropic, it must be transparent. Even if a material is transparent and optically anisotropic, there are cases where other factors limit the applicability of the method. For example, proportionality between $d(\Delta n)/dT$ and $C_P$ breaks down for certain pseudo-low dimensional systems and dilute magnetic systems at their percolation threshold.[62]

**Extraction of $\alpha$ from Experiment**

The challenge of measuring data of suitable quality in the critical region around $T_C$ is probably only surpassed by the difficulty in properly analyzing it. Numerous factors conspire to present a tricky task when performing analysis of data in the critical region. Two impediments are particularly challenging. First, the models used to fit $C_P$, or any data which is proportional to $C_P$, contain a large number of fit parameters. In general, more fittable parameters allow us to obtain a statistically-good fit with ease, but the best-fit solution might be unphysical or non-sensical. This means that the best-fit solution cannot be blindly accepted, and we need to know
when to constrain certain fit parameters and re-fit the data. Second, there is no proven method for knowing over which temperature ranges to fit critical behavior \textit{a priori}. We develop some basic guidelines, but still must fit over many different reduced temperature ranges and empirically decide which range provides the best and most reliable answer.

**Critical Expressions for Heat Capacity.** The scaling form of the thermodynamic free energy in Equation (1.4) does not include contributions from irrelevant variables such as \( u \) with associated non-linear scaling field \( g_u \). By including \( u \) in the free energy, we are able to obtain a more general expression

\[
F_S(T, h, u) = |g_t|^2 - \alpha Y \pm \left( \frac{g_h}{|g_t|} \Delta, g_u |g_t|^\theta_u \right), \tag{1.22}
\]

where the irrelevant-variable exponent obeys \( \theta_u > 0 \).[14] We recalculate \( C_P \) from Equation (1.22)

\[
C_P \simeq \frac{A_\pm}{\alpha} |t|^{-\alpha} \left[ 1 + E_\pm |t|^\chi \right] + B + Dt, \tag{1.23}
\]

which includes a non-analytic correction term, where \( \theta_u \) is more commonly called \( \chi \). For every known universality class, \( \chi = 0.5 \pm 0.1 \).[14, 65] Most experiments are unable to truly penetrate the asymptotic critical temperature region (where Equation (1.14) is sufficient), and it becomes necessary to include the non-analytic correction term, called the confluent singularity, to access it. When we consider the \( \alpha = 0 \) case, we are unaware of a corresponding correction, so the most general \( C_P \) expression remains
Equation (1.19):

\[ C_P \simeq -A_\pm \log |t| + B + D t. \] (1.24)

Each parameter in the expressions for \( C_P \) must be well understood, because a fit with so many parameters has the potential for unphysical least-squares solutions. Therefore, the range of acceptable values for each parameter must be known. For example, \( A_+ \) and \( A_- \) are never constrained, but the ratio \( A_+/A_- \sim 0.5 - 1.5 \) is typically observed.[66] The scaling-law hypothesis states that critical-exponent \( \alpha \) is equal on both sides of \( T_C \). At one time, there was some question about the validity of this hypothesis and many studies incorrectly concluded that \( \alpha_- \neq \alpha_+ \).[67, 68] It is sometimes an interesting exercise to check whether \( \alpha_- = \alpha_+ \) by allowing \( \alpha \) to be different in the fit on each side of \( T_C \).[69] However, it is perfectly justifiable to assume the constraint \( \alpha_- = \alpha_+ \) from the beginning of the analysis. Concerning the confluent singularity, it is common to constrain \( \chi = 0.5 \), or to a similar value, and fit over \( E_- \) and \( E_+ \). As far as we are aware, thermodynamics does not constrain the values of \( E_\pm \) (they can be negative or positive). There are many instances in the literature where the constraint \( B_- = B_+ = B \), suggested by Equation (1.23), was not imposed.[67, 70, 71] When \( \alpha < 0 \), the anomaly is finite at \( T_C \) (\( C_P(T_C) = B \)). Thus \( B_- = B_+ = B \), because otherwise, there would be a discontinuity at \( T_C \), which is only acceptable for \( \alpha = 0 \). Renormalization-group calculations extend the generality of this constraint into the region where \( \alpha > 0 \),[40, 69] so in general, there is only one value of \( B \). This is also true of \( D \), though this has never been disputed in the
literature. Both $B$ and $D$ must be positive because they represent the phonon and electronic contributions to heat capacity. The final parameter in Equation (1.23) is the critical temperature $T_C$, which is tacitly present in the reduced temperature terms. Fortunately, it is one of the easiest parameters for which to obtain an initial guess. $T_C$ will be very near the temperature of maximum $C_P$, but because of data rounding in that vicinity, the true $T_C$ is often about 1 mK higher than the temperature of the maximum.[65]

**Critical Temperature Region.** Critical behavior is observed in an asymptotic “critical temperature region” that has yet to be defined. In order to make general statements about the size of the critical region for any transition, it is advantageous to think in terms of the reduced temperature $t$, which is normalized by $T_C$. The schematic in Figure 7 provides a summary. It is difficult to state exactly when critical behavior begins, but it is generally somewhere between $10^{-2} < |t| \leq 10^{-1}$ for all transitions.[27] Then as $T_C$ is approached, a variety of effects distort the anomaly and mask the expected critical behavior. For example, earth’s magnetic field ($\sim 0.5$ Oe) causes minor rounding of the anomaly for $|t| \leq 10^{-3}$ in ferromagnets.[69] because critical behavior is defined only for zero applied field.[32] This is not a problem for antiferromagnets whose critical behavior is immune to the effect of modest applied fields.[32] For all magnetic materials, however, even a modest level of inhomogeneities
and defects (especially dislocations), which are present in all samples, create an impenetrable barrier for \(|t| \leq 10^{-4}\) where the behavior of the anomaly is hopelessly distorted from ideal critical behavior.[72] Magnetic domains must be larger than the correlation length \(\xi\), which diverges as \(T \to T_C\), for thermodynamic properties to exhibit undistorted critical behavior.[27] Therefore, significant broadening is expected to occur when \(\xi \geq L\) where \(L\) is the characteristic size of domains. Defects limit the size of magnetic domains so it is beneficial to measure the highest quality samples possible in order to maximize the temperature range over which critical behavior is exhibited. It is the goal of every experiment studying critical behavior in a magnetic

\[ t = (T - T_C)T_C \]
system to reach the $|t| = 10^{-4}$ threshold. Other systems, such as the superfluid transition in $^4$He, are able to exhibit undistorted critical behavior to $|t| \sim 10^{-7}$ where the effect of earth’s gravity becomes a limiting factor.[72] It is for this reason, there have been numerous experiments to measure the heat capacity of the superfluid transition in microgravity environments to extend the critical temperature range.[73]

**Least-Squares Fitting Procedure.** The best way to fit data with either Equation (1.23) or (1.24) is by using a non-linear Levenberg-Marquardt algorithm to do least-squares fitting. A great procedure is described in References [38, 40, 69], which has been adopted by most studies. We briefly summarize it here. The procedure begins by fitting Equation (1.23), without the confluent singularity ($E_- = E_+ = 0$), over increasingly-large temperature regions until the critical region is maximized without sacrificing fit quality. The confluent singularity is then included, which corrects the best-fit parameters and increases the asymptotic region over which a good fit for Equation (1.23) may be obtained (again the data is fit over many different temperature ranges). Assuming the solution consists of acceptable fit parameter values, this is the critical behavior that is published.

**Historical Application of Dilatometry**

An overview of various thermodynamic measurements used to extract the critical-exponent $\alpha$ was already presented. However, thermal expansion was not considered in that discussion. We now present a brief overview covering the limited historical
application of thermal expansion to the study of critical behavior, which sets the
stage for the rest of this work.

The ability of techniques such as capacitance-based dilatometry to measure ther-
mal expansion with astounding resolution makes it a useful tool to study critical
behavior. Historically, there have been very few who have recognized this potential
even after the precision and accuracy required to quantitatively study critical behav-
ior was achieved. It seems that those experimentalists who studied critical behavior
(specifically those interested in extracting $\alpha$) relied on heat-capacity measurements,
while those who measured thermal expansion were uninterested in applying their data
to study critical behavior.

With the exception of recent work conducted by the Neumeier group at Montana
State University, there are only two examples of which we are aware where thermal
expansion measurements were applied to study the critical behavior of a magnetic
system. The first of these was conducted by Philp et al. who studied the hydrated
antiferromagnetic salts MnCl$_2$·4H$_2$O and MnBr$_2$·4H$_2$O.[67] Their measurements were
performed with a dilatometer in the vicinity of $T_N$ (1.62 K and 2.12 K, respectively),
and they measured single crystals of both systems along each of the three principle
crystallographic directions of their monoclinic crystal structures. Unfortunately, in
their fits of linear thermal-expansion data, they relaxed the constraint imposed by
the scaling hypothesis and allowed $\alpha_- \neq \alpha_+$. Their conclusion for each material was
that $\alpha_- = 0$ (logarithmic divergence) and $\alpha_+ \simeq 0.32$ and 0.40, respectively, which
is a gross violation of scaling.[67] A heat-capacity study of the critical behavior of both materials was later conducted, concluding that $\alpha \simeq 0.125$ for each.[65] This result not only satisfies the scaling hypothesis, it classifies both materials as three-dimensional Ising antiferromagnets. The thermal-expansion study of Philp et al. did discover that the critical exponent $\alpha$, flawed as it was, appeared to be the same along each crystallographic direction. We are unaware of any theoretical evidence which suggests this must be true in general, but it is certainly intuitive to expect that the same characteristics of critical behavior exhibited by the volume coefficient of thermal expansion are exhibited along each principal crystallographic axis.

A few years later, the classic cubic antiferromagnet $\text{RbMnF}_3$ was measured by Golding with a dilatometer.[74] His data is of high quality, but the corresponding critical-behavior analysis he conducted was also flawed. Like Philp et al., Golding concluded that $\alpha_- \neq \alpha_+$ with values $\alpha_+ = 0.007 \pm 0.02$ and $\alpha_- = -0.100 \pm 0.03$. This same thermal-expansion data was later reanalyzed by Kornblit and Ahlers[38] in tandem with a critical-behavior study of the heat capacity using the same $\text{RbMnF}_3$ crystal measured by Golding. They introduced confluent singularity terms to their fit and obtained $\alpha = -0.15 \pm 0.16$ after adjusting $T_N$ significantly from Golding’s best-fit value for $T_N$. This critical exponent was entirely consistent with their heat-capacity study for which they obtained $\alpha = -0.14 \pm 0.01$.[38] Unfortunately, the uncertainty of $\alpha$ from the analysis of thermal expansion is more than 100% and covers multiple universality classes.
Beyond these two examples, there are a few successful cases where thermal expansion has been applied to study critical behavior in non-magnetic transitions. For example, Ahlers successfully used it to study the superfluid transition in $^4$He finding $\alpha = -0.026 \pm 0.004$.[72] And Pasler et al. studied critical fluctuations around the superconducting phase transition in YBa$_2$Cu$_3$O$_{7-\delta}$ finding $|\alpha| \leq 0.018$.[15] Each of these transitions therefore belongs to the three-dimensional XY universality class. In general, the history of applying thermal-expansion measurements to the study of critical behavior is limited and sparse, though it could play a more important role if thermal-expansion measurements were more widely conducted and suitable strategies for applying them were developed.

**Thesis Statement and Outline of Thesis**

The history of applying thermal-expansion measurements to the study of critical behavior is remarkably limited. Those few studies which do exist could be improved by implementing strategies to analyze the data with specific suitability to thermal expansion in mind. Perhaps the existence of a few successful test cases of such an analysis would provide sufficient evidence to convince even the most stubborn of the validity of the overall concept and prompt similar studies on other materials. It is therefore our objective to support the following thesis statement: *Analysis of high-resolution measurements of thermal expansion is a legitimate method to study critical phenomena in antiferromagnetic systems.* By legitimate, we mean thermal expansion
is as, or more valid, than other measurements like heat capacity to study classical critical phenomena. To support this thesis statement, we successfully study the critical behavior exhibited by antiferromagnetic CaMn$_2$O$_4$, Bi$_2$CuO$_4$, and $\alpha$-Mn with thermal expansion. Antiferromagnetic systems are not as susceptible as ferromagnetic materials to long-range dipole contributions which adjust the behavior away from ideal critical behavior predicted by theory. Therefore, antiferromagnetic systems typically make better test cases to compare experiment with theory.

The organization of this dissertation follows a logical progression starting with Chapter 2 where the concept of crystal growth by the floating-zone technique is introduced. Single-crystalline test systems CaMn$_2$O$_4$ and Bi$_2$CuO$_4$ were grown by this technique. Details and tricks concerning the implementation of the floating-zone method are reviewed which have been gained from extensive experience with successful and unsuccessful attempts to grow crystals of many different materials. In Chapter 3, the characterization techniques we used to assess the quality of our crystals are discussed including x-ray techniques and iodometric titration. Particular emphasis is placed on the orientation of single crystals which played an important role in this work because we measured thermal expansion along the distinct, principle crystallographic axes of our crystals (along lattice-parameter directions). Our single crystals were oriented with high precision using strategies discussed in detail and simulated Laue patterns generated by a program we wrote specifically for this purpose. In Chapter 4, a description of experimental measurement techniques is provided including
vibrating-sample magnetometry, heat capacity by the thermal-relaxation technique, and high-resolution dilatometry. Each of these measurements, especially the latter two, play integral roles in this work. The concept of thermal expansion is discussed from a theoretical and practical perspective in Chapter 5 to introduce relevant details regarding this relatively enigmatic physical property. Following our discussion of thermal expansion, we review the important thermodynamic relationships between thermal expansion and heat capacity in Chapter 6. The Pippard relation justifies the study of critical behavior with thermal expansion by scaling $\Omega T$ with $C_P$. Details regarding the uniqueness of scaling parameters and the equivalence of the Pippard and Ehrenfest relations, which to our knowledge have never before been addressed, are emphasized. Given justification to use thermal expansion to study critical behavior which is solidly grounded in thermodynamics, we consider the consequences of doing so in Chapter 7. Potential advantages and disadvantages, compared relative to heat capacity, are discussed and strategies uniquely suited to study critical behavior with thermal expansion are developed. In the course of this analysis, we produce a critical expression for $\Delta V/V$ in order to quantitatively investigate the detrimental effect numerically differentiating $\Delta V/V$ data to obtain $\Omega$ has on the critical behavior exhibited by $\Omega T$. Having considered potential strategies and relevant details, we test these ideas on thermal-expansion data in the vicinity of $T_N$ from three antiferromagnetic systems. In Chapter 8, we study the textbook antiferromagnetic transition of single-crystalline CaMn$_2$O$_4$. The critical behavior exhibited by $\lambda \Omega T$
is studied as is the behavior of $\lambda_i \mu_i T$ along each principle axis of the orthorhombic crystal structure ($\lambda$ and $\lambda_i$ are scaling constants). The results are fully consistent with all known predictions for the three-dimensional Ising universality class. We also fit thermal-expansion data $(\Delta L/L)_i$ along each principal crystallographic axis with our new critical expression demonstrating that the critical temperature region does extend to the $|t| \sim 10^{-4}$ boundary. Following this successful application of thermal expansion, we study the critical behavior of single-crystalline Bi$_2$CuO$_4$ in Chapter 9. Using the same strategies employed for CaMn$_2$O$_4$, we demonstrate that the transition in Bi$_2$CuO$_4$ also belongs to the three-dimensional Ising universality class. This conclusion settles a long-standing question by suggesting Bi$_2$CuO$_4$ exhibits easy-axis anisotropy rather than easy-plane anisotropy and provides a second successful test case. Finally, the limitations of studying critical behavior with a polycrystalline sample are demonstrated when we investigate the antiferromagnetic transition of $\alpha$-Mn in Chapter 10. $\alpha$-Mn has extremely complicated crystal and magnetic structures and we examine the possibility that its magnetic phase transition belongs to an $n \geq 4$ universality class. We conclude that the transition in $\alpha$-Mn most likely belongs to either the three-dimensional Heisenberg or three-dimensional $n = 4$ universality class. Having produced three successful examples, we feel justified in our conclusion that we have offered sufficiently-convincing evidence that the application of thermal expansion to study critical behavior in antiferromagnetic systems is a valid, useful technique.
SINGLE-CRYSTAL GROWTH WITH THE FLOATING-ZONE METHOD

Introduction to Single-Crystal Growth

The growth of single crystals has been a major area of research for more than a century and the perfection of crystal quality continues to drive progress in technology and discoveries of a subtle physical nature. For example, one of the major differences between the Nobel prize winning discoveries of the quantized Hall effect[6] and the more general fractional quantized Hall effect[75] was simply an improvement in sample quality!

There exist numerous techniques to grow single crystals, most of which, precipitate crystals from a molten solution. These include such well-known techniques as the Bridgman-Stockbarger,[76, 77] Czochralski,[78] high-temperature solution (flux), and floating-zone methods.[79] Some crystals can also be grown from vapor as is done in the vapor-transport method.[80, 81, 82] Furthermore, it is possible in some metals to grow large single-crystalline grains in a polycrystalline sample simply from extended anneals at temperatures sufficiently close to the melting temperature.[83] Therefore, synthesis of single crystals is possible from all three phases of matter: solid, liquid, and gaseous. However, we restrict our attention in this chapter to the floating-zone method and thus shall only consider growth from molten solutions.

While it is not our intention to provide a complete description of the theory of crystal growth from the melt, there are a few fundamentals which warrant a brief
treatment. We begin by considering a liquid just above its melting temperature \( T_m \). As the temperature of the melt is lowered to \( T_m \), the free energies of the melt and solid phases are identical so we expect the system to begin the solidification/crystallization process wherein molten and solid phases coexist in thermodynamic equilibrium. However, if the temperature is decreased carefully, it is possible for the system to remain entirely molten at temperatures below \( T_m \). This metastable state is referred to as supercooled or undercooled. A supercooled system is described by essentially the same physics as a supersaturated solution, so it is common among crystal growers to refer to a supercooled state as supersaturated. We adhere to this practice henceforth. At \( T_m \), the chemical potentials \( \mu = (\partial G/\partial n)_{P,T} \) of the molten and solid/crystalline phases (\( \mu_\ell \) and \( \mu_c \), respectively) are equal. Note that \( G \) is the Gibb’s free energy and \( n \) is particle number. However, in the supercooled state, there exists a non-zero difference between chemical potentials \( \Delta \mu = [\mu_\ell(T) - \mu_\ell(T_m)] - [\mu_c(T) - \mu_c(T_m)] \), which is referred to as the supersaturation.[84] Crystallization from the melt is driven by the magnitude of \( \Delta \mu \).

It is energetically favorable for a supercooled liquid to solidify, but to produce a high-quality single crystal, nucleation must develop first. The formation of a new phase, such as a crystal in equilibrium with a supersaturated melt, requires the appearance of small clusters from which the crystal may be constructed. This is nucleation. Nucleation may be homogeneous or heterogeneous depending on whether it occurs in the absence or presence of foreign particles or matter, respectively. For
example, in the floating-zone method, the presence of the interface between a polycrystalline seed rod and the molten zone allows for heterogeneous nucleation. In general, nucleation is a slow process, but heterogeneous nucleation is faster than homogeneous nucleation because the foreign matter acts as a pre-existing scaffold from which the crystal may build upon. In homogenous nucleation, thermal fluctuations drive the spontaneous formation of tiny crystals where local supersaturation levels are maximum.

Following nucleation, self-assembly of the crystal is initiated. The equilibrium shape of a growing crystal is determined by thermodynamics. The work of formation has a volume term, \((P_c - P_\ell) V_c = n(\mu_\ell - \mu_c)\), which is gained when \(n\) atoms, driven by supersaturation, transfer from the ambient liquid phase to the crystal\.[84] There is also a surface term which represents the energy spent creating the new crystal-melt interface\.[84] According to the Wulff rule\.[85] the equilibrium distance between a given crystal face and the center of the crystal is proportional to its surface energy. A simple way to yield the equilibrium shape, then, is to draw vectors normal to all crystallographic planes which originate at the crystal center and have magnitudes corresponding to the plane’s surface energy. If planes are drawn perpendicular to all vectors at their tips, the polyhedron with the smallest volume is the equilibrium form for the crystal and contains only facets with the lowest surface energies\.[84] Those vectors which extend beyond the equilibrium polyhedron or whose tips end on its
vertices correspond to crystallographic planes which do not belong to the equilibrium form.

![Cubic Kossel crystal with face sites at \(\{1 0 0\}\), step sites at \(\{1 1 0\}\), and kink sites at \(\{1 1 1\}\).](image)

Figure 8. Cubic Kossel crystal with face sites at \(\{1 0 0\}\), step sites at \(\{1 1 0\}\), and kink sites at \(\{1 1 1\}\).

The final subject we shall consider in our brief introduction to crystal growth from the melt is that of growth kinetics. Each crystallographic plane has a distinct growth rate which depends on its surface energy and leads to the equilibrium topology of the crystal. But how do atoms know where to incorporate themselves in a growing crystal’s surface and how can we quantify the growth rate of crystalline planes? Consider a structure composed of cubic blocks as a model for a growing crystal (see Figure 8). We are able to identify three distinct positions wherein a new block may be placed: kink sites, step sites, and face sites. A block incorporated into this structure has a “chemical bond” with one, two, or three other blocks, respectively, depending on whether it is in a face, step, or kink site. Though we shall not consider the
details which are aptly described elsewhere,[84, 86] it is known that crystals prefer to assemble themselves by filling kink sites. The growth speed of a crystallographic face depends then on its intrinsic density of kink sites.[84] For example, in Figure 8, the \{1 1 1\} planes offer the greatest density of kink sites, the \{1 1 0\} planes offer less density, and there are no kink sites on faces such as \{1 0 0\}. Thus, the \{1 1 1\} and \{1 1 0\} faces will grow until the crystal is a cube bounded by the \{1 0 0\} faces.

In the presence of low levels of supersaturation, a smooth face can theoretically be entirely resistant to growth. However, defects such as dislocations are always present and allow for a limited number of kink sites on otherwise smooth faces.

**Image Furnace**

An NEC Machinery Corporation model SC1-MDH optical image furnace with a two-lamp, two-mirror configuration was used for all single-crystal growth experiments in this work. Image furnaces are somewhat rare in the United States mainly due to the combination of high cost and a general attitude which de-emphasizes sample synthesis.[87] The furnace works primarily on the principle that focused light from two halogen lamps can be used to locally melt a sample, so that both good electrical conductors and insulators can be grown. This is a marked improvement over the original floating-zone technique which relied on induction heating, and therefore could only grow crystals with good electrical conductivity.[88]
The furnace itself is quite large; weighing approximately 1200 kg (2645.55 lbs) and having dimensions $1.140 \times 1.170 \times 2.250$ m$^3$ ($3.75 \times 3.84 \times 7.38$ ft$^3$).[89] It is compartmentalized with access provided by four doors on the front (one each for the bottom and top sections and two doors in the middle). The top and bottom doors allow access to the shafts when it is necessary to remove and clean them while the middle doors provide direct access to the lamps, elliptical cavities, and the crystal boule itself. On the right-bottom panel, there is a flow meter and pressure gauge for monitoring atmosphere conditions during growth.

Figure 9. Schematic of the elliptical cavities and their ability to focus light from two halogen lamps positioned at the foci of the ellipse into a small volume in the center. This allows us to locally melt the tips of two polycrystalline rods.

To use focused light as a heating mechanism, two halogen lamps are aligned in such a way that the filament of each lamp is positioned at the focal point of an elliptical hemispheric cavity. When the two elliptical hemispheres are joined, they
form a single ellipse so that light emitted from each focal point is directed towards the center of the ellipse after a single reflection from the cavity walls. This is depicted schematically on the left side of Figure 9. Assuming proper alignment of the halogen lamps, the light is focused into a tight region at the elliptical cavity’s center called the heat zone. The interior walls of the cavity are covered with a thin layer of gold to improve reflectivity and ensure that the majority of the light emitted from the halogen lamps is focused into the heat zone instead of being absorbed. When using the maximum-power 3.5 kW lamps, temperatures of approximately 2150°C can be reached depending on the reflectivity of the sample, the growth atmosphere, and other properties.[89] The elliptical cavities are displayed from the side in Figure 10(a) and (b) in their open and closed configurations, respectively. The interior of an elliptical cavity with halogen lamp inside is highlighted in Figure 10(c).

The feed and seed rods, between which the molten floating zone resides, are mounted to an upper and lower stainless-steel shaft. The shafts are capable of independent motion but can also be programmed to move together. They are able to move up or down with speeds between 0.5 mm/hr and 18000 mm/hr and to rotate clockwise or counterclockwise with rotational speeds between 6 and 60 rpm.[89] These speeds and directions may be adjusted manually or programmed into a sequence with the image-furnace software.

The shafts and the feed and seed rods are isolated from the ambient atmosphere of the lab by a quartz tube which is 5 mm thick. The tube can be seen in Figure
Figure 10. Photographs (courtesy of the author) of the optical floating-zone furnace which depict its most important components.

10(d) and allows crystal growth to be conducted in most atmospheres (air, O₂, N₂, Ar, H₂, CO₂, etc.) with pressures ranging from a modest vacuum to 970 kPa (9.57 atmospheres).[89] The quartz tube also protects the inner surfaces of the elliptical cavities. Flow rates between 0.5 and 5 L/min are also accommodated by the system if optimized crystal growth requires an environment with flowing gas.[89]

The heat produced by the aligned halogen lamps increases the temperature of the lamps, shafts, quartz tube, and elliptical-cavity walls in addition to its intended function of locally melting the polycrystalline rods. Through the course of a typical growth experiment, which lasts between six hours and a few days, these other components are continually heated. To remove this unintentionally-added thermal energy,
the elliptical cavities, shafts, and surfaces in contact with the quartz tube are water cooled while an air cooling unit blows air over the halogen lamps.[89] The yellow and blue tubes in Figure 10(a) and (b) supply cooling water to the elliptical cavities and quartz-tube contact surfaces, respectively.

A CCD camera is mounted to the back wall of the image furnace as can be seen in Figure 10(a) and (c). This camera provides continual visual access to the growth. This allows the crystal grower to react immediately to any detrimental perturbations of the molten zone by manually adjusting growth parameters.

**Floating-Zone Technique**

![Diagram of floating-zone system](image)

Figure 11. Schematic of the floating-zone system which is made of a feed rod, molten zone, growing crystal, and seed rod.

The floating-zone technique was developed to grow large single crystals with high levels of chemical purity. At its foundation, the technique consists of melting the
tips of two vertically-oriented, collinear rods (both polycrystalline or the seed rod may already be a single crystal) until a molten zone is established by joining the liquefied ends. Thus a floating zone or liquid bridge, held together against gravity by surface tension, resides between the two solid rods as can be seen in Figure 11. It is of significant importance that the molten zone be mechanically stable and thermally homogenous before crystal growth begins. For the molten zone to be considered mechanically stable, it must not vibrate or wobble. These perturbations tend to be caused by poor rod alignment, curved rods, or solid pieces of feed rod suddenly descending into the molten zone. As part of the stability requirement, the molten zone should not be too large or small. If it is too large, excess melt can run down and over the side of the seed rod/grown crystal and if it is too small, the molten zone may collapse. The molten zone shape should be such that the minimum width is the same as the zone height. Theory says that a maximum zone height is proportional\([90]\) to \((\gamma/\rho g)^{1/2}\) where \(\gamma\) and \(\rho\) are the surface tension and density of the melt, respectively, and \(g\) is the local acceleration of gravity \(g = 9.81 \text{ m s}^{-2}\). To ensure thermal homogeneity, the feed and seed rods are counter-rotated which acts to stir the molten zone.\([90]\] A secondary effect of the rod counter-rotation is to keep the molten zone chemically homogeneous; a necessary condition for homogeneous crystals.

After stabilizing the molten zone, crystal growth is initiated by moving the upper and lower shafts (and therefore the system composed of the feed rod, molten zone, and seed rod) either downward or upward through the heat zone with controlled speeds.
It is conventional to grow in the downward direction. As the system (rods and molten zone) is moved down through the heat zone, the bottom portion of the molten zone will begin to solidify as it descends to a position in the vertical temperature gradient of the heat zone which allows solidification. As liquid leaves the molten zone to participate in the formation of the solid, it is replaced by liquid from the feed rod whose lower tip has descended to a position in the vertical temperature gradient which allows it to melt. The process continues until the feed rod is reduced to a stub a few millimeters in length. It is a dynamic process which requires skill and experience to achieve success. A successful growth results from selection of appropriate growth parameters combined with careful control of the molten zone.

An excellent review article on the topic of the floating-zone method, which includes references to all published accounts of crystal growth by this technique through 2008, is found in Reference [79].

**Traveling-Solvent Floating-Zone Technique**

Congruently-melting compounds can generally be grown quite easily with the floating-zone method. However, in the case of a material which melts incongruently, we must use the traveling-solvent floating-zone method. To explain this method, it is best to provide an example. Consider the pseudo-binary phase diagram between two generic oxides $\text{A}_2\text{O}_3-\text{BO}$ illustrated in Figure 12. According to the phase diagram, in principal we could grow single crystals of $\delta\text{-A}_2\text{O}_3$, BO, and $\text{A}_2\text{BO}_4$ from the melt.
While the first two melt congruently, $\text{A}_2\text{BO}_4$ decomposes: $\text{A}_2\text{BO}_4 \rightarrow \text{BO} + \text{Liquid}$, before melting completely. If we were to make a feed and seed rod with composition $\text{A}_2\text{BO}_4$, when we establish the molten zone (depicted by the vertical, dashed red line in Figure 12), the initial melt composition is $x \equiv x_B/(x_A + x_B) = 0.33$ ($\text{A}_2\text{BO}_4$). So according to the phase diagram, BO will precipitate as the feed and seed rods travel down through the zone. As this occurs, the molten zone loses BO and replaces it with $\text{A}_2\text{BO}_4$. Thus the chemical composition of the melt is not constant, but rather, can be made to follow the liquidus line on Figure 12 as it becomes A-rich. When $x = 0.20$, $\text{A}_2\text{BO}_4$ precipitates from the melt and $x$ remains constant because the feed rod supplies material which chemically compensates for the precipitated crystal. We say that the composition of the melt $x$ traveled along the liquidus line making it
possible to grow the incongruently-melting compound $A_2BO_4$. This is the origin of
the name *traveling-solvent* floating-zone method.

**Solid-State Preparation of Polycrystalline Rods**

One of the most frustrating aspects of crystal growth by the floating-zone method
is the need to manufacture polycrystalline rods. Dense, uniform rods from pre-
synthesized powder of the desired chemistry are quite difficult to produce for many
compounds. In fact, there are some materials for which we were unable to manufac-
ture rods at all despite numerous attempts. The most common impediment to rod
production is the inability to compact the powder sufficiently before the fragile rods
are placed in a furnace for a final reaction. However, there are two methods which we
have found work well for many compounds. The first is the standard cold isostatic
pressure technique that is commonly employed by the crystal-growth community and
the second is a method developed in White *et al.*[91] that is described herein in detail.

The cold isostatic pressure technique begins by placing a hollow latex tube with
a closed end inside a hollow aluminum cylinder, which is held fixed by a ring stand.
The inner volume of this cylinder acts as a mould for the powder. We cut the open
end of the latex tube so that it protrudes from the top of the aluminum tube a few
centimeters above its rim and then fold it over the rim. We then follow the pouring of
two or three spatula loads of powder into the latex tube via a funnel with manually-
applied uniaxial pressure from a metal rod with diameter $\sim 60-70\%$ that of the inner
diameter of the aluminum tube. Pressure must be applied over the entire surface of the powder to ensure sufficient compactification. This procedure is repeated until sufficient powder has been pressed so that the length of the powder column is \(\sim 5-10\) cm. The open end of the latex tube is then tightly tied (perhaps several times) and is affixed to an open scaffold made of aluminum wire. The scaffold, with the attached latex tube, is carefully placed in a large cylindrical chamber which has been filled with water and a piston compresses the water to apply hydrostatic pressure to the latex tube for about five minutes. The maximum pressure applied by the piston is around 35 MPa. Higher pressure may rupture or destroy the cylindrical chamber. The purpose of the scaffold is to maintain the powder column’s cylindrical shape. Without the scaffolding, the powder column often bends or distorts under the increased pressure. The scaffold is then carefully removed from the cylinder, the latex tube is detached from the scaffolding, and following a brief wait period to allow things to dry, the latex tube is manually cut away from the powder column with scissors or a scalpel. If the column of powder has managed to maintain its structural integrity to this point, the operation of this last step often breaks it into multiple pieces. A “successful” attempt generally yields \(\sim 70\%\) of the pressed powder column in one piece. Unfortunately, many attempts yield numerous tiny pieces of compacted powder which are of no use to a crystal-growth experiment.

As an alternative to packing rods in latex tubes and subjecting them to hydrostatic pressure, we have developed a second method which was briefly described in
Reference [91]. In this method, the powder is pressed inside $\text{Al}_2\text{O}_3$ or $\text{SiO}_2$ tubes, much like it was in the latex tubes. That is, the powder is pressed manually with a metal rod at intervals following two or three spatula loads of powder. The advantage of this method is that the tubes containing the packed rods may be immediately placed in the furnace for firing without handling the fragile powder columns. The tubes act as a mould to provide straight, uniform rods of the desired dimensions. Reaction temperatures are chosen carefully so that the powder column undergoes minimal reaction with the inner surface of the tube. The final reaction temperature must also consider the level of densification it will produce. The powder column must densify enough so that the reacted polycrystalline rods may be easily and safely removed afterwards, but if too much densification occurs, the rods may become crooked. On the other hand, if too little densification occurs, it may become impossible to remove the rods without damaging them. Contamination of the rods by aluminum diffusion from the
Al₂O₃ tube is a potential concern which has previously been addressed.[91] We found that trace amounts of aluminum on the order of a few percent do diffuse into the rods. However, it is uncertain how much of the aluminum diffused into the powder during its synthesis before it was pressed (Al₂O₃ crucibles are used in those reactions too). Furthermore, it was found in the case of CaMn₂O₄ that the trace amount of aluminum in the rods did not enter the growing crystal,[91] so aluminum contamination of crystals seems to be an improbable byproduct of this method. Representative polycrystalline rods of CaMn₂O₄, produced by this method, are displayed in Figure 13.

Experimental Growth Parameters

Crystal growth is often approached with an empirical focus. This can largely be attributed to its complex nature. The overwhelming number of experimental variables involved creates a phase space which must be approached with a combination of foreknowledge, intuition, and luck. Most growth parameters are directly controlled by the crystal grower, so the implications of each parameter must be fully understood. This is especially critical when attempting to synthesize a new material for the first time.

Feed- and Seed-Rod Chemistry

The chemistry of the feed and seed rods is established by the grower and may therefore contain any molar ratios necessary for success. However, once the rods are
made, we are stuck with our choice. Naturally, the phase diagram is the origin of any decision regarding rod chemistry. There is not a lot of freedom in this decision, however. To grow a congruently- (floating-zone method) or incongruently-melting compound (traveling-solvent floating-zone method), both methods require rods with approximately the stoichiometry of the desired crystal. We generally have a freedom of perhaps a few percent composition difference from stoichiometry, as illustrated in the following special cases.

If the vapor pressure of the material is high, we expect there to be some volatilization. This loss of material could potentially shift the composition of the melt into another region of the phase diagram (perhaps to a region where a different compound precipitates from the melt). This is what occurs in the growth of CaMn$_2$O$_4$ with stoichiometric rods.[91] In this case, loss of manganese-oxide vapor from the melt is compensated for with a minor molar excess in the polycrystalline rods.[91]

Another example of the benefits of slightly off-stoichiometry rods is found in the case of incongruently-melting compounds. Consider Bi$_2$CuO$_4$ with the pseudo-binary phase diagram in Reference [92]. Bi$_2$CuO$_4$ is a line compound which decomposes (in air) around 850° C (Bi$_2$CuO$_4$ → CuO + liquid). If the composition in the rods is not completely homogeneous and there are local regions which are slightly Bi-rich, those regions melt at a lower temperature $\sim$ 772° C. To promote high density rods, it is important to react them at temperatures just below the melting or decomposition temperature. But when we reacted stoichiometric Bi$_2$CuO$_4$ rods just below 850° C,
the “minor” local melting of Bi-rich regions generally caused the rod to react with, and stick to, the inner surface of the Al$_2$O$_3$ tube. However, when we introduced 1-2% excess CuO, the composition of the rods shifted away from the problematic region of the phase diagram, and we were able to react the rods above 772° C without trouble.

**Feed-Rod Density and Homogeneity**

A polycrystalline seed rod’s only purpose is to provide some melted material to form the bottom half of the initial molten zone and to provide a sturdy scaffold upon which to build a single crystal boule. Thus, as long as it is mechanically stable and properly aligned, its impact on the growth, following the establishment of the molten zone, is relatively limited. The feed rod, on the other hand, plays an important role in the growth procedure throughout the entire experiment. Besides its chemistry, which we have already discussed, the magnitude and homogeneity of the feed-rod’s density is quite important. We later derive the physics of the stable molten zone wherein the density of the feed rod $\rho_f$ and its time derivative $d\rho_f/dt$ both play roles. Of course, the molten zone is only stable when $d\rho_f/dt = 0$ meaning the feed rod provides a steady diet of melt (assuming the dimensions of the rod are also time-independent).

It is important to prepare rods as densely as possible. A feed rod with density less than 85-90% of its theoretical maximum will be porous and is able to suction molten material from the zone through a capillary effect. This detrimental action inhibits the zone from ever reaching an equilibrium state. Still worse, the stability of the molten
zone can suffer from this problem to such an extent that the zone may spontaneously collapse.

Feed-Rod Dimensions

Because they are ideally cylindrical, the dimensions of the feed rod can be characterized by two parameters: their length and diameter. Obviously, a longer feed rod has the potential to grow a longer crystal, but typically, a minimum of 5 cm length is all that is required of a feed rod. Single-crystal growth generally occurs after a few centimeters of solidification when one of the numerous initial grains finally dominates. There is theoretically no upper limit on feed rod length, though the methods we use to prepare them tend to limit them to $\sim 10$ cm.

There are a few points to consider regarding feed-rod width. In general, a wider rod is subjected to more of the horizontal temperature gradient, although reasonable widths of 5 - 7 mm in diameter are nearly insusceptible to internal temperature inhomogeneities. Though unnecessary, growths are easier if the feed- and seed-rod diameters are similar. As a rule of the thumb, the width of the rods should vary inversely with melt temperature. The reason for this rule is simple: The height of the melt zone is independent of rod dimension, however, the width of the zone does depend on the diameter of the rods. Since a stable molten zone requires the height and width of the zone be nearly the same, we tune the width of the rods to match the zone height. In Figure 14, we see that a constant zone height results in unstable
situations in the left and right cases. However, the center case has the most stable zone due entirely to the choice of rod dimension.

Figure 14. Schematic of the molten zones for rods of three distinct dimensions given a constant power output from the halogen lamps. The small and large rod diameters result in unstable molten zones, however, the zone with the medium rod diameter is most stable because the molten-zone width is about the same as its height.

More important than the size of rod dimensions, is the aforementioned requirement that the dimensions of the feed rod be uniform. Even if the density is constant within the rod, if the width (or more accurately, the cross-sectional area) of the feed rod contains any variations, the molten zone will receive an excess or deficit of melt and alter the dynamics of the zone. Depending on the severity of the dimensional non-uniformity, the stability of the molten zone could be jeopardized.

Halogen Lamp

The image furnace is equipped to operate with 500 W, 750 W, 1000 W, 1500 W, 2000 W, and 3500 W halogen lamps. Their names indicate the maximum power output from each lamp, though typically we limit ourselves to 90% of the advertised
power in order to conserve the lifetime of the lamps. We must consider the melting temperatures of the feed and seed rod when selecting a lamp size. Obviously the selected lamp must be able to supply enough power to initiate melting and maintain a molten zone. The optimal choice is the smallest halogen lamp which is able to meet this requirement. In general, the size of the filament scales with the maximum power of the lamp and a lamp with a larger filament is going to form a larger more spatially-diffuse heat zone. So there is a trade-off between the quality and size of the heat zone and the maximum power supplied to it. The optimal choice of halogen lamp is the best possible equilibrium between these two competing issues.

We have plotted the power output of several halogen-lamp sizes as a function of applied voltage in Figure 15. When setting and adjusting the halogen-lamp power output during a growth, we control the voltage across the lamps. We often know the proper power necessary for a growth experiment beforehand, and to set this power, we need only read off the voltage for the relevant lamp size from Figure 15.

Unfortunately, there is no simple method to convert the power of the lamps to a specific temperature. The temperature reached by the sample is a complicated function of the furnace configuration and sample-specific properties including thermal conductivity, opacity, the quality of its surface condition, and color.[88] In general, higher lamp power is required to melt samples with highly-reflective surfaces, low light absorption, or large diameters.[88]
Lamp and Polycrystalline-Rod Alignment

The alignment of the two halogen lamps and the co-alignment of the rotational axes of the feed and seed rods are set before a growth experiment. It is not required to perform an alignment of the lamps prior to each and every experiment. A realignment is implemented only after switching lamps or if the alignment appears to have drifted over the course of many crystal-growth experiments. The alignment of the lamps dictates the size and shape of the heat zone and therefore its quality. Optimal positioning of the lamp filaments in the foci of their respective hemispherical elliptical cavities minimizes the dimensions of the heat zone. Otherwise, the heat zone assumes an irregular shape and contains undesirable temperature gradients.

The co-alignment of the rotational axes of the feed and seed rods should be as precise as possible. This alignment is difficult because imperfections in the dimensions
and shape (such as bends) of the feed rod are typically present. However, if the maximum deviation between the centers of the feed and seed rods is kept to 1-2 millimeters or less under counter-rotation, the rods may be considered adequately aligned. There is always a little play in the position of the feed rod as a result of the way it is attached to the upper shaft. This allows it to self-correct for a small bend in its length if the original alignment is reasonable.

**Growth Atmosphere**

We control the growth environment by selecting an atmosphere and its pressure. Each choice influences the growth in several distinct ways that are detailed herein. We have grown single crystals in environments of air, O\(_2\), N\(_2\), Ar, Ar + 3% H, and CO\(_2\). Of course, we could grow crystals in other common environments such as He or even under a modest vacuum. The only real limiting factor is whether the environment poses a danger to the grower or the image furnace. From a general chemistry perspective, O\(_2\) is chosen when growing an oxide crystal and inert atmospheres such as N\(_2\) and Ar are appropriate for the growth of non-oxide crystals or oxides which are susceptible to accumulating undesirable excess oxygen. Strongly or weakly reducing atmospheres such as Ar + 3% H and CO\(_2\), respectively, are used when growing metal or inter-metallic crystals susceptible to oxidation, or when deliberately removing oxygen from oxides during a growth.

Looking beyond chemical considerations, each distinct atmosphere has its own thermal conductivity. Direct heat exchange between the molten zone and the gas
molecules surrounding it is therefore different for each atmosphere. A study by Koohpayeh et al.[88] demonstrated that, at a constant power output from the halogen lamps, the temperature reached in a polycrystalline rod of YFeO$_3$ increased as the environment was alternated through helium, oxygen, argon, and vacuum. Naturally, this conclusion simply reflected the relative magnitudes of thermal conductivity for those gases. Namely, that $\kappa_{\text{Ar}} < \kappa_{\text{O}} < \kappa_{\text{He}}$ and heat loss due to convection is almost completed eliminated under moderate vacuum conditions.

The thick wall of the quartz growth chamber allows us to implement environments ranging from modest vacuum to about 11 bar. Though most growth attempts take place at atmospheric pressure, this flexibility is advantageous for a few special cases. For example, if the vapor pressure of the rod material is large, a lower pressure would do little to inhibit volatilization. However, the rate of volatilization is reduced by increasing the growth-environment’s pressure. In most cases, 11 bar of pressure is insufficient to eliminate volatilization entirely, however, it may be enough to reduce it to acceptable levels. A second possible case occurs when the stability of a phase requires a certain pressure or when a first attempt to grow a new crystal relies on a phase diagram which has been determined at non-atmospheric pressures. In these cases, the pressure of the growth environment should reflect the chemistry suggested by available phase diagrams and other evidence.

Though chemistry dominates considerations regarding the pressure of the growth environment, it is important to be aware of the effect pressure has on other aspects
of the growth. For example, higher pressures lead to lower temperatures, given the same power output, because of the presence of a higher number of gas molecules which transport more heat away from the molten zone via convection. Higher pressures are also known to produce a sharper vertical temperature gradient along the heat zone, which could potentially cause cracks and a higher defect density to form in the growing crystal. There is no way to avoid these detrimental effects when chemistry constrains us to grow at elevated pressures. The best we can do is to be aware of their existence.

**Rotation Rates**

When considering rotation rates, we are able to select the directions and magnitudes of rotation for the upper and lower shafts. The shafts are always counter-rotated, because the purpose of rotation is to promote a chemically-homogenous melt and homogeneous temperature profile within the molten zone. Without counter-rotation, the molten zone is stirred mainly by Marangoni convection (also known as thermocapillary convection), which originates from surface-tension gradients induced by vertical temperature gradients. This form of convection is strongest just inside the melt/atmosphere interface so that mass and heat transport to the center of the molten zone is quite inefficient. As a result, a sharp, horizontal temperature gradient is established inside the melt. In contrast, simulations demonstrate that the temperature profile inside the molten zone is quite homogeneous when the rods are
counter-rotated. Furthermore, the Marangoni convection is suppressed by counter-rotation and the dominant forced convection effectively stirs the melt in such a way that it is chemically homogenous as well. Having established that counter-rotation is the best approach, we might ask if it is important whether the upper shaft is rotated counter-clockwise and the lower shaft clockwise or vice-versa. In our experience, this distinction is unimportant.

We next consider the magnitude of rotation, beginning with the ratio of the rotation rates of the upper and lower shafts. Lan et al. have published simulations of a rather extreme case of non-unity rotation ratio wherein the crystal is rotated and the feed rod is stationary and vice versa. These cases lead to undesirable horizontal thermal gradients in the molten zone, but it is unclear how a rotation rate which is closer to unity would influence the zone. All growth experiments conducted at Montana State have thus far used a ratio of 1.0. Because the implications of a non-unity rotation ratio are not very well understood, it is easier to remove a degree of freedom by choosing to keep the rotation rates of the upper and lower shafts identical. Therefore, we need only decide on one rotation magnitude. The central point to consider is that the shape of the melt-solid interface where crystal growth occurs is directly influenced by the rotation rate. In general, higher rotation rates lead to a convex interface shape, a more stable molten zone, and a more efficient heat and mass transport. We have found that acceptable rotation rates are 15-50 rpm.
Growth Speeds

Unlike respective rotation rates, the ratio of growth speeds for the upper and lower shafts are almost never unity. We discuss how to determine the proper ratio of the two speeds in the section on the physics of the stable floating zone so, for now, we need only consider the speed of one of the shafts. We generally think of selecting the descent speed of the lower shaft because this is what is referred to as the growth speed. In general, the growth speed should be as slow as possible. Crystals grown at higher speeds than necessary tend to have greater intrinsic defect density as well as macroscopic defects such as cracking of the boule due to imposed thermal stress. However, the properties of a crystal may require growth at higher speeds to minimize material loss due to volatilization or because the molten zone is impossible to stabilize due to the poor surface tension of the melt.[93] In either of these cases, the crystal quality is worse than it would be if these material-specific properties did not inhibit slower growth. In general, a reasonable growth rate is 0.5-2 mm/hour. For difficult cases, we have used higher growth speeds such as 5 or 10 mm/hour.[91, 93] However, it is ill-advised to grow much faster than 10 mm/hour.

Filter Configuration

This final parameter has nothing to do with the crystal growth itself, but if chosen poorly, may force the termination of a crystal-growth experiment before even beginning. The CCD camera which allows us to monitor the growth in real-time is filtered to cut down on the reflected light intensity. Without filtering, the camera
image is saturated by light to such an extent that nothing is visible. On the other hand, if the melting temperature of a compound is low, the power output required to melt it may be insufficient to penetrate through the filters with enough intensity to see much either. Thus, a poorly chosen filter configuration could leave the camera blinded by light or its absence. For this reason, there are actually two distinct filters available: a thick filter with a gold surface and a thin filter with a silver surface. This provides four distinct filter configurations which, listed in order of increasing filtering strength, are: no filters, silver filter only, gold filter only, or both filters. One of these filter configurations should be acceptable for any situation.

Establishment and Termination of the Molten Zone

The initial establishment of the molten zone sets the tone for the rest of the growth. Experience has taught us that a successful crystal growth owes much to the proper establishment of the molten zone. Termination of the zone at the end of an experiment, on the other hand, has little influence over the quality of the crystal. However, if the molten zone is terminated poorly, the liquid from the zone might blanket the top end of the crystal with what quickly becomes an unsightly polycrystalline blob. For these and other reasons, it is worthwhile to devote some attention to the proper manipulation of the molten zone at the beginning and end of a crystal-growth experiment.
The establishment of the molten zone is so paramount because, even given the correct choice of experimental growth parameters, it still takes time for the zone to reach equilibrium. For many experiments, the zone may eat a few centimeters of the feed rod before stability is attained. That being the case, it is preferable to establish the zone early and not adjust it at all throughout the entire experiment. When first attempting to grow a specific crystal, the zone may need to be adjusted frequently, as the parameters are optimized. However, the quality of the resulting crystal boule suffers dramatically compared to a crystal grown with a stable zone, which has not been frequently adjusted throughout the growth. Subsequent growth attempts should result in better stability of the zone during growth. If not, usually one of the experimental growth parameters is not optimal. We confronted one exception to this rule in the growth of Bi$_2$CuO$_4$, where the intrinsic surface tension of the melt is so low that zone stability is never truly attained.[93]

To establish the molten zone, we begin by melting the tips of the feed and seed rods. This step immediately follows a wait period of 30-60 minutes at about 90% of the power necessary to melt the rods to allow them to reach thermal equilibrium. The volume of melt on the tips of the feed and seed rods should be nearly identical so that the initial molten zone is as symmetric as possible. This is accomplished most easily if the the densities and dimensions of the rods are the same and their respective tips are placed symmetrically above and below the horizontal center line of the heat zone (usually by 2-3 mm). After the tips of the rods are completely molten, (they exhibit
a shiny, hemispherical surface) the feed and seed rods are carefully brought together. When they are close enough, the molten tips will spontaneously connect, forming a floating, liquid hourglass. It is at this point that the dimensions of the molten zone are manually set. The height of the zone should ideally be the same as the tapered width at the center of the zone and the volumes of the upper and lower portion of the zone should be similar. These requirements can be met by manually adjusting the position of the lower and/or upper rods. It is then possible to initiate growth by selecting the descent speed of the two shafts, however, before doing so, it is important to observe the zone. If over 10-15 minutes the molten zone’s characteristics (volume, stability, etc) remain constant, the growth is ready to proceed. However, if the zone is periodically unstable, or if the volume of the melt decreases (perhaps being drawn into a porous feed rod, for example), some experimental parameters or the nature of the zone itself may need to be adjusted before initiating growth.

At the conclusion of a crystal growth experiment (typically when only a few millimeters of feed rod remains) the molten zone is terminated. The most successful procedure for a clean termination of the zone involves the following steps. We first stop the descent of the upper and lower shafts and increase the rate of counter-rotation to \( \sim 50 \) rpm. Next, we manually lower the power output of the halogen lamps in a gradual and controlled manner, watching the response of the molten zone. The zone should respond by decreasing its volume and the interface between melt and solid should slowly converge towards the center from above and below. If this procedure
is continued, the molten zone will auto-separate at a time when there is little melt remaining in the zone. The counter-rotation of the upper and lower shafts results in a large shear stress at the tapered ends of the feed rod and crystal boule, which leads to separation when the surface tension of the remaining melt is no longer sufficient to maintain the floating zone. When termination of the zone finally ensues, the power output of the lamps is typically around 40-60% of the growth power and the small amount of melt remaining does not run down over the crystal boule. It is only after the zone has auto-separated that we manually move the feed rod and crystal away from the heat zone and power the lamps down completely.

**Physics of the Stable Floating Zone**

A stable molten zone has reached equilibrium, and in such a system, mass balance is satisfied. The mass entering the molten zone is compensated for by the mass leaving the zone. In terms of relevant physical parameters, this is expressed,

\[ \rho_f A_f dz_f = \rho_l A_c dz_c + m_{\text{vol}} + m_{\text{non-equil.}}, \tag{2.1} \]

where \( \rho_f \) and \( \rho_l \) are the densities of the feed rod and liquid, respectively. Volumes \( A_f dz_f \) and \( A_c dz_c \) are composed of cross-sectional areas and an infinitesimal vertical height and account for melt entering and leaving the zone, respectively. We use a general cross-sectional area because, though the feed and seed rods are cylindrical, a growing crystal will often assume an elliptical cross-sectional form.[91] \( m_{\text{vol}} \) and \( m_{\text{non-equil.}} \) represent mass loss due to volatility and various non-equilibrium processes,
respectively. If we take a time derivative of Equation (2.1), we obtain

\[ \rho_f A_f v_f = \rho_{\ell} A_c v_c + \frac{dm_{\text{vol}}}{dt} + \frac{dm_{\text{non-equl.}}}{dt}, \tag{2.2} \]

where we have assumed that \( \frac{d\rho_f}{dt} = \frac{d\rho_{\ell}}{dt} = \frac{dA_f}{dt} = \frac{dA_c}{dt} = 0 \) and \( v_c \) and \( v_f \) are the speeds of the lower and upper shafts, respectively. If the non-equilibrium term in Equation (2.2) can be ignored or, better, is zero, then we can rearrange the expression to something more useful

\[ \frac{v_f}{v_c} = \frac{\rho_{\ell} A_c}{\rho_f A_f} + \frac{1}{v_c \rho_f A_f} \frac{dm_{\text{vol}}}{dt}. \tag{2.3} \]

Equation (2.3) governs the equilibrium size of the growing crystal boule. We see immediately that \( v_f = v_c \) only in an extremely improbable case. This result may seem counterintuitive. Consider a common situation where there is no volatilization and where \( A_c = A_f \). Equation (2.3) reduces to \( \frac{v_f}{v_c} = \frac{\rho_{\ell}}{\rho_f} \), and since a solid phase seems more dense than its liquid phase, we conclude that \( v_f < v_c \). This is not correct in general, however. Covalently-bonded materials have higher densities in their liquid phase than as solids, so the more intuitive result \( v_f > v_c \) is recovered.\[94\] We have tested Equation (2.3) for many materials and found it governs the equilibrium growth of crystals very well.
SAMPLE CHARACTERIZATION

Laue Method of X-Ray Diffraction for Single-Crystal Orientation

History and Introduction

Wilhelm Röntgen discovered x-rays in 1895 at the University of Würzburg[95]. He was later awarded the first Nobel Prize in Physics in 1901 for this discovery. Röntgen named them x-rays because their nature was unknown at the time. This issue was not fully clarified until 1912 when Max Laue (he became Max von Laue in 1913) first learned of the thesis work of graduate student P. P. Ewald. Ewald’s dissertation provided theoretical calculations describing the physics of how visible electromagnetic waves (light) might scatter from an array of harmonic oscillators. Laue wondered about the possible interaction of electromagnetic waves of smaller wavelength with this primitive crystal model, leading him to his hypothesis of crystal diffraction. He reasoned that if a crystal is built from periodically arranged atoms which could scatter electromagnetic radiation and if x-rays had a wavelength on the order of the interatomic spacing in that crystal, then x-rays should be diffracted by crystals[96]. He developed his experiment with Walter Friedrich and Paul Knipping at the Ludwig Maximilians University of Munich. They placed a copper sulfate (CuSO₄) crystal between an x-ray beam and a photographic plate and successfully observed diffraction spots produced by transmitted x-rays[97]. Max von Laue earned the 1914...
Nobel Prize in physics for this experiment which simultaneously demonstrated the periodic nature of crystals with spacing on the order of x-ray wavelengths (Å) and the wave nature of x-rays, themselves.

Laue developed a system of three equations, now referred to as Laue’s Equations, to describe x-ray diffraction by crystals.[97] However, a graduate student named W. L. Bragg derived a more concise diffraction condition later that same year.[98] Bragg’s law, as it came to be known, is a geometric solution for constructive interference between phase-coherent, monochromatic x-rays of wavelength $\lambda$, which scatter from atoms arranged in crystallographic planes spaced a distance $d$ apart from one another when the incident x-ray beam makes an angle $\theta$ with the planes under consideration. Bragg’s law is written

$$n\lambda = 2d \sin \theta,$$  \hspace{1cm} (3.1)

where $n$ is referred to as the order of diffraction. The order of diffraction can be any integer between one and the highest integer less than or equal to $2d/\lambda$; this condition being imposed because $\sin \theta$ cannot be greater than unity. W.L. Bragg and his father W.H. Bragg were awarded the 1915 Nobel Prize for their use of Equation (3.1) to solve the first crystal structures from diffraction patterns recorded using the Laue method of x-ray diffraction.

Though the technology and methods of modern x-ray diffraction experiments have advanced far beyond these primitive initial experiments conducted in the early years of the twentieth century, the technique developed by Laue is still relevant, mostly
in unaltered form, to the task of single-crystal orientation. Every diffraction pattern observed using the Laue method results from a unique orientation of the crystal relative to the incident x-ray beam. (Symmetries in the crystal structure will lead to some degeneracy in the patterns. For example, we expect the Laue patterns for (1 0 1) and (1 0 1) to exhibit the same spatial symmetries, though the intensities of comparable spots are not expected to be the same.) The orientation of the crystal is defined by the directions of the lattice parameters: a, b, and c within (or relative to) the crystalline sample. Careful analysis of the diffraction pattern indirectly leads to the solution of the crystal’s orientation - knowledge generally required for a meaningful description of the crystal’s physical properties.

The Laue method of x-ray diffraction is naturally divided into two techniques: transmission and back-reflection. Transmission Laue diffraction was the original method used by Laue himself. However, for the successful implementation of a transmission experiment, a thin crystal, which does not readily absorb x-rays, is required. If this requirement is not satisfied, back-reflection Laue diffraction may still be effectively employed. The main difference between these two techniques is found in the geometry of their setups, with a secondary difference being the amount of sample which participates in diffraction. While transmission Laue diffraction probes the entire depth of the crystal (x-rays transmit through the sample), back-reflection Laue diffraction probes only a thin layer at the surface of the crystal. All Laue x-ray
diffraction experiments relevant to this work were conducted with a back-reflection setup.

**Experimental Setup**

![Diagram](image)

Figure 16. (a) Schematic of a generic back-reflection Laue diffraction system, and (b) photograph (courtesy of the author) of the back-reflection setup at Montana State University.

The experimental setup of a back-reflection Laue system is displayed in Figure 16. In a back-reflection experiment, polychromatic radiation is finely collimated and directed through a detector (a Laue camera loaded with Polaroid 57 or Fuji FP-3000B film). The x-rays diffract from a single crystal which has been mounted on a goniometer and those diffracted beams which intersect the plane occupied by the film are recorded. If the distance between the sample and film $D$ is known, and the distance between a Laue spot and the center of the film $r$ is measured, the Bragg
angle $\theta$ as defined in Equation (3.1) can be calculated

$$\tan(180^\circ - 2\theta) = \frac{r}{D}. \quad (3.2)$$

Knowledge of this angle provides no relevant information to the task of orientation in general, however. Given $\theta$ for a specific Laue spot, if the wavelength $\lambda$ participating in diffraction was known, Equation (3.1) could be used to calculate an inter-planar spacing $d$. This spacing could then be identified with a crystallographic plane $(hkl)$, and it is precisely this indexing of spots which solves the Laue pattern and determines the sample’s orientation. However, polychromatic radiation is used in single-crystal diffraction techniques like Laue because each crystallographic plane has its own fixed Bragg angle and variation of $\lambda$ is the only way to satisfy Equation (3.1) for more than a few crystallographic planes. This means we do not know which x-ray wavelength $\lambda$ participated in diffraction to produce a given Laue spot and we must solve the pattern by some other method.

**Basics of a Back-Reflection Laue Pattern**

A typical back-reflection Laue pattern is composed of Laue spots which arrange themselves along hyperbolas and lines[99] as seen in the sample photograph displayed in Figure 17(a). The reason for this is demonstrated in Figure 17(b), where the concept of a zone axis is introduced. A zone axis is a crystallographic direction which is orthogonal to the plane-normal vectors of two or more crystallographic planes. The Laue spots lying on the same line or hyperbola originate with diffraction from
crystallographic planes which are mutually orthogonal to a single zone axis, collectively referred to as planes of a zone. The angle $\phi$ between the zone axis and the direction of the incident x-ray beam determines whether the Laue spots will form a hyperbola or line. If $\phi$ is 90°, a line is formed; otherwise, a hyperbola is formed. It follows that Laue spots lying on the intersections of hyperbolas and lines originate from crystallographic planes whose normal vectors are orthogonal to two or more zone axes. For this to be possible, the crystallographic planes causing such Laue spots are undoubtedly of low Miller-index order.
Back-Reflection Laue Experiments

The first step in conducting any Laue-diffraction experiment is to choose an initial crystal orientation (relative to the incident beam) in which to mount the sample to a goniometer. Ideally, the symmetries of the unit cell are reflected in the morphology of the crystal in the form of facets. These facets are macroscopic representations of crystallographic planes whose Miller indices are typically of order less than four. In addition to facets, some crystals will cleave when struck or cut and the highly-reflective plane which is revealed is also generally a macroscopic manifestation of a crystallographic plane with low Miller-index order. When fortunate enough to deal with a sample exhibiting facets or containing a cleavage plane, the most efficient strategy is to initially secure the sample to a goniometer so that the x-ray beam is perpendicular to one of them. Unfortunately, artificially synthesized samples, such as those grown by the floating-zone method, are often irregularly shaped. This provides few obvious choices for an initial orientation unless a cleavage plane exists. If there are no obvious starting orientations available, it is best to mount the sample to the goniometer in an orientation encouraged by the sample’s natural morphology. This is usually the growth direction of the crystal boule in the case of samples grown by the floating-zone method.

After choosing an orientation, the crystal surface perpendicular to the incident beam should be polished, except when the x-ray beam is incident on a facet or cleaved surface. Because the back-reflection technique probes the crystal’s surface, it should
be flat and clean. This condition is inherently satisfied by facets and cleavage planes in general. Next, a distance $D$ between the sample and the film is selected. Typical distances are between 30 and 50 mm. The Polaroid film (dimensions of $88.8 \times 114.5$ mm$^2$) subtends a solid angle of about 2.1 steradians when $D$ is 50 mm and 3.3 steradians when $D$ is 30 mm as calculated by

$$\Omega = 88.8D \int_{-57.25}^{57.25} \frac{d\zeta}{(\zeta^2 + D^2)\sqrt{\zeta^2 + 44.4^2 + D^2}}. \quad (3.3)$$

The hemisphere, which is centered on the position where the x-ray beam is incident on the crystal’s surface and intersects the film, subtends $2\pi$ steradians. Therefore, 33.3% of the space back-reflected x-rays could possibly occupy is sampled by the Polaroid film when $D$ is 50 mm. When $D$ drops to 30 mm, the amount of space sampled by the film increases to 52.5%. Any distance between 30 and 50 mm is usually adequate. The crucial point is that the distance must be accurately measured and consistent throughout the process of orienting a sample. In all back-reflection experiments performed as part of this work, $D$ was nearly 40 mm.

Finally, suitable settings for the molybdenum x-ray tube and exposure times must be selected. The settings depend on the quality of the sample surface. For example, high-quality, specular crystal surfaces generally require a less intense x-ray beam than a low-quality surface because the diffuse background due to surface reflection is large. Common x-ray tube settings for the voltage are between 20-50 kV and 35 mA is typical for the current. The intensity of the x-ray beam $\Gamma$ is proportional to the
applied current and the applied voltage squared \[99\]

\[ \Gamma \propto IV^\Lambda \quad \Lambda \simeq 2. \quad (3.4) \]

If x-ray tube settings are not optimal for a given experiment, coarse adjustments of the beam intensity are made by changing the voltage and fine adjustments are made by modifying the current. The exposure time also influences the intensity of the Laue spots. Laue-spot intensity is roughly proportional to exposure time,\[100\] but the background intensity is also proportional to exposure time. If the background becomes too intense, the film is overexposed and Laue spots are poorly visible. On the other hand, exposure times that are too short result in underexposed film with weak Laue spots and no observable background. We found an intermediate exposure time of 10-15 minutes resulted in an optimal signal to background ratio.

The film used in most projects relevant to this work was manufactured by Polaroid. Polaroid 57 film is designed and packaged for compatibility with our Laue camera. However, with the advent of the age of digital cameras, Polaroid discontinued manufacture of the instant developing film for which it became so famous in order to focus on the more profitable digital technology industry instead. This occurred early in 2008, and the last Polaroid 57 film produced was released in February 2008. Fortunately, Fuji manufactures its FP-3000B film which is similar to the Polaroid film in many ways. Most importantly, it is a high speed film (3200 ISO) and has similar dimensions. However, it is packaged for compatibility with a Fuji camera which cannot be used for x-ray experiments. To use the Fuji film, it is inserted into our Polaroid
Laue camera in a dark room and, after the x-ray exposure, is developed manually in the dark room. This is a tedious process, born of necessity, in which about 10 minutes in the dark room is required for each exposure. But until Polaroid or another company manufactures Polaroid 57 film, this is the only cost-effective solution.

Simulation of Laue Patterns

Before we discuss how to analyze a Laue pattern, we turn our attention to the details of an important tool used to orient single crystals. The ability to compare experimental photographs with Laue patterns, simulated for known orientations, has obvious advantages. In the past, compilations of simulated Laue patterns were published in books referred to as Laue atlases.[101] But published patterns for common crystal structures in a few high-symmetry orientations cannot satisfy the needs of an experimentalist orienting novel or uncommon materials because a Laue pattern depends on the Bravais lattice (including lattice-parameter values), sample to film distance $D$, and sample orientation with respect to the incident x-ray beam.[100] We describe an algorithm, adapted from Marín and Diéguez[100] with some modifications, which calculates the positions of Laue spots for any crystal in any orientation located a distance $D$ from the film. A complete simulation should also reflect the unique intensity of each Laue spot. However, we have chosen not to address the individual intensities of Laue spots because it is complicated[100] and because it is only important when distinguishing between otherwise identical patterns such as those for $(2 1 1)$ and $(2 \overline{1} \overline{1})$, for example. For our purpose, it was sufficient to orient the $a$
axis of a crystal, without worrying about our inability to make the subtle distinction between (1 0 0) and (1 0 0).

Figure 18. Schematic which defines the relationship between a fixed three-dimensional coordinate system with its origin at the volume diffraction center of the crystal (O; $\vec{x}$, $\vec{y}$, $\vec{z}$) and a fixed two-dimensional coordinate system with its origin in the center of the film (O$'$; $\vec{x}'$, $\vec{y}'$). The direction of the incident x-ray beam is indicated by an arrow.

Before Laue-spot coordinates are calculated, suitable reference frames must be defined. There are four reference frames to consider: (O; $\vec{x}$, $\vec{y}$, $\vec{z}$) is fixed to the laboratory with its origin at the volume diffraction center of the initial position of the crystal, (O$'$; $\vec{x}'$, $\vec{y}'$) is fixed to the laboratory and has its origin in the center of the plane in which the film resides, and the direct-space (O; $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$) and reciprocal-space lattice parameters (O; $\vec{b}_1$, $\vec{b}_2$, $\vec{b}_3$) of the crystal, which are fixed to the sample. Note that $\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$ correspond to the a, b, and c axes, respectively. The positions of the two frames, (O; $\vec{x}$, $\vec{y}$, $\vec{z}$) and (O$'$; $\vec{x}'$, $\vec{y}'$), do not move relative to one another or to the laboratory during the experiment. They have well defined positions with respect
to one another as displayed in Figure 18. The lattice parameters, direct-space and reciprocal, could be in any arbitrary orientation with respect to \((O; \vec{x}, \vec{y}, \vec{z})\), though they have well-defined orientations with respect to one another through the definition of the reciprocal lattice vectors. To simplify the calculations, it is convenient to start with two assumptions about the orientation of the crystal reference frame \((O; \vec{a}_1, \vec{a}_2, \vec{a}_3)\) with respect to \((O; \vec{x}, \vec{y}, \vec{z})\): (1) the \(\vec{a}_1\) axis is coincident with the \(\vec{x}\) axis and (2) the \(\vec{a}_2\) axis is in the \(\vec{x}-\vec{y}\) plane. These assumptions, displayed in Figure 19, characterize an initial crystal orientation with respect to \((O; \vec{x}, \vec{y}, \vec{z})\) from which we later generalize to any orientation.

Figure 19. Initial orientation of the crystal, characterized by its direct-space coordinate system, relative to the fixed \((O; \vec{x}, \vec{y}, \vec{z})\) coordinate system.

After defining an initial orientation, we calculate expressions, referenced to \((O; \vec{x}, \vec{y}, \vec{z})\), for the direct-space lattice-parameter vectors. It is convenient to adopt the
notation of Equation (3.5)
\[ \vec{a}_1 = a_1 \hat{i} \]
\[ \vec{a}_2 = a_{2x} \hat{i} + a_{2y} \hat{j} \]
\[ \vec{a}_3 = a_{3x} \hat{i} + a_{3y} \hat{j} + a_{3z} \hat{k}, \]

where the unit vectors \( \hat{i}, \hat{j}, \hat{k} \) are coincident with the \( \vec{x}, \vec{y}, \vec{z} \) axes, respectively.

Employing elementary vector analysis, expressions for \( a_{2x}, a_{2y}, a_{3x}, a_{3y}, \) and \( a_{3z} \) are obtained as calculated in Appendix A (see calculations leading to Equation (A.6)).

\[ a_{2x} = a_2 \cos \gamma \]
\[ a_{2y} = a_2 \sin \gamma \]
\[ a_{3x} = a_3 \cos \beta \]
\[ a_{3y} = a_3 \frac{\cos \alpha - \cos \gamma \cos \beta}{\sin \gamma} \]
\[ a_{3z} = a_3 \left[ \sin^2 \beta - \left( \frac{\cos \alpha - \cos \gamma \cos \beta}{\sin \gamma} \right)^2 \right]^{1/2} \]

Expressions for a vector perpendicular to arbitrary crystallographic plane \((hkl)\), given the orientation defined in Figure 19, are calculated next. This calculation makes use of the reciprocal lattice vectors of the crystal and is detailed in Appendix A (see calculations leading to Equation (A.10)). The vector normal to crystallographic plane \((hkl)\) is \( \vec{n}_{hkl} = n_1 \hat{i} + n_2 \hat{j} + n_3 \hat{k} \) and is expressed with respect to reference frame \((O; \vec{x}, \vec{y}, \vec{z})\). It has components
\[ n_1 = ha_{2y}a_{3z} \]
\[ n_2 = -ha_{2x}a_{3z} + ka_{1z} \]
\[ n_3 = h(a_{2x}a_{3y} - a_{2y}a_{3x}) - ka_{1z} + la_{1y} \]
We stress that these vector components are only valid when the crystal is in the orientation specified by Figure 19. To calculate the plane-normal vectors for an arbitrary crystal orientation, we note that any vector referenced to frame \((O; \vec{x}, \vec{y}, \vec{z})\) can be rotated about the \(\vec{z}\) axis by angle \(\alpha'\) followed by a rotation about the \(\vec{y}\) axis by angle \(\beta'\) until it is parallel to the \(\vec{x}\) axis. When a diffraction pattern is needed for a crystal in the \((HKL)\) orientation, the vector perpendicular to crystallographic plane \((HKL)\), \(\vec{n}_{HKL}\), is calculated from Equation (3.7) and then the angles \(\alpha'\) and \(\beta'\) which rotate \(\vec{n}_{HKL}\) into coincidence with the \(\vec{x}\) axis are calculated. Identical rotations by \(\alpha'\) and \(\beta'\) of all other plane-normal vectors \(\vec{n}_{hkl}\) corresponding to crystallographic planes \((hkl)\) being considered for diffraction have the mathematical effect of rotating the crystal from its \((100)\) initial orientation (see Figure 19) to its new \((HKL)\) orientation. Operating on the plane normal vectors \(\vec{n}_{hkl}\) with the appropriate operators \((\alpha'\) rotation followed by \(\beta'\) rotation) provides new expressions for the plane-normal vectors given the new crystal orientation \((HKL)\). We call these vectors \(\vec{c}_{hkl}\) to distinguish them from \(\vec{n}_{hkl}\).

To this point, we have derived expressions for the plane-normal vectors \(\vec{c}_{hkl}\) for any Bravais lattice in any orientation. The physics of diffraction is incorporated by the next step. Derivations of Bragg’s law are typically done in two-dimensional space for simplicity as in Figure 20(a). It is useful to note that the x-ray beam is incident on the planes \((hkl)\) with the exact angle \(\theta\) the diffracted beam leaves those same planes. This, combined with the observation that diffraction takes place within a
single spatial plane (there are no other angles besides the Bragg angle \( \theta \) to consider), makes the three-dimensional generalization of x-ray diffraction trivial. To calculate the vector which describes the diffracted x-ray beam, we simply rotate a vector, which is anti-parallel to the incident beam, 180° about the plane-normal vector for the crystallographic plane \((hkl)\) being considered. This rotation is displayed in Figure 20(b).

The mathematical machinery to rotate an arbitrary vector about a second arbitrary vector by an arbitrary angle was elegantly derived, without reference to any specific coordinate system, to describe the kinematics of rigid body motion - specifically rotation. On page 162 of Goldstein’s *Classical Mechanics*,[102] the solution is reported for the rotation of vector \( \vec{r} \) about unit vector \( \hat{n} \) by angle \( \Phi \).

\[
\vec{r}' = \vec{r} \cos \Phi + \hat{n}(\hat{n} \cdot \vec{r})(1 - \cos \Phi) + (\vec{r} \times \hat{n}) \sin \Phi \tag{3.8}
\]
The expression simplifies to
\[ \vec{r}' = -\vec{r} + 2\hat{n}(\hat{n} \cdot \vec{r}), \] (3.9)
when \( \Phi = 180^\circ \). The diffracted-beam vector from plane \((hkl)\), referenced to \((O; \vec{x}, \vec{y}, \vec{z})\), can be calculated by substitution of \(\vec{x}\), which is anti-parallel to the direction of the incoming x-ray beam (see Figure 18), for \(\vec{r}\) and the plane-normal vector \(\vec{c}_{hkl}\) for \(\hat{n}\) after normalizing it. The result is the diffracted-beam vector which we denote \(\vec{c}_{hkl}'\).

After the diffracted-beam vectors are calculated for all crystallographic planes being considered for diffraction, the final step is to determine where these vectors intersect the plane occupied by the film. In other words, we calculate the coordinates of the Laue spots in the reference frame of the film \((O'; \vec{x}', \vec{y}')\). The details of the calculation are reported in Appendix A (see calculations leading to Equation (A.14)).

If we write the diffracted beam from plane \((hkl)\) in the form \(\vec{c}_{hkl}' = c'_1 \hat{i} + c'_2 \hat{j} + c'_3 \hat{k}\) and the sample to film distance is \(D\), then the Laue-spot coordinates in reference frame \((O'; \vec{x}', \vec{y}')\) are
\[ \left(-D \frac{c'_2}{c'_1}, D \frac{c'_3}{c'_1}\right). \] (3.10)

With Laue-spot coordinates calculated for all relevant planes, the back-reflection diffraction pattern is easily generated. This algorithm is able to calculate a Laue pattern for a sample with any Bravais lattice in any orientation with respect to the incident x-ray beam. However, we must address one subtle point about Laue patterns. Consider the situation as presented in Figure 21. The orientation of a cubic sample (where, by orientation, we mean the x-ray beam is anti-parallel to the
Figure 21. (a) Generic cubic crystal with [0 0 1] oriented out of the board and (b) the same crystal rotated 45° about [0 0 1]. In a Laue x-ray diffraction experiment with incident beam going into the plane of the page, each orientation results in the same Laue pattern ((0 0 1) orientation), though the patterns are rotated 45° with respect to one another.

The normal vector of the orientation plane is (0 0 1) in both (a) and (b) of Figure 21, but they have been rotated about [0 0 1] by 45° with respect to one another. Will they produce the same Laue pattern? The answer is yes if the definition of “pattern” requires only that the spatial relationship between Laue spots (symmetry) be preserved. However, the patterns will be rotated by 45° with respect to one another. To simulate a Laue pattern, one need only select a crystallographic plane to be perpendicular to the incident x-ray beam (by definition, this is the orientation direction). However, this does not completely define the orientation as demonstrated by the example in Figure 21. In the algorithm described herein, the initial orientation displayed in Figure 19 takes away the extra degree of freedom. The main point we are trying to convey is that two Laue patterns, which are identical in every way except that they are rotated (in the plane of the film) by a finite angle with respect to one another, result from experiments wherein the same crystallographic plane
was oriented perpendicular to the incident x-ray beam. Therefore, a simulated Laue pattern, generated by the algorithm we described, will typically not match a correctly-corresponding experimental pattern until it is rotated within the plane of the film.

We have written a program in the Java language which implements this algorithm called LauePatternSim.java and uses an instantiable class LaueCalc.java. The program outputs a simulated Laue pattern via a GUI interface. As an example, we simulated Laue patterns for the (1 0 0), (1 1 0), and (1 1 1) orientations of a generic cubic crystal and the results are displayed in Figure 22.

Analysis of Laue Patterns

**Determining Orientation.** Determining the orientation of a single crystal by back-reflection Laue x-ray diffraction requires a good understanding of elementary crystallography. Analysis of as many as a dozen Laue patterns from different orientations might be required to unambiguously identify the orientation of the $a$, $b$, and $c$ axes relative to the crystal. It all begins with the Laue pattern collected from the initial orientation. Unless this orientation is chosen wisely or is particularly fortuitous, analysis of the first pattern will generally require great care. The first step is to locate the most important Laue spots in the pattern, which we will study further by taking a second Laue photograph. As discussed previously, important Laue spots result from diffraction from crystallographic planes which are perpendicular to two or more high-symmetry zone axes. Therefore, they lie at the intersection of two or more lines.
Figure 22. Laue-pattern simulations for a generic cubic crystal with orientations (a) (1 0 0), (b) (1 1 0), and (c) (1 1 1).
or hyperbolas of Laue spots and tend to stand out. There may be more than one Laue spot that fits this description and the way to decide which is most important is to study the Laue spots around them. If two mutually-perpendicular lines of spots intersect at a Laue spot, it is probably the best Laue spot to study. This is especially true if there is a small region running parallel to one of the lines which is conspicuously void of other Laue spots. However, it may be difficult to determine whether two lines are mutually-perpendicular if their intersection is far from the pattern’s center where the angles between them become distorted. If there are multiple choices among the possible Laue-spot candidates, none of which are obviously more important than the others, we typically just select one to study.

Once the next Laue spot is chosen, we rotate the goniometer until the Laue spot appears in the center of the new pattern. Our goniometer is such that if we identify a vector that runs vertically through it with the $\vec{z}$ axis of a cartesian coordinate system, it can rotate about the $\vec{z}$ axis and about an axis in the $\vec{x} - \vec{y}$ plane. We rotate about the $\vec{z}$ axis by angle $\alpha'$ and the axis in the $\vec{x} - \vec{y}$ plane by angle $\beta'$. To calculate these angles, we measure the position of the Laue spot we wish to study $(x', y')$ relative to $(O'; \vec{x}', \vec{y}')$, where the origin is defined by the four black pin-hole dots in every photograph. We then calculate the plane-normal vector $\vec{n}$ of the crystallographic plane corresponding to the Laue spot, relative to $(O; \vec{x}, \vec{y}, \vec{z})$,

$$\vec{n} = \left( \frac{1 + \mu}{2}, \frac{x'}{2D}, \frac{y'}{2D} \right),$$

(3.11)
where $\mu$ is defined by

$$\mu \equiv \sqrt{1 + \left(\frac{x'}{D}\right)^2 + \left(\frac{y'}{D}\right)^2}. \quad (3.12)$$

$\vec{n}$ and $\mu$ are functions of the Laue-spot position as well as the distance between the film and crystal $D$. If $\vec{n} = (n_1, n_2, n_3)$, then the absolute values of the new goniometer angles are

$$|\alpha'| = \left| \tan^{-1}\left(\frac{n_2}{n_1}\right) \right| \quad (3.13a)$$

$$|\beta'| = \left| \tan^{-1}\left(\frac{n_3}{\sqrt{n_1^2 + n_2^2}}\right) \right|. \quad (3.13b)$$

The direction of rotation is not calculated, but rather is determined by inspection of the Laue-spot position with respect to the center of the photograph. Rotation order matters because the operators representing these two rotations do not commute. Care must be taken to be sure that the rotation by $\alpha'$ always precedes that of $\beta'$.

When a Laue pattern for the new orientation is collected, the important Laue spot from the previous pattern is obscured by the beam spot, but the hyperbolas that intersected it in the previous pattern are now visible as lines. There are a few important tools that we employ to identify the orientation of the new Laue pattern. The pattern is first compared with simulated Laue patterns for high-symmetry orientations, which are obtained from a program like LauePatternSim.java. It is tempting to simply compare and contrast numerous simulations with the experimental pattern, but we need a more quantitative method to confirm orientations, because even a close
match to a simulated pattern only provides a good hypothesis. Our more sophisticated approach to crystal orientation involves the use of a stereographic projection on a Wulff net. A stereographic projection looks deceivingly like a Laue pattern, but is actually a projection of points on a unit circle representing crystallographic planes. The spatial arrangement of the points is dictated by the angles between the crystallographic planes which are represented by them and by the inherent symmetry of the crystal structure. Generating the stereographic projection provides two advantages which we exploit to identify the orientation of a Laue pattern. First, the angles between lines of Laue spots in the stereographic projection are the same as corresponding angles between lines in the Laue pattern. Making this comparison is generally the easiest way to determine the orientation of high-symmetry patterns such as deciding between (1 0 0) and (1 1 0) in a cubic crystal for example (see the distinct angles between major lines in Figure 22(a) and (b), respectively). Second, if the line which connects two important Laue spots runs through the center of the pattern (always true for the center spot and any other spot in the pattern), we can use Equation (3.13) to calculate the angle between the crystallographic planes responsible for each Laue spot. We do this by measuring the distance between the spots and calling it $x'$. Then, we calculate an angle as if we were going to rotate from (0,0) to $(x',0)$ where $\alpha'$ is the angle between the crystallographic planes. Given this angle, we compare the angles between crystallographic planes on the stereographic projection and search for matches. If there is a complete match (when angles between lines
of Laue spots, general symmetry, and angles between a few high-profile Laue spots are all consistent with the stereographic projection), it is likely the orientation has been solved. However, additional patterns from other orientations may be required to unambiguously identify the lattice-parameter directions for a crystal.

**Characterization of Crystal Quality.** The character of Laue spots is indicative of the quality of the portion of the single crystal being probed by the x-ray beam. We previously calculated the position of a Laue spot in a pattern, but this assumes the position of a Laue spot may be defined by a point. In an ideal world, a Laue spot is a dimensionless point, but the influence of parameters such as temperature and modest strain result in a finite size for, and elliptical distortion of, Laue spots. The position we calculated was really just the center of the Laue spot. When Laue spots appear as streaks or are severely elongated, the crystal is strained.[99] Unfortunately, we cannot really quantify the strain by the shape of the Laue spots, but this distortion’s presence or absence says much about the quality of the crystal. It is also common to observe Laue spots which are comprised of multiple, smaller spots at approximately the same position. Each spot represents diffraction from the same crystallographic plane but each originates from different grains with slight misorientation with respect to one another. Low-angle grain boundaries or twinning are responsible for this observation.[99]
The Bragg condition for diffraction, \( n\lambda = 2d\sin\theta \), contains two experimentally-accessible parameters. While the crystal structure defines the various \( d \)-spacings between planes and \( n \) describes the order of diffraction for a given Bragg reflection, we are able to control \( \lambda \) (wavelength of x-ray radiation) and \( \theta \) (crystal orientation). In Laue experiments, we could only choose a fixed orientation between the x-ray beam and the sample because we were working with a single crystal. To satisfy the Bragg condition, then, we were forced to use polychromatic radiation so that most planes could participate in diffraction. This configuration is reversible, however, if we use monochromatic radiation and sample all orientations with respect to the x-ray beam. This may be accomplished either by rotating a single crystal through all orientations during an experiment or by measuring a sample composed of small crystalline grains that are arranged in all orientations. The latter experiment is what is meant by powder x-ray diffraction.

Sample preparation for a powder x-ray diffraction measurement is simple, though one unfortunate consequence is that it is destructive to the sample. A sample is ground into a fine powder with mortar and pestle until the grain sizes are minimized. The powder is then affixed to a glass slide with a thin film of petroleum jelly by dusting the powder on the jelly surface and then gently tapping excess powder away. This procedure is repeated several times until there is a thin, even layer of powder
with excellent surface coverage. Once the powder is in the jelly, it must not be handled directly. The grains should be distributed over all possible orientations and any tampering with the powder already adhered to the slide may influence the distribution. The glass slide and petroleum jelly contribute a smooth background to the x-ray pattern which is characteristic of amorphous materials.[99]

The diffraction experiment is run with an x-ray diffractometer in $2\theta$-mode. X-ray radiation is produced via a standard Cu x-ray tube with 45 kV and 40 mA settings. The x-ray beam incident on the sample is dominated by Cu-K$_\alpha_1$ radiation ($\lambda = 1.540562$ Å), but also contains some Cu-K$_\alpha_2$ ($\lambda = 1.544390$ Å). Typical experiments scan from 10° to 70°, but the $2\theta$-range depends on the expected crystal structure. The data is in the form of intensity in counts per second as a function of $2\theta$.

Fundamentals of a Diffraction Pattern

A powder x-ray diffraction pattern is composed of a set of peaks, called Bragg reflections, each with its own position ($2\theta$) and intensity. Application of Bragg’s law allows for the calculation of Bragg-reflection positions using the known crystal structure ($d$’s) of the material and the experimental wavelength $\lambda$. But the intensity of Bragg reflections is more complicated to calculate. The x-ray pattern produced by a diffractometer may be simulated by calculating the intensity of the Bragg reflection from plane ($hkl$) with[99]

$$I = |F_{hkl}|^2 p \left( \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \right) e^{-2M}. \quad (3.14)$$
There are five important factors (polarization, structure, multiplicity, Lorentz, and temperature) which influence the intensity as calculated by Equation (3.14). We discuss each of these factors briefly.

The scattering of an x-ray beam by an electron was first described by J. J. Thomson.\cite{Thomson1907} He discovered that the ratio of the coherently scattered and incident beam intensity was proportional to a factor $\frac{1}{2} (1 + \cos^2 2\theta)$ where $2\theta$ is the same angle used in Bragg’s law. This term became known as the polarization factor. Of course, x-rays may scatter with an electron incoherently via the Compton effect, but incoherent scattering does not participate in diffraction so we ignore it.

When we consider x-ray scattering from an atom, the complexity increases. The nucleus may be completely ignored because it is far too massive to participate in scattering, but an atom with atomic number $Z$ contains $Z$ electrons which do participate. A simple guess that the intensity is just $Z$ times the scattering intensity from one electron is actually correct for $2\theta = 0$. However, the electrons are arranged about the atom in such a way that partial interference can occur between scattered x-rays from different electrons. Therefore, the intensity is not generally proportional to scattering from one electron. We define a quantity called the atomic scattering factor or atomic form factor $f$ as the ratio of the amplitude of the wave scattered by an atom and the amplitude of the wave scattered by one electron. Thus $f$ describes a kind of scattering efficiency for a given element. Values of $f$ are tabulated in sources.
such as Reference [99], but in general, $f$ is a monotonically decreasing function of $\sin \theta / \lambda$.

When atoms are periodically arranged in a crystal structure, we consider x-ray scattering from a unit cell. Bragg's law is traditionally derived for diffraction from continuous planes, but in reality, diffraction originates with coherent scattering from discrete atoms. Thus, we need to calculate scattering due to the specific arrangement of atoms in a crystal structure. Diffraction from “plane” $(hkl)$ is a function of the fractional atomic position $(u_n, v_n, w_n)$ and the atomic form factor $f_n$ for the $n$th atom. Summing over all $N$ atoms in the unit cell, the structure factor for Bragg reflection $(hkl)$ is calculated

$$F_{hkl} = \sum_{n=1}^{N} f_n e^{2\pi i (hu_n + kv_n + lw_n)}.$$  

(3.15)

The structure factor wields a powerful influence over the intensity of Bragg reflections. For example, diffraction patterns for materials with cubic crystal structures have surprisingly few Bragg reflections. This is because $F_{hkl} = 0$ for a large number of $(hkl)$ planes. In the case of a body-centered cubic crystal with one atom in its basis, $F_{hkl} = 0$ for any plane where $h + k + l$ is an odd number.[99] This effectively forbids half of all planes from participation in diffraction.

The multiplicity factor $p$ originates from the possible equivalency of planes of high symmetry. For example, a powder containing material with a cubic crystal structure might allow diffraction from $(1 \ 0 \ 0)$, $(0 \ 1 \ 0)$, and $(0 \ 0 \ 1)$ (more concisely written \{1 0 0\}). But the $d$-spacings of those three planes are identical so, according to the
Bragg condition for diffraction, they occur at the same position $2\theta$ and their identical intensities add together ($p = 3$). In this way, $p$ accounts for equivalent permutations of planes for which $d$ and $|F_{hkl}|^2$ are the same.

X-ray diffraction ideally occurs at a well defined angle $\theta$ given well-defined $d$ and $\lambda$, but in reality, all Bragg reflections have finite width and $\theta$ is identified as the angle where the Bragg reflection has maximum intensity. An angle $\theta + \delta\theta$ may still result in diffraction if $\delta\theta$ is sufficiently small. To model this, a geometric term called the Lorentz factor $(4 \sin^2 \theta \cos \theta)^{-1}$ is introduced. This is often combined with the polarization factor to produce the Lorentz-polarization factor

$$\frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}.$$  \hspace{1cm} (3.16)

The final factor relevant to the calculation of the intensity of Bragg reflections accounts for thermal vibrations of atoms. Thermal motion of atoms effectively decreases the intensity of reflections because the perfect, instantaneous periodicity of the lattice is degraded. It also causes the background to increase through temperature-diffuse scattering. Traditionally, the temperature is considered in the intensity calculation by modifying the atomic form factor $f$ so that it becomes $f = f_0 e^{-M}$ where $f_0$ is the form factor as previously described. Then, because $|F|^2$ is proportional to $f^2$, we multiply the intensity by the Debye-Waller factor $e^{-2M}$, which was first considered by Peter Debye[104] and later modified and improved by Ivar Waller.[105] $M$ depends on the amplitude of thermal vibration and the scattering angle $\theta$ and is approximately
described by

\[ M = \frac{6h^2T}{mk_B\Theta_D^2} \left[ \phi(x) + \frac{x}{4} \right] \left( \frac{\sin \theta}{\lambda} \right)^2, \]  
\[ (3.17) \]

where \( \Theta_D \) is the Debye temperature, \( k_B \) is the Boltzmann constant, \( x = \Theta_D/T \), and \( \phi(x) \) is

\[ \phi(x) = \frac{1}{x} \int_0^x \frac{\xi}{e^\xi - 1} \, d\xi. \]  
\[ (3.18) \]

Analysis of Experimental Patterns

Powder x-ray diffraction patterns are a material’s fingerprint. The positions and intensities of Bragg reflections are characteristic of a material, and an unknown powder is typically identified by comparison with entries in pattern databases or to a simulated pattern generated for a reasonable guess by programs such as PowderCell.\[106\] The observation of spurious Bragg reflections generally indicates the presence of one or more impurity phases within the sample. Calculation of the ratio of the Bragg reflections with largest magnitude for each phase provides a rough estimate for the relative quantity of parent and impurity phases in the sample.

Serious analysis of experimental diffraction patterns is conducted by comparing the diffraction pattern with the intensity calculation of Equation (3.14). Powerful programs such as PowderCell\[106\] and GSAS\[107\] fit the experimental pattern using a non-linear, least-squares regression algorithm called Rietveld refinement.\[108\] The crystal structure of a sample including space group, atomic positions, bond lengths, bond angles, and many other properties are extracted from the correct employment of
the Rietveld-refinement technique. However, Rietveld refinement of our experimental
diffraction patterns was not conducted in the course of this work. Instead, it was
sufficient to compare experimental patterns with a simulated pattern generated by
PowderCell.[106]

Iodometric Titration

Introduction

Iodometric titration is one of several techniques borrowed from analytical chem-
istry which have become standard in materials science. The popularity of the tech-
nique stems from its low cost and simple experimental procedure. Iodometric titra-
tion is mainly used to determine the oxygen content in compounds with possible
oxygen non-stoichiometry and is as precise as, or better than, thermogravimetric
analysis.[109]

A compound is built from two or more elements in specified ratios (the sto-
ichiometry) which depend on possible oxidation states and the satisfaction of charge
 neutrality. For example, simple ionic compounds such as NaCl or KI are chemi-
cally stable because charge neutrality is clearly satisfied (the oxidation states of their
constituent ions are Na\(^+\), Cl\(^-\), K\(^+\), and I\(^-\)). However, when we consider an oxide
containing a transition metal, the story is more complicated. Consider an archetypic-
ical ternary oxide \(\text{A}_a\text{B}_b\text{O}_c\) where A and O ions are each present in a single, well-known
oxidation state, but B is a transition metal with two or more possible oxidation states.
$A_aB_bO_c$ is perfectly stoichiometric when all B ions are $B^{+\eta}$. But through anneals in various conditions, $A_aB_bO_c$ can become oxygen deficient or rich ($A_aB_bO_{c+\delta}$ where $\delta$ is positive definite). Because the ratio $A/B$ is conserved, charge neutrality requires some B ions to adjust their oxidation states to compensate for the change in oxygen content. It is not surprising then that physical properties are often highly sensitive to oxygen non-stoichiometry.[110] Precise knowledge of the oxygen content is typically necessary for any meaningful study of such a material.

Iodometric titration is a form of redox titration in which iodine ($I_2$) is titrated with a sodium thiosulfate ($Na_2S_2O_3$) solution. This may be contrasted with iodimetric titration which titrates *with* $I_2$.[111] Iodometric titration relies on the ability of $I_2$ to oxidize thiosulfate ($S_2O_3$) into tetrathionate ($S_4O_6$) in the reaction[111, 112]

$$2S_2O_3^{-2} + I_2 \rightarrow 2I^- + S_4O_6^{-2} \quad (3.19)$$

The volume of $Na_2S_2O_3$ titrant ($\Delta V$) required to fully convert all $I_2$ to iodide ($I^-$) in Equation (3.19) is measured. Starch is used as an indicator so that the solution turns transparent from dark blue when all $I_2$ has been reduced. Because the concentration of the $Na_2S_2O_3$ solution is known ($C_t$), we can calculate how many mol of $I_2$ were reduced. The amount of $I_2$ present, produced through redox reactions involving the mixed oxidation-state ion (B in our example), is uniquely a function of the respective quantities of the mixed oxidation states present in the material (fraction of B ions that are $B^{+\eta}$). In this way, iodometric titration indirectly establishes the ratio of the
mixed oxidation states (or average valence of B) and, by requiring charge neutrality, can provide a precise measure of the oxygen content ($\delta$).

Any transition-metal oxide has the potential for oxygen non-stoichiometry and, in theory, iodometric titration could be used to determine its oxygen content. However, the nature of the experiment excludes certain compounds from consideration. First, the sample must be soluble in a dilute HCl solution. Ruthenium, chromium, niobium, and titanium oxides generally do not meet this requirement. Second, the compound must contain only one element with multiple oxidation states, and that element may only have two assumed oxidation states within the compound. For example, this excludes cuprates containing bismuth such as Bi$_2$CuO$_4$, Bi$_2$Sr$_2$CaCu$_2$O$_8$, and Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$, because bismuth and copper may both assume multiple oxidation states: Bi$^{+3}$, Bi$^{+5}$, Cu$^{+2}$, and Cu$^{+3}$. Iodometric titration is most commonly applied to manganese,[91] copper,[113] nickel,[114] and cobalt oxides[115].

**Experimental Procedure**

The experimental procedure described herein is adapted from Reference [113]. Before titration experiments are performed, we prepare a few solutions. To begin, we boil approximately 2 L of deionized H$_2$O to get rid of excess CO$_2$, and then we allow a day for the H$_2$O to cool (in a sealed container) to ensure the accuracy of each solution’s concentration. Then, the following solutions are prepared:

- 2.0 M KI Solution: 16.60 g of granular KI are weighed out and placed in a 50 ml volumetric flask, after which, $\sim$ 25 ml of H$_2$O is added to the flask to dissolve
the KI crystallites. The reaction $\text{KI} + \text{H}_2\text{O} \rightarrow \text{K}^+ + \text{I}^- + \text{H}_2\text{O}$ is strongly endothermic. Finally, the flask is topped off to the 50 ml line with H$_2$O. This solution is only stable for $\sim 6$ hours before it begins to yellow, indicating the presence of I$_2$. When this yellowing is observed, it must be prepared again.

- 2.0 M HCl: Generally, we dilute a stronger concentration of HCl such as 6 or 12.1 N HCl (N or normality is equivalent to molarity in HCl) to prepare the 2.0 M HCl solution.

- 0.01 N Na$_2$S$_2$O$_3$ Solution: This solution must be prepared with great accuracy. We weigh out 2.4 g of Na$_2$S$_2$O$_3$·5H$_2$O, place it in a 1000 ml volumetric flask, and swirl in some H$_2$O to dissolve the crystals. The solution is then topped off exactly to the 1000 ml line. The concentration of the solution must be known to at least five significant figures and should be around $C_t \sim 9.6 \times 10^{-3}$ mol/L. If kept sealed and in a dark environment, the Na$_2$S$_2$O$_3$ solution may remain functional for as long as a month.

- Starch-Indicator Solution: The starch-indicator solution is prepared freshly each day titrations are performed. We weigh out $\sim 1$ g of soluble starch and add $\sim 20$ drops of H$_2$O to the powder from a pipette. This mixture is stirred with a toothpick until it becomes a viscous paste. While stirring, we heat 100 ml of H$_2$O on a hot plate and add the paste after the H$_2$O reaches a rolling boil. The solution is boiled for one minute and then allowed to cool.
After the solutions have been prepared, we grind the sample into a fine powder with mortar and pestle. Each titration requires 10-20 mg of powder so it is best to have ~ 100 mg of powder for multiple titrations. The titration procedure goes as follows. We first weigh out 10-20 mg of powder in a test-tube style beaker and record the mass \( m \) (±0.1 mg). A magnetic stirrer is added to the beaker and then the top of the beaker is covered and sealed by a silicon sheet. Through this silicon sheet, we insert both a single hollow needle (to relieve overpressure) and a needle attached to the end of a tube which supplies Ar gas to the beaker. The air in the beaker is then purged for about five minutes with a gentle Ar flow. We allow the gas flow to continue throughout the experiment so that titration is conducted in an inert environment. Using needle-tipped syringes filled with 2.0 M HCl and 2.0 M KI solutions, we next add 6 ml of KI followed by 6 ml of HCl (1 cc = 1 ml), and stir the solution vigorously for ~ 30 minutes using the magnetic stirrer. The solution becomes a dark yellow or orange color during this step due to the presence of I\(_2\). This is because HCl dissolves the sample and then redox reactions between Cl\(^-\) and the B ions produce Cl\(_2\). This Cl\(_2\) simultaneously reacts with I\(^-\) to produce I\(_2\) through the reaction

\[
\text{Cl}_2 + 2\text{I}^- \rightarrow 2\text{Cl}^- + \text{I}_2, \quad (3.20)
\]

resulting in the yellowish-orange color of the solution. After checking that the powder has been completely dissolved following 30 minutes of stirring, we add ~ 1 ml of the starch indicator and the contents of the beaker become dark blue or purple. We are
then ready to titrate, so we record the initial volume of the Na$_2$S$_2$O$_3$ titrant (use a 50 ml calibrated buret whose tip penetrates the silicon cover by a hole in its center) and titrate drop-wise. When the end point is near, the solution lightens in color becoming weakly pink. At this point, it is best to let the solution sit a few minutes between each subsequent drop to watch the time-dependent effect of the color change. When the solution is fully transparent, the end point has been reached and we record the final volume on the buret and calculate $\Delta V = V_f - V_i$. This process should be repeated multiple times to assure a consistent and reliable result with good statistics.

**Experimental Analysis**

As detailed in the previous section, we dissolve $m$ mg of powder in HCl/KI solution under flowing Ar and titrate with $\Delta V$ ml of NaS$_2$O$_3$ solution with concentration $C_t$. The next step is to calculate the oxygen content ($\delta$) as a function of $m$, $\Delta V$, $C_t$, molecular weight $W$, and the stoichiometry of the material. Of course, the following calculations contain some strict assumptions about the material so, on a cautionary note, other sample characterization techniques should precede titration to ensure the sample is single phase with the correct stoichiometry and is free of significant chemical impurities. Otherwise, titration results, calculated in the following manner, could be misleading and incorrect. It is instructive to consider a generic transition metal oxide $A_aB_bO_{c+\delta}$. The stoichiometric compound ($\delta = 0$) contains $A^{+\epsilon}$, $B^{+\eta}$, and $O^{-2}$ ions, but oxygen non-stoichiometry allows for possible $B^{+\lambda}$ or $B^{+\sigma}$ where $\sigma < \eta < \lambda$. If we consider $A_aB_bO_{c+\delta}$, it is convenient to express the
chemical formula $A_a^+ [B_1^{+\eta} B_2^{+\lambda}] b O_{c+\delta}$, whereas if we consider $A_a B_b O_{c-\delta}$, it becomes $A_a^+ [B_1^{+\eta} B_2^{+\lambda}] b O_{c-\delta}$. Returning to our example, after $A_a B_b O_{c\pm\delta}$ powder is dissolved in the HCl/KI solution, all free $B^{+\lambda}$ or $B^{+\eta}$ ions are reduced to $B^{+\sigma}$ by reactions with chloride ($Cl^-$)

$$a_1 B^{+\eta} + a_2 Cl^- \rightarrow a_3 Cl_2 + a_4 B^{+\sigma}$$

$$b_1 B^{+\lambda} + b_2 Cl^- \rightarrow b_3 Cl_2 + b_4 B^{+\sigma},$$

where $a_i$ and $b_i$ ($i = 1, 2, 3, 4$) are coefficients which balance the reactions. Obviously, conservation of mass requires $a_1 = a_4$, $a_2 = 2a_3$, $b_1 = b_4$, and $b_2 = 2b_3$. It is convenient to define $\phi \equiv a_1 = a_4$ and $\psi \equiv b_1 = b_4$. Then, conservation of charge requires $\eta a_1 - a_2 = \sigma a_4$ and $\lambda b_1 - b_2 = \sigma b_4$, which become $\phi(\eta - \sigma) = a_2$ and $\psi(\lambda - \sigma) = b_2$.

The balanced reactions are then

$$\phi B^{+\eta} + \phi(\eta - \sigma) Cl^- \rightarrow \frac{\phi}{2}(\eta - \sigma) Cl_2 + \phi B^{+\sigma}$$

$$\psi B^{+\lambda} + \psi(\lambda - \sigma) Cl^- \rightarrow \frac{\psi}{2}(\lambda - \sigma) Cl_2 + \psi B^{+\sigma}. $$

The required principles of conservation provide an under-determined set of $a_i$ and $b_i$ leaving $\phi$ and $\psi$ as free parameters.

We consider first the case of $A_a B_b O_{c+\delta}$ ($A_a^+ [B_1^{+\eta} B_2^{+\lambda}] b O_{c+\delta}$). If $\gamma$ mol of $A_a B_b O_{c+\delta}$ is dissolved in the HCl/KI solution, before $B^{+\lambda}$ and $B^{+\eta}$ ions are reduced to $B^{+\sigma}$, we have $\gamma b$ mol of B composed of $\gamma b(1 - \alpha)$ mol of $B^{+\eta}$ and $\gamma b\alpha$ mol of $B^{+\lambda}$. Therefore, we identify $\phi \equiv \gamma b(1 - \alpha)$ and $\psi \equiv \gamma b\alpha$. $Cl_2$ is produced by the following reactions
via Equation (3.22)

\[
\gamma b(1 - \alpha)B^{+\eta} + \gamma b(1 - \alpha)(\eta - \sigma)Cl^- \rightarrow \frac{\gamma b}{2}(1 - \alpha)(\eta - \sigma)Cl_2 + \gamma b(1 - \alpha)B^{+\sigma}
\]

\[
\gamma b\alpha B^{+\lambda} + \gamma b\alpha(\lambda - \sigma)Cl^- \rightarrow \frac{\gamma b}{2}\alpha(\lambda - \sigma)Cl_2 + \gamma b\alpha B^{+\sigma}.
\]

(3.23)

The amount of Cl$_2$ produced is \(\frac{\gamma b}{2}(1 - \alpha)(\eta - \sigma)\) mol which sums to \(\frac{\gamma b}{2}\{(\eta - \sigma) + \alpha(\lambda - \eta)\}\) mol Cl$_2$. As Cl$_2$ is produced, it subsequently reacts with I$^-$ to produce I$_2$ by the following reaction via Equation (3.20)

\[
\frac{\gamma b}{2}\{(\eta - \sigma) + \alpha(\lambda - \eta)\}Cl_2 + \gamma b\{(\eta - \sigma) + \alpha(\lambda - \eta)\}I^- \rightarrow \\
\gamma b\{(\eta - \sigma) + \alpha(\lambda - \eta)\}Cl^- + \frac{\gamma b}{2}\{(\eta - \sigma) + \alpha(\lambda - \eta)\}I_2.
\]

(3.24)

Therefore, the amount of free I$_2$ evolved is uniquely a function of \(\gamma, b, \eta, \lambda, \sigma,\) and \(\alpha\).

If \(\xi\) mol of NaS$_2$O$_3$ are required to convert all I$_2$ back to I$^-$ by the following reaction via Equation (3.19)

\[
\gamma b\{(\eta - \sigma) + \alpha(\lambda - \eta)\}S_2O_3^- + \frac{\gamma b}{2}\{(\eta - \sigma) + \alpha(\lambda - \eta)\}I_2 \rightarrow \\
\gamma b\{(\eta - \sigma) + \alpha(\lambda - \eta)\}I^- + \frac{\gamma b}{2}\{(\eta - \sigma) + \alpha(\lambda - \eta)\}S_4O_6^-,
\]

(3.25)

then \(\xi = \gamma b\{(\eta - \sigma) + \alpha(\lambda - \eta)\}\). Solving for \(\alpha\), we find

\[
\alpha = \frac{\xi}{\gamma b(\lambda - \eta)} - \frac{\eta - \sigma}{\lambda - \eta}.
\]

(3.26)

Only \(\xi\) and \(\gamma\) have not yet been defined in explicit experimental or chemical terms.

If the concentration of the NaS$_2$O$_3$ solution is \(C_t\) and it took \(\Delta V\) ml to convert all I$_2$ to I$^-$, then \(\xi = C_t\Delta V\) and if the mass of A$_aB_bO_{c+\delta}$ is \(m\) and it has molecular weight
W, then \( \gamma = \frac{m}{W} \). This leads to a useful expression for \( \alpha \)
\[
\alpha = \frac{C_t \Delta V}{mb(\lambda - \eta)} W - \frac{\eta - \sigma}{\lambda - \eta} \tag{3.27}
\]

This is not the final calculation of \( \alpha \), because we have failed to address the subtle point that \( W \) is the total molecular weight of \( A_n B_b O_{c+\delta} \) and therefore \( W \) is a function of \( \delta \). We write \( W = W|_{A_n B_b O_c} + \delta W|_O \) where the first term is the molecular weight of the stoichiometric compound and the second term is the molecular weight of the excess oxygen.\(^{[116]}\) Then \( \alpha \) becomes
\[
\alpha = \frac{\chi}{b(\lambda - \eta)} [W|_{A_n B_b O_c} + \delta W|_O] - \frac{\eta - \sigma}{\lambda - \eta} \tag{3.28}
\]

where it is convenient to combine the experimental parameters by defining \( \chi \equiv \frac{C_t \Delta V}{m} \).

\( \delta \) is a function of \( \alpha \), which can easily be calculated by imposing charge neutrality on \( A^+_{\alpha} [B^{\eta}_{1-\alpha} B^{\lambda} \alpha]_0 O_{c+\delta} \). The result is \( \{a \epsilon + b \eta - 2c\} + ab(\lambda - \eta) = 2\delta \). However, the bracketed term is zero because it represents the stoichiometric case. The relationship between \( \alpha \) and \( \delta \) is therefore
\[
\alpha b(\lambda - \eta) = 2\delta. \tag{3.29}
\]

Solving for \( \delta \) and substituting it into Equation (3.28) provides
\[
\alpha = \frac{\chi}{b(\lambda - \eta)} [W|_{A_n B_b O_c} + \frac{\alpha b}{2}(\lambda - \eta)W|_O] - \frac{\eta - \sigma}{\lambda - \eta} \tag{3.30}
\]

and re-solving for \( \alpha \) gives
\[
\alpha = \frac{\chi}{b(\lambda - \eta)} W|_{A_n B_b O_c} - \frac{\eta - \sigma}{\lambda - \eta} 1 - \frac{\lambda}{2} W|_O \tag{3.31}
\]
Using Equation (3.29), we can also express it in terms of $\delta$

$$\delta = \frac{\chi W|_{A_a B_b O_c} - \frac{b}{2}(\eta - \sigma)}{1 - \frac{\chi}{2} W|_O}.$$  \hspace{1cm} \text{(3.32)}$$

Equation (3.32) calculates the excess oxygen of $A_aB_bO_{c+\delta}$ characterized by $\delta$, in terms of chemical and experimental parameters. When we consider $A_aB_bO_{c-\delta}$ (more conveniently written $A_{1-\alpha}^+[B_{1-\alpha}^+\lambda B_{1-\alpha}^+\lambda]_b O_{c+\delta}$), the procedure is identical to the case of excess oxygen except that only $B^{+\eta}$ produces $I_2$. The calculation results in equations for $\alpha$

$$\alpha = \frac{1 - \frac{\chi}{b(\eta - \sigma)} W|_{A_a B_b O_c}}{1 - \frac{\chi}{2} W|_O},$$ \hspace{1cm} \text{(3.33)}$$

and $\delta$

$$\delta = \frac{\frac{b}{2}(\eta - \sigma) - \frac{\chi}{2} W|_{A_a B_b O_c}}{1 - \frac{\chi}{2} W|_O}.$$ \hspace{1cm} \text{(3.34)}$$

The symmetry in $\delta$ between Equations (3.32) and (3.34) is intuitively appropriate.

While this method of calculating $\alpha$ and $\delta$ may seem a bit esoteric, the general results of equations (3.31), (3.32), (3.33), and (3.34) are valid for most materials. For example, compounds such as $La_2CuO_4$ have $B = Cu$, $\lambda = 3$, $\eta = 2$, $\sigma = 1$, and $b = 1$, and calculation of $\alpha(\chi)$ and $\delta(\chi)$ is trivial. Even compounds where the transition metal has only two oxidation states, such as $La_2NiO_4$ or $La_2CoO_4$ with $B = Ni, Co$, $\lambda = 2$, $\eta = \sigma = 1$, and $b = 1$, lend themselves to calculation of $\alpha(\chi)$ and $\delta(\chi)$ by this method.
EXPERIMENTAL TECHNIQUES

Vibrating-Sample Magnetometry

Magnetization was measured as a function of temperature by vibrating-sample magnetometry within the Physical Properties Measurement System (PPMS). The resolution[117] of the magnetometer is $\sim 10^{-6}$ emu and the temperature range in which measurements are made is between 1.9 and 400 K (or 300 to 1000 K with a special oven option). Temperature is swept at rates between 0.01 and 12 K/min during a measurement, though our typical default rate was 0.1-1 K/min.[118] A superconducting magnet supplies fields between $\sim 0$ Oe (there is a small remnant field) and 90000 Oe (9 T). The magnet is a longitudinal superconducting solenoid, which is composed of a Nb-Ti alloy embedded in Cu.[118] The magnetic field produced by the magnet is estimated to have 0.01% uniformity over a 5.5 cm region,[118] which covers most of the region relevant to the measurement. Samples are affixed to a quartz or G-10 sample paddle with a solution of Duco cement diluted with acetone, which contributes a negligible background on the order of $10^{-6}$ emu. The sample paddle is attached to a long sample rod and is driven by a linear transport motor at 40 Hz through a coil-set puck. The puck contains detection coils, in which a voltage is induced by a changing magnetic flux, and a thermometer to monitor sample temperature.
Theory of Operation

A magnetometer measures an induced voltage in a conductive loop which encompasses a changing magnetic flux. The induced voltage according to the flux rule is given by

$$V_{\text{coil}} = -\frac{d\Phi}{dt} = -\left(\frac{d\Phi}{dz}\right)\left(\frac{dz}{dt}\right), \quad (4.1)$$

where the minus sign is due to Lenz’s Law. Because the linear transport motor drives the sample through the coil set so that the vertical position of the sample obeys $z(t) = A \cos(2\pi ft)$ where $A$ is the amplitude of oscillation (generally 1-3 mm) and $f$ is the frequency (40 Hz), we can easily calculate $(dz/dt)$. On the other hand, $(d\Phi/dz)$ is difficult to calculate, but it depends on the DC magnetic moment of the sample $M$. In fact, it is proportional to $M$ with a coupling constant $C$ (units of Oe m emu$^{-1}$).[117] The voltage induced in the coil set

$$V_{\text{coil}} = 2\pi fCM A \sin(2\pi ft), \quad (4.2)$$

is amplified and lock-in detection allows the coefficient of the sinusoidal voltage response to be accurately measured. With the exception of $M$, all the terms in the coefficient are constant and known, so $M$ is easily extracted.

Experimental Operation

When measuring magnetization, there are only a handful of experimental choices which must be made. The most important experimental factors include the size and shape of the sample and the amplitude of oscillation $A$. Other decisions regarding
parameters have little influence on the quality of data if they are approached with common sense. For example, during a temperature-dependent magnetization experiment, the temperature sweep rate should not exceed $\sim 1$ K/min because the sample fails to attain a quasi-static thermodynamic equilibrium.

Without a doubt, the most influential experimental parameter is the shape and size of the sample. The magnetometer is calibrated with a cylindrical Pd standard, and as a result, the ideal sample is cylindrically-shaped.[117] However, the samples we measured were parallelepiped bars because it is prohibitively difficult to machine oxide single crystals into cylinders. There is a small error associated with using bars instead of cylinders (negligible for antiferromagnets), but to our knowledge, there are no calculations available which describe it. Furthermore, it is outside the scope of this work to produce one here, but it is a fact which warrants some level of awareness. On the other hand, the length of the sample is a factor over which we generally do have control. A smaller sample length results in more accurate data, but it also produces less signal.[117] These competing factors must be weighed against one another and considered on a sample by sample basis. The lengths of samples used in measurements relevant to this work were kept to a few millimeters without sacrificing resolution because they had sufficiently-large intrinsic signals. A smaller oscillation amplitude results in higher accuracy, especially as the sample length gets longer.[117] We used the default amplitude of 3.0 mm for our measurements.
Thermal-Relaxation Calorimetry

The PPMS heat-capacity option uses the thermal-relaxation technique to measure heat capacity at constant pressure between 1.9 and 400 K and in applied fields between 0 and 9 T.[119] Use of a Helium-3 insert can extend the low end of the accessible temperature range to \( \sim 0.4 \) K.

Heat Capacity Puck

The heat-capacity puck (see Reference [119] for details) consists of a copper frame from which eight delicate platinum wires suspend a \( 3 \times 3 \) mm\(^2\) alumina platform. On the underside of the platform, there is a resistive heater and a thermometer. The sample sits on the sample platform, to which it is mechanically and thermally coupled via Apiezon thermal grease, and from where we can introduce heat pulses and measure its temperature locally. The eight wires not only provide electrical connection to the platform’s thermometer and heater, they also provide a thermally conductive route between the platform and the thermal bath (the puck frame which has its own thermometer). A copper cap for the puck functions as a radiation shield to insulate the experiment thermally.

Theory of Operation

The thermal-relaxation technique is a conceptually simple method used to measure \( C_p \). We begin with a sample, which is in equilibrium with a thermal bath at temperature \( T_b \) (the temperature of the puck frame), and introduce a heat pulse.
This is accomplished by driving a constant current between a few nanoamps and a few milliamps through the platform heater for a given period of time \( t_0 \). Thus, a constant power \( P_0 \) is supplied for \( t_0 \) seconds, which raises the sample temperature to \( T_0 \equiv T_b + \Delta T \) as measured by the platform thermometer. Good thermal contact between the platform and sample is ensured by the use of Apiezon thermal grease. At time \( t_0 \), the current is shut off so that the supplied power drops from \( P_0 \) to zero and the temperature of the sample begins to decay from \( T_0 \) toward \( T_b \) (see Figure 23). The chamber pressure is kept at \( \sim 0.01 \) mTorr so there is negligible convective cooling, and the thermal conductance between the sample platform and thermal bath is dominated by the platinum wires which connect them.

This process is repeated multiple times for each temperature and, by fitting the time-dependent decay of the sample temperature with a model, a value for \( C_P \) is extracted. We correct for the heat-capacity contributions of the thermal grease and sample platform by measuring their combined heat capacity before placing the sample on the platform, and subtracting it from the measurement which includes the sample. This background contribution is referred to as the addendum. The quality of thermal coupling between the sample and platform decides which of the two temperature-decay models are used to extract \( C_P \). The simple model (one decay constant) is used for “perfect” thermal coupling and the two-tau model \(^{TM} \) (two decay constants) is appropriate for more realistic thermal coupling.
In the simple model, the time-dependence of the temperature of the platform/sample system obeys

$$C_t \frac{dT}{dt} = -K_w(T - T_b) + P(t)$$

$$P(t) = \begin{cases} P_0 & 0 \leq t \leq t_0 \\ 0 & t > t_0 \end{cases}, \quad (4.3)$$

where $C_t$ is the total heat capacity of the sample, grease, and platform, $K_w$ is the thermal conductance of the wires supplying heat pulses to the platform, $T_b$ is the temperature of the thermal bath (puck frame), and $P(t)$ is the power from the heater. Equation (4.3) is a separable, ordinary differential equation and can be solved by integration. The solution is

$$T(t) = \frac{P_0}{K_w} \left( 1 - e^{-\frac{K_w}{C_t} t} \right) + T_b \quad 0 \leq t \leq t_0 \quad (4.4a)$$

$$T(t) = (T_0 - T_b) e^{-\frac{K_w}{C_t} (t-t_0)} + T_b \quad t > t_0, \quad (4.4b)$$

where $T_0 = T(t_0)$ is the highest temperature reached before the current is turned off, as calculated in Equation (4.4a). The solution for $T(t)$ is plotted in Figure 23.

Non-linear, least-squares fitting of the temperature-decay curve allows us to extract a value for $C_t$ and the sample’s heat capacity is calculated by subtracting $C_{\text{addenda}}$ from $C_t$. Note that $C_t/K_w$ forms a natural time constant in Equations (4.4a) and (4.4b), which we define as $\tau$.

When the thermal coupling between the sample and platform is less than ideal, the two-tau modelTM is used. In this model, the temperature relaxation between the sample and platform and between the platform and the thermal bath are considered
separately, leading to the coupled differential equations

\[ C_p \frac{dT_p}{dt} = P(t) - K_w (T_p(t) - T_b) + K_g (T_s(t) - T_p(t)) \] (4.5a)
\[ C_s \frac{dT_s}{dt} = -K_g (T_s(t) - T_p(t)) , \] (4.5b)

where \( C_p \) is the heat capacity of the platform (not to be confused with \( C_P \) which is generic heat capacity at constant pressure), \( C_s \) is the heat capacity of the sample, \( P(t) \) is defined as it was in Equation (4.3), and \( T_p \) and \( T_s \) are the temperatures of the platform and sample, respectively. In the limit \( T_s \to T_p \), we recover Equation (4.3) from Equation (4.5a). The solutions for Equations (4.5a) and (4.5b) take a simple form that we could probably have guessed from the name of the model: \( T_x(t) = A_x + B_x e^{-t/\tau_1} + D_x e^{-t/\tau_2} \) where \( x \) represents either the platform or sample and \( A_x, B_x, D_x, \tau_1, \) and \( \tau_2 \) are constants. While the form of the solution is simple, the expressions for the constants are quite complicated. For example, using the technique of Laplace
Transforms, the characteristic time constants were calculated

\[ \frac{1}{\tau_1} = \frac{1}{2} \left[ \frac{K_g + K_w}{C_p} + \frac{K_g}{C_s} \right] - \frac{1}{2} \sqrt{\left[ \frac{K_w + K_g}{C_p} - \frac{K_g}{C_s} \right]^2 + 4 \frac{K_g^2}{C_s C_p}} \]

\[ \frac{1}{\tau_2} = \frac{1}{2} \left[ \frac{K_g + K_w}{C_p} + \frac{K_g}{C_s} \right] + \frac{1}{2} \sqrt{\left[ \frac{K_w + K_g}{C_p} - \frac{K_g}{C_s} \right]^2 + 4 \frac{K_g^2}{C_s C_p}} \],

where \( \tau_1 > \tau_2 \). Despite the difference in complexity of the two models, the procedure used to measure \( C_P \) (heat capacity of the sample at constant pressure) is equivalent for both: the time-dependent temperature relaxation is fit by the model and \( C_P \) is extracted from the characteristic time constant(s). The software that runs the measurement fits the data with both models and then selects the results from the one providing the best fit. When the sample coupling, which is defined by \( 100 \times \frac{K_g}{(K_g + K_w)} \%) \), is less than 100%, the two-tau model \( ^{\text{TM}} \) generally provides the best fit. However, when sample coupling is sufficiently close to 100%, the simple model is typically better. In rare cases where the sample coupling drops below 90%, the results are unreliable and the sample must be re-measured.

**Measurement Details**

There are several important considerations regarding the measurement of heat capacity which warrant some attention. The most salient points include the requirements on sample size and character, the choice of thermal grease, and strategies to accurately measure heat capacity in the vicinity of a phase transition. We discuss each of these subjects in turn.
The dimensions and character of a sample must meet certain requirements, imposed by the technique, in order to measure $C_P$. Most importantly, the puck is designed to accommodate samples with mass between 1 and 200 mg and with surface area smaller than the $3 \times 3$ mm$^2$ platform. But there are additional points to consider even for samples which meet these requirements. First, the rise and decay times of the sample temperature increase with increasing sample mass, which extends the total measurement time of the experiment. Heat capacity is an inherently slow measurement and, for particularly massive samples, a $C_P$ curve from 2 to 300 K may take upwards of three to four days (including the addendum measurement). This point tends to encourage smaller samples when measurement time is expensive. Second, the size of a sample must be deliberately prepared so that its thermal diffusion time is small compared to the relevant time constants ($\tau$'s). Samples with low thermal conductivity, for example, must be relatively flat (sample dimension perpendicular to the platform is small compared to dimensions parallel to it) to compensate for long thermal-diffusion times. Other than size considerations, the sample surface chosen to form the interface with the platform must be polished smooth and flat and be free of defects which could impede thermal conduction.

The choice of Apiezon thermal grease depends on the temperature region where $C_P$ is measured. N-grease, which melts not far above room temperature, is typically used at low temperature ($0 \leq T \leq 305$ K) while H-grease is more appropriate above 305 K.[119] The heat capacity of N-grease is well behaved at low temperature ($T <$
200 K)[121], but there are features which appear between 200 and 325 K with a poorly-reproducible character, culminating in a large anomaly centered at $\sim 295$ K.[122] Therefore, high resolution measurements in this temperature region must be approached with caution. If N-grease must be used (if measurements at low temperature are necessary), this problem can be minimized by using as little grease as possible and sampling the addenda densely. In general, it is best to minimize the amount of grease used (typical volumes are less than 1 mm$^3$).

Heat capacity is a sensitive probe of phase transitions, but measuring the sharp anomalies in $C_P$ in the vicinity of a phase transition is exceedingly challenging. This is mainly a consequence of an assumption made in the thermal-relaxation technique, that $C_P$ is constant in the temperature range $T_b$ to $T_b + \Delta T$. In reality, $C_P(T)$ is temperature-dependent and the extracted $C_P$ value associated with $T_b$ is an average of $C_P(T)$ throughout the $\Delta T$ temperature range being measured. When measuring around sharp, diverging anomalies, this averaging effect results in a broader anomaly with artificially-reduced magnitude.[123] To minimize this effect, it is best to select a small $\Delta T$ and measure with high data density. Far away from a phase transition, the default rise $\Delta T/T_b = 2\%$ is fine, but around the transition, we typically use $\Delta T/T_b \sim 0.5\%$. It is also important to approach $T_C$ carefully so that no measurement goes through it (avoid the situation $T_b < T_C < T_b + \Delta T$). This latter point is especially important when measuring a first-order phase transition.[123] The simple and two-tau models$^{TM}$ anticipate a smooth, well-behaved relaxation curve. However, if the
temperature decays through $T_C$ in a first-order phase transition, the latent heat causes
the temperature to remain constant at $T_C$ for a finite time before the latent heat has
been released and further loss of thermal energy results in decreasing temperature
again. The models are unable to fit such behavior and the resulting measurement is
extremely poor.[123]

High-Resolution Dilatometry

Introduction

The measurement of thermal expansion may be approached with a variety of tech-
niques including, x-ray or neutron diffraction,[124] optical interferometry,[125] and
capacitance dilatometry.[126] While each has its own set of advantages and disadvan-
tages, the measurements reported herein were made with a three-terminal capacitance
method (high plate, low plate, and ground). At the foundation of the capacitance-
dilatometer technique is a dilatometer cell consisting of two closely-spaced parallel
plates. The plates form a capacitor, which obeys the simple physics of the parallel-
plate capacitor wherein capacitance $C$ is a function of the plate area $A$, distance
between the plates $d$, and the permittivity $\epsilon$ of the medium existing between the
plates

$$C(T) = \epsilon(T) \frac{A(T)}{d(T)}.$$  \hspace{1cm} (4.7)

Equation (4.7) is valid only when $A \gg d$ so that fringe-field effects around the outer
edges of the capacitor plates make a negligible contribution to the total measured
capacitance. This condition is maintained by the design[127] of our cell. A dilatometry technique uses Equation (4.7) to correlate $C(T)$ with a changing gap between the capacitor plates $d(T)$, and the latter quantity corresponds to the thermal expansion or contraction $\Delta \ell / \ell$ of the sample being measured.

**Dilatometer-Cell Design**

The design of the capacitance-dilatometer cell used to measure the data for this work is the last in a long series of iterations.[127, 128] Most of the design and testing work, as well as manufacture of the cells, was completed at Montana State University. A schematic of the cell design is reprinted in Figure 24 from J. J. Neumeier, R. K. Bollinger, G. E. Timmins, C. R. Lane, R. D. Krogstad, and J. Macaluso, Rev. Sci. Instrum. 79, 033903 (2008) with permission from the American Institute of Physics and Dr. John Neumeier. As can be seen in Figure 24(a), the cell is constructed from four distinct parts, all made of fused quartz. These parts include two L-shaped pieces (one stationary and one mobile) and two springs. The angled wedge in Figure 24 is a necessary accessory, but is not considered to be part of the cell. Capacitor plates are made from vapor-deposited gold on the two L-shaped pieces (with a thin layer of chromium underneath to help the gold adhere to the cell). The low capacitor plate, deposited on the stationary L-shaped piece, is displayed in Figure 24(a) with a guard ring etched into the gold around the parameter of the plate. The guard ring is grounded which reduces fringe-field effects.[127] The high plate is on the mobile L-shaped piece and is not directly visible in Figure 24(a), though its location is
obvious when we view the assembled cell in Figure 24(b). The two L-shaped pieces are assembled by gluing two quartz springs to the positions indicated in Figure 24(b) with a Na$_2$SiO$_3$ solution. The springs hold the cell together in such a way that the capacitor plates remain parallel with high precision and they apply tension when we establish a gap by seating a sample. The sample sits within the valley at the top of the cell seen in Figure 24(b). Typically, the sample is not large enough to span the entire width of the valley, so a wedge with the proper dimensions is selected and inserted between the sample and the valley wall of the stationary L-piece. A 3° angle is cut in that valley wall and the wedge has a corresponding 3° angle. As it is gently pushed between the sample and the wall, the wedge and sample collectively span the valley, and push the mobile L-shaped piece away from the stationary piece against
the tension supplied by the quartz springs. This action establishes the capacitance gap $d$.

**Measurement Details**

The measurement of thermal expansion using our experimental setup is described in Reference [127], but we supplement that information with a brief description of several aspects of the experiment herein. When a sample is loaded into the dilatometer cell, we establish a gap between the capacitor plates. A typical installation gap leads to a capacitance reading of 15-25 pF. After allowing the capacitance to stabilize, we install the thermal-expansion probe into a cryostat, which has been dedicated to thermal-expansion measurements. The cryostat has an inner sample chamber, surrounded by a narrow vacuum space, which is subsequently surrounded by a region for cryogenic liquids.

After installing the probe, the sample space is heated slowly to a maximum of 350 K by a 60 Ω manganin resistive heater, which is wrapped around the bottom of the sample chamber tube, and powered by a DC power supply set to 15-20 V. While heating, a turbo pump evacuates the sample chamber for 16-20 hours until it reaches $\sim 10^{-6}$ mbar. However, in the initial stages of pumping/heating, three helium gas flushes are conducted at 30 minute intervals. Any residual gas bakes off the probe and sample-chamber surfaces (some are first knocked off by the helium gas flushes) and is removed by the turbo pump so that we start with a clean environment in the sample chamber. We carefully cool the sample chamber from $\sim 350$ K to room
temperature by transferring a modest amount of liquid nitrogen to the cryogen space. Upon reaching room temperature, the sample chamber is flooded with 50 mbar of helium exchange gas, the vacuum space is pumped out with the turbo pump for 5 minutes, and 50 mbar of helium exchange gas is added to the vacuum space. Liquid nitrogen is then transferred cautiously and intermittently to maintain a cooling rate no higher than 3-4 K/min down to ∼80 K. Once this temperature is reached, the liquid nitrogen is blown out of the cryogen space with an overpressure of nitrogen gas, and 5-8 L of liquid helium is transferred. The system is able to reach a low temperature of ∼5-6 K due to the imperfect ability of the helium exchange gas to communicate 4.2 K to the sample and thermometers. This is especially true when some of the exchange gas condenses on the inner cryostat walls.

Capacitance is measured by an Andeen-Hagerling precision capacitance bridge, which can measure a stable capacitance (units of pF) in the sixth digit after the decimal point. This corresponds to a resolution for ∆L/L on the order of 0.1 Å for a sample 1-2 mm long! [127] This resolution is ∼1000 times better than the highest resolution diffraction measurements. The astonishing resolution of the bridge is a consequence of its isolated internal reference capacitor. Temperature is measured with a Lakeshore 340 temperature controller which simultaneously measures the resistances of platinum and Cernox™ resistive thermometers. The platinum thermometer has low sensitivity (defined by $S = (dR/dT)^{-1}$) below ∼50 K, but typical metallic resistance with higher sensitivity above. The Cernox™, on the other hand, is a
semiconducting thin-film resistor, so its sensitivity is high at low temperature and decreases monotonically with increasing temperature. Each resistor was calibrated against a standard thermometer from the PPMS and is affixed to a quartz block at the same height as the sample. The deliberate placement of the thermometers puts them at roughly the same position as the sample in the vertical and horizontal temperature gradients. Because the sensitivity of each thermometer is optimal in different temperature ranges, we use the Cernox™ thermometer exclusively below 50 K, and then perform a weighted average of the two thermometers above 50 K

\[ T = \frac{S_{\text{Cer}}T_{\text{Cer}} + S_{\text{Pt}}T_{\text{Pt}}}{S_{\text{Cer}} + S_{\text{Pt}}}, \]  

(4.8)

where subscript Cer corresponds to Cernox™ and subscript Pt refers to platinum.[127]

It would be ideal to measure capacitance on both warming and cooling, but we are unable to control the cooling rate from 77 down to 5 K, so the measurement on cooling is not useful in this range. Our standard procedure is to measure on warming once the cryostat has reached its lowest temperature and is stable. The 60 Ω resistive heater, run by the Lakeshore temperature controller now, is activated and the sample chamber begins to warm. Initially, a Labview program controls the power output of the heater blindly with no feedback in such a way as to warm the sample chamber at a stable, uniform rate of 0.20(1) K/min for 6000 seconds.[127] Its ability to maintain the 0.2 K/min warming rate is contingent on the pressures inside the sample and vacuum spaces and the volume of liquid helium in the cryogen chamber. This is why we are so careful to keep the conditions of the cryostat as
reproducible as possible. After 6000 seconds, a feed-back routine is adopted, which carefully monitors the warming rate at 20 Hz and adjusts the power output in response to deviation from 0.2 K/min.[127] The Lakeshore measures the resistance of the two thermometers every 50(2) ms while the capacitance bridge averages $2^{N-1}$ points (we use $N = 7$) to output a capacitance data point every 5.2 s.[127] In the 5.2 s required for the capacitance bridge to produce a capacitance data point, 104 temperature readings are collected. These 104 data are averaged to yield the temperature. Therefore, every 5.2 s, a capacitance and temperature data point, which are averages of 64 and 104 individual datum, respectively, are collected.[127] However, to increase the resolution and decrease experimental noise further, we average between 1 and 10 of these data to yield the final data point. For example, if we average 10, then every 52 s we get a data point, and with the warming rate fixed at 0.2 K/min, we have a data point every $\sim 0.17$ K. We can increase the data density at the expense of resolution by decreasing the number of data points averaged.

Calibration of Dilatometer Cell

In order to calculate a change in capacitor gap $\Delta d$ from a change in capacitance $\Delta C$, and thereby infer a change in the sample length $\Delta L$, the calibration factor $\epsilon A$ (see Equation (4.7)) must be determined for each dilatometer cell. To determine $\epsilon A$ for a given cell, we first measure the background contribution, referred to as the empty-cell effect, followed by an annealed copper standard.
The empty-cell effect is a measurement of the capacitance between 5 and 350 K when a fused-quartz wedge, large enough to establish a gap $d$ and apply tension to the quartz springs, is seated instead of a sample. The quartz wedge has the same thermal expansion as the dilatometer cell so there is no differential thermal expansion. Therefore, the measurement accounts primarily for non-parallellicity of the quartz springs and imperfections in the machining of the cell, as well as the temperature-dependent behavior of the gold capacitor-plate areas, the quartz springs, and the sodium-silicate glue which affixes the springs to the cell.[127] The empty-cell effect is smooth, reproducible, and small (140 times smaller than the empty-cell effect for a copper dilatometer cell).[127]

After measuring the empty-cell effect, we measure the thermal expansion of high-purity, annealed copper as a reference material.[127] The thermal expansion of quartz is zero at 300 K and 79.2 K as we will later show, so at these two temperatures, $\Delta L/L$ is entirely attributable to the thermal expansion of copper. We take advantage of this fact by overlapping published copper data[129] with our measured $\Delta L/L$ at 79.2 and 300 K, after subtracting the empty-cell effect and accounting for the differential thermal expansion between quartz and copper.[127] We discuss the details of this procedure next.

Before attempting to extract $\epsilon A$ from the empty-cell and copper measurements, we confront two subtle points. First, we need access to accurate measurements of the *absolute* thermal expansion ($\Delta L/L$) of both fused-quartz and copper, and second,
we need an appropriate function with which to fit discrete sets of data so that we can work with them. The absolute $\Delta L/L$ for copper has been published in the range 2-320 K with a three-terminal capacitance dilatometer[129] and the absolute coefficient of thermal expansion ($\mu \equiv d/dT(\Delta L/L)$) of fused-quartz is published in the temperature range 6-273 K as studied with laser interferometry[125] and 273-473 K from capacitance dilatometry.[130] If we integrate $\mu(T)$ with respect to $T$ and set the integration constant so that $\Delta L/L = 0$ at 300 K, we calculate a suitable $\Delta L/L$ data set for fused-quartz. As far as fitting the discrete data is concerned, any mathematically complete set of polynomials would work, but we have found Chebyshev polynomials of the first kind to be the most useful. The Chebyshev polynomials, $T_0(x)$, $T_1(x)$, ..., $T_n(x)$, are mutually orthogonal over the interval [-1,1] and can approximate a function $f(x)$ better and in fewer terms than most other sets of polynomials.[131] Like other complete sets of polynomials, any smooth, differentiable function $f(x)$ may be expressed as an infinite series

$$f(x) = \sum_{i=0}^{\infty} a_i T_i(x).$$  \hspace{1cm} (4.9)
Typically, we use a maximum of six terms to fit our data. The first six Chebyshev polynomials of the first kind are

\begin{align}
T_0(x) &= 1 \\
T_1(x) &= x \\
T_2(x) &= 2x^2 - 1 \\
T_3(x) &= 4x^3 - 3x \\
T_4(x) &= 8x^4 - 8x^2 + 1 \\
T_5(x) &= 16x^5 - 20x^3 + 5x.
\end{align}

We fit the $\Delta L/L$ data for fused-quartz[125, 130] and copper[129], and the capacitance data for our empty-cell and copper-standard measurements, piecewise with $\sum_{i=0}^{5} a_i T_i(T)$ (see Reference [127]). The quartz fit is displayed in the inset of Figure 25.

After all the discrete data sets are fit, we use them to calibrate the cell. The fit to the empty-cell measurement, $C_{\text{empty cell}}(T)$, is first normalized to the copper data at its lowest measured temperature $T'$

$$C_{\text{normalized empty cell}}(T) = \left[ \frac{C(T) - C(T')}{C(T')} \right]_{\text{empty cell}} \times C_{\text{Cu}}(T').$$

(4.11)

This step calculates the percentage change of the capacitance exhibited by the empty cell and then scales it with the capacitance of the copper measurement. The copper data is then corrected for the empty-cell effect by subtracting the normalized empty-cell capacitance (Equation (4.11)) from the copper data

$$C_{\text{corrected Cu}}(T) = C_{\text{Cu}}(T) - C_{\text{normalized empty cell}}(T).$$

(4.12)
Figure 25. $\Delta L/L$ for fused-quartz (the line is a guide for the eye). The inset highlights the two temperatures where $\Delta L/L = 0$ and the line is our piecewise Chebyshev-polynomial fit.

The next step is to make a rough attempt at calibrating the dilatometer cell without accounting for the thermal expansion of quartz. To accomplish this, we invoke the simple expression for the parallel-plate capacitor (Equation (4.7))

$$C(T) = \frac{\epsilon A}{d(T)}. \quad (4.13)$$

If we ignore the differential expansion between quartz and copper (referred to as the relative effect[127]), the change in length $\Delta L$ comes from changes in the capacitance gap

$$\Delta L = d(T) - d(300). \quad (4.14)$$
We can approximate the capacitor gap at any temperature by solving Equation (4.13) for $d(T)$

$$d(T) = \frac{\epsilon A}{C(T)},$$  \hspace{1cm} (4.15)

and, after substituting it into Equation (4.14) and normalizing $\Delta L$ by the length of the copper sample at 300 K, Equation (4.14) becomes

$$\left( \frac{\Delta L}{L} \right)_{Cu} = \frac{\epsilon A}{L_{Cu \ 300}} \left[ \frac{1}{C_{corrected \ Cu}(T)} - \frac{1}{C_{corrected \ Cu}(300)} \right].$$  \hspace{1cm} (4.16)

A rough dilatometer-cell calibration is performed by estimating values for $\epsilon A$ until $\Delta L/L$ from Equation (4.16) overlaps the published copper data[129] at 79.2 and 300 K.

However, an accurate dilatometer-cell calibration requires us to account for the differential thermal expansion between quartz and copper and then to refine the approximate value for $\epsilon A$ we found in the previous step. To this end, we derive an expression to replace Equation (4.16). We begin by expressing the change in the capacitor gap as

$$\Delta d = d(T) - d(300).$$  \hspace{1cm} (4.17)

But $\Delta d$ can also be expressed in terms of the difference between the change in the length of the copper sample and the change in length of the quartz (the relative effect discussed in Reference [127])

$$\Delta d = (\Delta L)_{Cu} - (\Delta L)_{Quartz}.$$  \hspace{1cm} (4.18)
Substitution of Equation (4.18) into Equation (4.17) allows us to solve for the change in length of the copper sample

\[(\Delta L)_{Cu} = d(T) - d(300) + (\Delta L)_{Quartz}.\quad (4.19)\]

If we substitute Equation (4.15) into Equation (4.19) and normalize by the length of copper at 300 K, we obtain

\[\left(\frac{\Delta L}{L}\right)_{Cu} = \frac{1}{L_{Cu}} \left[ \frac{\epsilon A}{C_{corrected\ Cu}(T)} - \frac{\epsilon A}{C_{corrected\ Cu}(300)} + (\Delta L)_{Quartz} \right]. \quad (4.20)\]

At 300 K, \(L_{Cu}(300) = L_{Quartz}(300) + d(300)\),[127] and we can rearrange this relationship to get unity

\[1 = \frac{L_{Cu}(300) - d(300)}{L_{Quartz}(300)}. \quad (4.21)\]

We multiply the \((\Delta L)_{Quartz}\) term in Equation (4.20) by one (Equation (4.21)) to obtain the final expression for \(\Delta L/L\), which includes the relative effect of the thermal expansion of quartz

\[\left(\frac{\Delta L}{L}\right)_{Cu} = \frac{1}{L_{Cu}} \left[ \frac{\epsilon A}{C_{corrected\ Cu}(T)} - \frac{\epsilon A}{C_{corrected\ Cu}(300)} + (L_{Cu}(300) - d(300)) \left(\frac{\Delta L}{L}\right)_{Quartz} \right]. \quad (4.22)\]

If the temperature-dependent thermal expansion of quartz was zero, Equation (4.22) reduces to Equation (4.16) as it should. The only terms for which we have no published results or cannot measure directly in Equation (4.22) are \(\epsilon A\) and \(d(300)\). However, we estimate \(d(300)\) using Equation (4.15) by substituting in \(C_{corrected\ Cu}(300)\) and \(\epsilon A\) as determined by Equation (4.16). We then iteratively search for an optimized
value for $\epsilon A$ which properly overlaps the published copper data[129] with Equation (4.22) at 79.2 and 300 K. Each time a new value of $\epsilon A$ is calculated, it is used to estimate $d(300)$ for the next iteration until a self-consistent solution is obtained.

**Converting Raw Data to $\Delta L/L$**

As was the case with the copper measurement, we correct for the empty-cell and relative effects. First, we normalize the empty-cell data to the measurement

$$C_{\text{normalized empty cell}}(T) = \left[ \frac{C(T) - C(T')}{C(T')} \right]_{\text{empty cell}} \times C_{\text{sample}}(T').$$

(4.23)

The Chebyshev-fitted empty-cell data is normalized to the lowest temperature $T'$ measured for the sample, after which, the corrected data is calculated by subtracting the normalized empty-cell capacitance from the measured capacitance

$$C_{\text{corrected sample}}(T) = C_{\text{sample}}(T) - C_{\text{normalized empty cell}}(T).$$

(4.24)

We next calculate the temperature dependence of the uncorrected capacitor gap using the cell calibration constant $\epsilon A$

$$d_{\text{uncorrected}}(T) = \frac{\epsilon A}{C_{\text{corrected sample}}(T)}.$$

(4.25)

To correct the capacitor gap for the relative effect, we include the thermal expansion of quartz

$$d_{\text{corrected}}(T) = d_{\text{uncorrected}}(T) + (L_{\text{sample}}(300) - d_{\text{uncorrected}}(300)) \left( \frac{\Delta L}{L} \right)_{\text{Quartz}},$$

(4.26)
where it should be noted that the proper units of the measured length of the sample at 300 K are in \( \mu \text{m} \). Finally, the fully corrected \( \Delta L/L \) data is described by

\[
\left( \frac{\Delta L}{L} \right)_{\text{sample}} = \frac{d_{\text{corrected}}(T) - d_{\text{corrected}}(300)}{L_{\text{sample}}(300)},
\]

which is equivalent to Equation (4.22).
Though we are all aware that pipes may burst when water inside them freezes in winter or that the same amount of air in a raft has a bigger volume on a warm day than on a cool day, not many people invest much thought to the phenomenon of thermal expansion. In fact, looking beyond its obvious relevance to engineering problems, the intrinsic value of thermal expansion as a thermodynamic parameter, worthy of study in its own right, is probably underestimated by the contemporary scientific community. Chief among the many useful properties that make it relevant to the study of solid state systems is that it is a remarkably-sensitive probe of phase transitions.

**Introduction to Thermal Expansion**

**Mechanisms of Thermal Expansion**

The thermal expansion of solids is dominated by contributions from quantized vibrations of the lattice (phonons), though smaller contributions come from conduction electrons or cooperative ordering of spins when either is present. The study of lattice dynamics is therefore at the heart of understanding thermal expansion. At absolute zero temperature, the ions in a *classical* crystal lattice are completely at rest in their equilibrium positions ($\vec{r}_{i,0}$ relative to some coordinate system where $i$ indexes ionic positions), and the equilibrium potential energy, calculated over the entire lattice,
is $U_{\text{Eq}}$. When the crystal’s equilibrium temperature is raised to a finite value, the introduction of thermal energy causes the ions to oscillate about their equilibrium positions so that their instantaneous positions $\vec{r}_i$ deviate from $\vec{r}_{i,0}$ by $\vec{R}_i = \vec{r}_i - \vec{r}_{i,0}$.

To account for this thermal motion, a correction term is added to $U_{\text{Eq}}$, which is a function of $\vec{R}_i$. If oscillations are small ($|\vec{R}_i|$ small compared to ion-ion spacing), then the first non-zero term in a Taylor series expansion of the correction potential about equilibrium is quadratic in $\vec{R}_i$.[132] The total lattice potential energy may be written[132]

$$U = [U_{\text{Eq}} + U_2] + U_3 + U_4 + \ldots ,$$

(5.1)

where subscripts indicate potential energy terms quadratic, cubic, and quartic in $\vec{R}_i$. The terms in the bracket represent the potential energy of a completely harmonic lattice. The higher order terms, collectively referred to as anharmonic, are small enough compared to the harmonic terms, that they are often not retained. This is referred to as the harmonic approximation and, in practice, a harmonic lattice sufficiently reproduces most phenomena which depend on lattice dynamics. However, retention of the anharmonic terms is required to theoretically describe the observed imperfect agreement of $C_P$ with the law of Dulong and Petit, volume- and temperature-dependence of elastic constants, non-equivalence of adiabatic and isothermal elastic constants, non-infinite thermal conductivity, and the phenomenon of thermal expansion.[132, 133]

To appreciate the influence of an anharmonic term in the lattice energy, it is illustrative to consider an example discussed by Kittel.[133] Consider a classical oscillator
with potential energy $U(x) = cx^2 - gx^3 - fx^4$ where $x$ is the displacement from ionic equilibrium positions (defined at $T = 0$ K). While the $cx^2$ term is obviously harmonic, the $x^3$ term accounts for asymmetric mutual repulsion of ions and the $x^4$ term represents softening of vibrations at large amplitudes. The average displacement of ions $\langle x \rangle$ in this one-dimensional solid can be calculated using elementary statistical physics

$$\langle x \rangle = \frac{\int_{-\infty}^{\infty} xe^{-U(x)/k_BT} dx}{\int_{-\infty}^{\infty} e^{-U(x)/k_BT} dx}.$$ (5.2)

To lowest order, the average displacement is

$$\langle x \rangle = \frac{3g}{4c^2} k_B T,$$ (5.3)

where we see the harmonic $x^2$ and anharmonic $x^3$ pre-factor terms play a role.[133]

Only an anharmonic potential with finite $g$ (where $g$ is relevant compared to $c^2$) results in non-zero thermal expansion $\langle x \rangle \neq 0$ in this example.

All microscopic theories of thermal expansion rely on the anharmonicity of the lattice potential energy, however, we may also consider thermal expansion from an entirely macroscopic perspective as is done in Reference [126], assuming nothing about microscopic potentials. This alternative description assumes that thermal expansion proceeds by two physically-intuitive steps and allows us to introduce the Grüneisen parameter. Consider a solid in which the temperature is increased by an amount $dT$ in an isochoric process (volume $V$ is constant). Obviously, this requires an input of
energy $dU$ per unit volume, which we describe by rearranging the definition of $C_V$

\[
\left( \frac{1}{V} \right) dU = \left( \frac{C_V}{V} \right) dT. \tag{5.4}
\]

In response to the addition of thermal energy, the pressure inside the solid changes (though not necessarily increases) by

\[
dP = \left( \frac{C_V}{V} \right) \left[ \frac{\partial P}{\partial (U/V)} \right]_V dT. \tag{5.5}
\]

Then, if the internal pressure of the solid is allowed to relax to its original value $P$ in an isothermal process (temperature $T + dT$ is constant), the final change in relative volume is calculated by using the definition of isothermal compressibility ($\chi_T \equiv -\left( \partial \ln V/\partial P \right)_T$) and Equation (5.5)

\[
\frac{dV}{V} = \chi_T dP = \frac{\chi_T C_V}{V} \left[ \frac{\partial P}{\partial (U/V)} \right]_V dT. \tag{5.6}
\]

The term in brackets is the Grüneisen parameter,[134] which we define

\[
\gamma(T, V) = \left[ \frac{\partial P}{\partial (U/V)} \right]_V. \tag{5.7}
\]

Therefore, the volume coefficient of thermal expansion $\Omega$ is

\[
\Omega = \frac{\gamma \chi_T C_V}{V}. \tag{5.8}
\]

From Equation (5.8), it is apparent that $\Omega$ is a function of compressibility, heat capacity, and Grüneisen parameter. This is a logical and reasonable result. The stiffness of the lattice, which thermal expansion must work against, is embodied by $\chi_T$ and the higher the heat capacity of the solid, the more energy input is required
to change the solid by one unit of temperature. Some of this energy cost goes into the lattice and its thermal expansion.

The Grüneisen parameter[134] $\gamma(T,V)$ is dimensionless and typically maintains a value between 1-10 throughout the entire experimental range.[126] There are, however, a few anomalous situations where $\gamma$ is known to diverge, such as in MgB$_2$ at low temperature,[128] and in the vicinity of a quantum phase transition in heavy-fermion systems.[135] From an experimental standpoint, $\gamma$ is obtained from Equation (5.8) by substituting in data for $\Omega$, $C_V$, and $\chi_T$. It is sometimes helpful to plot $\gamma$ as a function of temperature when comparing the behavior of distinct but related materials. The definition of $\gamma$ in Equation (5.7) is not the most instructive description of $\gamma$, but $\gamma$ can also be defined microscopically. In fact, each phonon mode $j$ has its own individual Grüneisen parameter

$$\gamma_j = -\frac{d \ln \omega_j}{d \ln V}, \quad (5.9)$$

where $\omega_j$ is the vibrational frequency of the phonon mode and $V$ is the volume of the sample. The total phonon Grüneisen parameter $\gamma$ is a weighted average of all mode Grüneisen parameters $\gamma_j$

$$\gamma = \frac{\sum_j C_j \gamma_j}{\sum_j C_j}, \quad (5.10)$$

where $C_j$ is the heat-capacity contribution of the $j^{th}$ phonon mode.

Given an expression for $\Omega$, we are able to explore some basic concepts regarding thermal expansion. Using Equations (5.8) and (5.10), it is possible to make some general claims about the behavior of thermal expansion in the limits of low
and high temperature. At low temperature, only acoustic phonon modes with long
wavelengths (low energy) are populated in non-negligible numbers.\[126\] Therefore,
$\Omega$ has the same temperature-dependent behavior as heat capacity in this limit: $\Omega \simeq a_3 T^3 + a_5 T^5 + a_7 T^7 + \ldots$, where $a_i$ are constants.\[126\] At high temperature ($T \gg \Theta_D$),
$\Omega$ asymptotically approaches a constant value, because $\gamma$ saturates. The behavior of
$\gamma$ at high temperature is given by $\gamma = \gamma_\infty + b_{-2} T^{-2} + b_{-4} T^{-4} + b_{-6} T^{-6} + \ldots$, where
$\gamma_\infty$ is the asymptotic value $\gamma$ takes at infinite temperature and $b_i$ are constants.\[136\]
In addition, the other two components of Equation (5.8) ($\chi_T$ and $C_V$) asymptotically
approaches a constant value at high temperature, so for $T \gg \Theta_D$, $\Omega$ is roughly tem-
perture independent. Between these two extreme limits, the behavior of thermal
expansion varies richly from system to system and is quite complicated to calculate.

To this point, we have focused on the role of phonons in thermal expansion. How-
ever, for non-insulating crystals, there is also a small electronic contribution that is
typically only important at low temperature when phonons are frozen out. In cal-
culating the thermal expansion of a generic metallic system, Ashcroft and Mermin
assumed a free electron gas to model conduction electrons.\[132\] They calculated that
$\Omega$ (with lattice and electronic contributions) is proportional to $\gamma C_V^{\text{Latt}} + (2/3) C_V^{\text{Elec}}$, where $\gamma$ is the Grüneisen parameter.\[132\] Based on this calculation, the electronic con-
tribution to thermal expansion exhibits the same behavior as it does in heat capacity;
namely, the electronic contribution to the coefficient of thermal expansion is linear in
temperature. This contribution becomes significant when $\gamma C_V^{\text{Latt}} \sim (2/3) C_V^{\text{Elec}}$, which
occurs at low temperature (γ is usually on the order of unity). The electronic contribution is not often studied, but the first to do so was Andres.\[137\] We can define an electronic Grüneisen parameter γ_e\[138\] using Equation (5.8) and the electronic contributions to Ω and C_V. The electronic Grüneisen parameter is most relevant to the study of heavy-fermion systems wherein the mass of electrons is renormalized and the electronic contribution to Ω and C_V is very important.

Besides phonon and electronic contributions to thermal expansion, there is also a finite coupling between magnetic moments and the elasticity of the lattice. Magnetoelastic coupling, as it is commonly known, is responsible for thermal expansion’s response to phase transitions involving magnetic ordering. This topic is discussed in detail in a later section.

**Structurally-Anisotropic Crystals**

Materials with cubic crystal symmetry exhibit the same thermal-expansion behavior along *any* arbitrary crystallographic direction which is measured. Their thermal expansion is, therefore, isotropic. However, as the symmetry of a crystal is lowered, measurements along distinct crystallographic directions can exhibit different behaviors. This anisotropy can be quite large or very weak, but it is always present in materials with low crystal symmetry. To gain an intuitive feeling for how anisotropy is built into thermal expansion, we exploit some published calculations[139, 140] of the thermal-expansion coefficient along lattice-parameter directions. The simplest
non-trivial crystal structure we can study is that of axial crystals (tetragonal, hexagonal, and trigonal/rhombohedral Bravais lattices), which have two distinct thermal-expansion coefficients. If we assume a layered structure with layers stacked perpendicular to \( c \), the coefficients of thermal expansion are

\[
\mu_\perp = \frac{C_V}{V} \left[ \frac{(C_{11} + C_{12}) \gamma_\perp}{(C_{11} + C_{12}) C_{33} - 2C_{13}^2} - \frac{2C_{13} \gamma_\parallel}{(C_{11} + C_{12}) C_{33} - 2C_{13}^2} \right], \tag{5.11a}
\]

\[
\mu_\parallel = \frac{C_V}{V} \left[ \frac{C_{33} \gamma_\parallel}{(C_{11} + C_{12}) C_{33} - 2C_{13}^2} - \frac{C_{13} \gamma_\perp}{(C_{11} + C_{12}) C_{33} - 2C_{13}^2} \right], \tag{5.11b}
\]

where \( C_{ik} \) are elastic constants, \( \parallel \) and \( \perp \) are defined in reference to the \( a \) axis, and the Grüneisen parameters \( \gamma \) are weighted averages of the mode Grüneisen parameters

\[
\gamma_{\perp,j} = -\frac{1}{2} \left( \frac{\partial \ln \omega_j}{\partial \ln c} \right)_a \tag{5.12a}
\]

\[
\gamma_{\parallel,j} = -\frac{1}{2} \left( \frac{\partial \ln \omega_j}{\partial \ln a} \right)_c. \tag{5.12b}
\]

From Equation (5.11), it is clear that anisotropic thermal expansion is a result of the interplay between the elastic constants and the thermal stress coefficients, which are proportional to \( \gamma \).[126] Similar calculations can be made in an analogous fashion for orthorhombic crystal structures,[126] however, we are unaware of any general expressions which have been published for monoclinic and triclinic crystal structures.

Empirically, we observe relatively large thermal-expansion anisotropy in many systems. The best way to quantify anisotropy is to add or subtract constants to each thermal-expansion data set (in an orthorhombic system, for example, these would be \( \Delta a/a, \Delta b/b, \) and \( \Delta c/c \)) so that they are all zero at room temperature and then compare their magnitudes at the lowest measured temperature. In conducting this
kind of analysis for real data, we see the axis with largest expansion is larger by a factor of 11, 7.5, 6, 5.3, 7.5, and 23 than the axis with the smallest expansion in \( \text{Na}_x\text{CoO}_2 \) (with \( x = 0.75 \) and 0.80),[71] \( \text{CaMn}_2\text{O}_4,[141] \) \( \text{Bi}_2\text{CuO}_4,[93] \) \( \text{Li}_{0.9}\text{Mo}_6\text{O}_{17},[142] \) and \( \text{La}_2\text{NiO}_4\delta,[143] \) respectively. On the other hand, some materials with anisotropic crystal structures, such as \( \text{SrNbO}_{3.41} \), exhibit a relatively weak 1.4 thermal-expansion anisotropy.[144] The manifestation of anisotropy is often such that most axes exhibit conventional thermal expansion while one axis exhibits negative thermal expansion over small or large temperature regions. For example, this scenario is observed in low-dimensional molybdenates \( \gamma\text{-Mo}_4\text{O}_{11} \) and \( \text{Li}_{0.9}\text{Mo}_6\text{O}_{17},[142, 145] \) In layered systems, the anisotropy is strongest between in-plane and out-of-plane directions with the out-of-plane direction generally having a larger thermal expansion.[71, 93, 142, 143] One notable exception is \( \text{CaMn}_2\text{O}_4 \) where the crystallographic direction perpendicular to the layers has the smallest thermal expansion.[141] These layered systems exhibit significant thermal-expansion anisotropy because the phonon modes, embodied by \( \gamma_j \), running parallel and perpendicular to the layers are so distinct.

A low crystal symmetry creates the opportunity for scenarios with large thermal-expansion anisotropy, however, it is not a necessary consequence. Large or intriguing thermal-expansion anisotropy is the result of a combination of low crystal symmetry and anomalous phonon modes. The latter can only be predicted and studied on a case by case basis.
Negative Thermal Expansion

The lattice of most materials expands as the temperature of the material is increased. However, some materials exhibit unconventional behavior where the opposite occurs and the lattice shrinks with increasing temperature. This phenomenon is referred to as negative thermal expansion. Negative thermal expansion is most-commonly observed in systems at low temperature where sufficient anomalous phonon modes γ_j can sometimes dominate the weighted sum in Equation (5.10). However, there are also strange materials, such as ZrW_2O_8, that exhibit negative thermal expansion over the entire temperature range over which they are thermodynamically stable.[140]

From theory, we gain a superficial understanding of the origins of negative thermal expansion. Consider the coefficient of thermal expansion Ω as calculated in Equation (5.8) for a generic system. Thermodynamic requirements constrain χ_T, C_V, and V to be positive for all temperatures, so negative thermal expansion must arise from negative γ. The total phonon Grüneisen parameter γ is calculated in Equation (5.10) as a weighted sum of γ_j parameters for each phonon mode j. Since the heat-capacity contribution of each phonon mode C_j is positive, the only way γ can be negative is if the weighted sum is dominated by phonon modes with negative γ_j.

It is logical next to identify which factors lead to negative γ_j. If we consider the dynamic interaction between a pair of ions, we can identify three distinct behaviors: bond-stretching, tension, and bond-rotation effects.[126, 140] The bond-stretching
mechanism occurs when a phonon mode has its vibration polarized parallel to the line connecting two ions. For a typical interatomic potential between the two ions, this interaction leads to positive $\gamma_j$.[126] However, when the vibration of a phonon mode is polarized perpendicular to the line between two ions, we observe the tension effect. Transverse oscillations increase the absolute distance between the two ions causing tension, and the lattice reacts with a tendency towards attraction to relieve it. Phonon modes causing the tension effect generally have negative $\gamma_j$.[126] Finally, the bond-rotation interaction is a composite of the bond-stretching and tension effects with less relevance to thermal expansion than the previous two effects from which it is constructed. It is adequately treated in Reference [140] so we do not discuss it here.

We have briefly introduced these effects as if they occur independently. However, real interactions between two ions typically have vibrational components both parallel and perpendicular to the line between them simultaneously. For most interactions between ions, the bond-stretching mechanism outweighs the tension component. Those modes where the tension effect outweighs the bond-stretching mechanism generally have lower frequencies and are thus preferentially occupied at low temperature.[126] It is for this reason that negative thermal expansion is most often observed at low temperature.
Thermal Expansion in the Vicinity of a Phase Transition

Heat capacity is sometimes referred to as a response function due to its sensitivity to phase transitions. But compressibility and thermal expansion are also response functions. The connection between thermal expansion and a structural phase transition is intuitive, but it is less obviously connected to other types of phase transitions. However, we have previously noted that phonon, electronic, and spin degrees of freedom are all intimately coupled to thermal expansion. Therefore, thermal expansion should sensitively probe any type of phase transition. In the vicinity of a first-order phase transition, a discontinuous jump is measured in $\Delta L/L$. When measuring a second-order phase transition, $\Delta L/L$ displays an abrupt change in slope but is continuous across $T_C$. In this latter case, the coefficient of thermal expansion $\Omega$ exhibits either a power-law divergence (critical behavior) or a discontinuous jump, as in the case of the transition between superconductivity and the normal state.

While we could study many types of phase transition with thermal expansion, this work is focused on antiferromagnetic order and its accompanying critical behavior. Magnetoelastic coupling connects the magnetic moments of a solid to lattice degrees of freedom and provides a measurable response in thermal expansion. The response has been calculated from first principles by Callen and Callen.[146] They found that the magnetic component of the coefficient of thermal expansion is

$$\Omega_{\text{magnetic}} \propto \frac{d}{dT} g_{fg} (T, H),$$

(5.13)
where $g_{fg}(T, H)$ is the isotropic correlation function defined by

$$g_{fg} = \frac{\sqrt{3} \langle \vec{S}_f \cdot \vec{S}_g \rangle}{S (S + 1) (2S + 1)}.$$ \hspace{1cm} (5.14)

The subscripts indicate ionic sites $f$ and $g$, which are occupied by interacting magnetic moments. To fully appreciate this result, it is useful to consider a specific material and calculate its thermal expansion. Callen and Callen[146] considered cubic ferromagnets EuO and EuS, and, using the two-spin cluster approximation, calculated that the magnetic contribution to thermal expansion and heat capacity in these systems is

$$\Omega_{\text{magnetic}} = \frac{N \sqrt{3}}{S (S + 1) (2S + 1)} \left[ z_1 \tilde{D}^\alpha (1, 2) \frac{d}{dT} \langle \vec{S}_1 \cdot \vec{S}_2 \rangle + z_2 \tilde{D}^\alpha (1, 3) \frac{d}{dT} \langle \vec{S}_1 \cdot \vec{S}_3 \rangle \right]$$

$$C_{V,\text{magnetic}} = N z_1 J_{12} \frac{d}{dT} \langle \vec{S}_1 \cdot \vec{S}_2 \rangle + N z_2 J_{13} \frac{d}{dT} \langle \vec{S}_1 \cdot \vec{S}_3 \rangle,$$ \hspace{1cm} (5.15a) \hspace{1cm} (5.15b)

where $\tilde{D}^\alpha (f, g)$ represents magnetostriction, $N$ is ions per unit volume, and $z_1$ and $z_2$ are numbers of nearest and next-nearest neighbors, respectively. Ions 2 and 3 are the nearest and next-nearest neighboring ions, respectively, to representative ion number 1. This result suggests that $\Omega_{\text{magnetic}}$ and $C_{V,\text{magnetic}}$ have identical temperature-dependence and, though this calculation was made for specific materials, the result is general. If we understand the response of heat capacity to a phase transition, we understand the response of thermal expansion as well because they are similar. In Chapter 7, we derive general expressions for the response of $\Delta V/V$ to antiferromagnetic order assuming the transition exhibits standard critical behavior.
Interpretation of $\Delta L/L$ Measured for Polycrystalline Samples

Not all compounds can be synthesized in single crystal form, and many of those which can are too small to be measured by dilatometry. When a sample of interest falls into this category, sometimes the best alternative is to measure a high-quality polycrystalline sample instead. Interpreting the result of such a measurement gets to the heart of the definition of a polycrystal.

By definition, polycrystals are composed of a single phase, but are inhomogeneous in the sense that the size and orientation of grains or crystallites vary widely over a small length scale. In such a heterogeneous solid, there are local stress and strain fields which, unless the crystallites have cubic crystal symmetry, change non-uniformly in response to changes in temperature or applied stress. Thus, measurements of bulk physical properties on a polycrystalline sample cannot be expected to match analogous measurements on a single crystal. Early methods due to Voigt and Reuss modeled the behavior of a polycrystal assuming an isotropic distribution of crystallite orientation, and they are still used today as approximations or limits on the true values of bulk physical properties. The central difference between the methods is that Voigt assumed that change in strain is uniform across the macroscopic sample while Reuss assumed changes in stress were uniform. If we consider a polycrystal with isotropic orientation (no preferred orientation), the values of the volume coefficient of thermal expansion are calculated $\Omega_R$ and $\Omega_V$ by the Reuss and
Voigt methods respectively[126] (do not confuse $\Omega_V$ with the coefficient of volume thermal expansion at constant volume)

$$\Omega_R = \mu_1 + \mu_2 + \mu_3$$  \hspace{1cm} (5.16a)

$$\Omega_V = 3 \sum_{\alpha=1}^{6} \left( \sum_{\lambda=1}^{3} c_{\lambda \alpha}^T \right) \mu_\alpha / \sum_{\alpha=1}^{3} \sum_{\lambda=1}^{3} c_{\lambda \alpha}^T,$$  \hspace{1cm} (5.16b)

where $c_{\lambda \alpha}^T$ are elastic stiffness moduli. In the Reuss model, $\Omega_R$ is simply three times the unweighted average of the linear coefficients of thermal expansion along all principle crystallographic directions (the example assumes an orthorhombic structure) and agrees fairly well with most measurements of polycrystals. The Voigt expression for $\Omega_V$ weights the small expansion of elastically-stiff directions more heavily and is more suited to describing the thermal expansion of composite materials.[126]

Reuss probably could have written down his formula for $\Omega$ without deriving it. When we measure $\Delta L/L$ of a polycrystal, we pick up contributions from all orientations, so some kind of average over distinct crystallographic directions makes sense. Then, multiplication of the average by three yields the volumetric coefficient $\Omega$. This procedure was tacitly employed when it was previously assumed that $\Delta V/V = 3 \Delta L/L$ for polycrystal data.[70, 149]

When a sample is ground into powder for an x-ray diffraction scan, the pattern is often plagued by anomalous intensities of peaks resulting from preferential orientation. The magnitude of this problem depends in part on how well the powder sample was prepared. Analogously, some preferential orientation might be avoided by careful synthesis of polycrystalline samples, but it cannot be completely avoided.
Furthermore, when a compound has a large intrinsic thermal-expansion anisotropy, even minor amounts of preferential orientation can be amplified until $\Omega_R$ is no longer an acceptable approximation. To correct this problem, the orientation distribution function (ODF) can be introduced to weight the Reuss model depending on the specific preferential orientation of a sample. The analytic form of the ODF is constructed from a series expansion over generalized spherical harmonics $T_{l}^{m',m}(\phi_1, \Phi, \phi_2)$ using the Euler angles $\phi_1$, $\Phi$, and $\phi_2$, and has the form[150]

$$f(\phi_1, \Phi, \phi_2) = \sum_{l=0}^{\infty} \sum_{m'=-l}^{l} \sum_{m=-l}^{l} t_{l}^{m',m} T_{l}^{m',m}(\phi_1, \Phi, \phi_2),$$

(5.17)

where $t_{l}^{m',m}$ are expansion coefficients. A complete and proper analysis of a polycrystalline sample should ideally include the ODF, however, the complexity of the procedure to obtain it generally inhibits consideration of the ODF when reporting bulk measurements like thermal expansion. Instead, most people simply rely on the Reuss method. This has also been our convention, but we acknowledge the possibility that preferential orientation causes the Reuss method to be a poor approximation.

**Calculation of $\Delta V/V$ for Single-Crystalline Samples**

Dilatometry methods, including the one employed for this work, are unable to measure $\Delta V/V$ directly. Instead, measurements are made of the linear thermal expansion $\Delta L/L$ along important crystallographic directions. However, $\Delta V/V$ and its temperature derivative $Ω$ typically play a more fundamental role in thermodynamics than their linear counterparts. So it is important to calculate $\Delta V/V$ from various
measurements of $\Delta L/L$. The question then arises: How many and which crystal-
lographic directions should be measured and how should they be used to calculate
$\Delta V/V$? The answer depends on the underlying crystal symmetry of the sample.

For any crystal, the volume of its unit cell depends on the classification of its Bra-
vais lattice. A triclinic lattice has the lowest symmetry of any Bravais lattice and its
volume contains all six possible degrees of freedom (three lattice parameters and three
angles). But with increasing symmetry, crystallographic constraints on the angles $\alpha$,
$\beta$, and $\gamma$, and the lattice parameters $a$, $b$, and $c$ decrease the number of independent
degrees of freedom until there is one for cubic lattices, two for tetragonal, hexago-
nal, and trigonal/rhombohedral lattices, three for orthorhombic lattices, and four for
monoclinic lattices. These degrees of freedom are explicitly displayed in Table 4. To

<table>
<thead>
<tr>
<th>Bravais Lattice</th>
<th>Unit Cell Volume $V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$V = a^3$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$V = a^2c$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$V = \sqrt{3/2}a^2c$</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>$V = a^3\sqrt{1 - 3\cos^2\alpha + 2\cos^3\alpha}$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$V = abc$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$V = abc\sin\beta$</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$V = abc\sqrt{1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma}$</td>
</tr>
</tbody>
</table>

maintain the symmetry properties of its lattice as a function of temperature, a crystal
has no more unique linear thermal expansion coefficients $\mu_i \equiv d(\Delta L_i/L_i)/dT$ than the
number of degrees of freedom intrinsic to the volume of its Bravais lattice. Therefore,
associated with all non-cubic Bravais lattices are multiple, distinct $\mu_i$, and while they need not exhibit substantially different temperature-dependent behaviors, they are often anisotropic. To determine $\Delta V/V$, we require as many distinct measurements of $\Delta L/L$ as there are degrees of freedom in the lattice.

We next decide along which crystallographic directions to measure $\Delta L/L$. The lattice parameters form a convenient, complete description of the lattice so it is obvious that we should measure along lattice parameter directions. For structures without angular degrees of freedom (cubic, tetragonal, hexagonal, and orthorhombic), these directions will always be sufficient to determine $\Delta V/V$. However, to determine $\Delta V/V$ for rhombohedral, monoclinic, and triclinic crystals, additional, non-lattice-parameter directions must be measured to account for these extra degrees of freedom. We address this issue after first providing an example of how to calculate $\Delta V/V$ for a more simple system.

Consider an orthorhombic crystal with room-temperature lattice parameters $a$, $b$, and $c$. The temperature-dependent change in the volume of its unit cell from room temperature to $T$ is calculated

$$\Delta V(T) = (a + \Delta a(T))(b + \Delta b(T))(c + \Delta c(T)) - abc. \quad (5.18)$$

If we factor out the room-temperature lattice parameters and divide by the room-temperature volume $abc$, we yield

$$\Delta V/V = (1 + \Delta a(T)/a)(1 + \Delta b(T)/b)(1 + \Delta c(T)/c) - 1. \quad (5.19)$$
When we expand Equation (5.19), keeping only terms linear in $\Delta$-quantities, we arrive at a first order calculation for $\Delta V/V$

$$\Delta V/V \simeq \Delta a(T)/a + \Delta b(T)/b + \Delta c(T)/c.$$  \hspace{1cm} (5.20)

For an orthorhombic crystal, simply adding the linear thermal expansions along the three lattice parameters produces $\Delta V/V$. A similar procedure allows us to calculate $\Delta V/V$ for the other Bravais lattices as summarized in Table 5. We omit the triclinic lattice due to its rarity in nature and to the messy character of the calculation. Furthermore, the experimental procedure required to accurately obtain $\Delta V/V$ for a triclinic lattice is so arduous, that anyone committed enough to undertake it would surely be committed enough to do the calculations themselves. We have also omitted the rhombohedral structure in Table 5, because it is generally more convenient to employ the rhombohedral-hexagonal transform, which allows the rhombohedral lattice to be described by an effective hexagonal unit cell.

Table 5. Volume thermal expansion for various Bravais lattices as a function of measurements of $\Delta L/L$ along lattice-parameter directions.

<table>
<thead>
<tr>
<th>Bravais Lattice</th>
<th>Volume Thermal Expansion $\Delta V/V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$\Delta V/V = 3(\Delta L/L)$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$\Delta V/V = 2(\Delta a/a) + \Delta c/c$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$\Delta V/V = 2(\Delta a/a) + \Delta c/c$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$\Delta V/V = \Delta a/a + \Delta b/b + \Delta c/c$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$\Delta V/V = (\Delta a/a + \Delta b/b + \Delta c/c)(\sin \beta(T)/\sin \beta) + (\sin \beta(T)/\sin \beta - 1)$</td>
</tr>
</tbody>
</table>
When we consider a monoclinic crystal structure, we must obtain the temperature-dependent behavior of crystallographic angle $\beta(T)$ in order to calculate $\Delta V/V$. This can be accomplished by an indirect procedure that requires a fourth, non-lattice-parameter measurement. While we could choose any direction, the analysis is simpler for a few well-chosen directions. The linear thermal expansion along an arbitrary crystallographic direction in a monoclinic crystal structure is calculated in Appendix B (see Equation (B.4))

$$
\left( \frac{\Delta L}{L} \right)_{hkl} = \frac{\sin \beta(T)}{\sin \beta} \left[ \frac{(h/a)^2 + (k \sin \beta/b)^2 + (l/c)^2 - 2hl \cos \beta/(ac)}{(h/a)\left(1 + \Delta a/a\right) + (k \sin \beta(T)/b)\left(1 + \Delta b/b\right) + (l/c)\left(1 + \Delta c/c\right)} - 1 \right].
$$

(5.21)

The choice of either $h = 0$ or $l = 0$ is advantageous because Equation (5.21) will contain only two terms in the denominator and numerator instead of four. For example, if we choose our fourth crystallographic direction to be $[hk0]$, $\Delta L/L$ is

$$
\left( \frac{\Delta L}{L} \right)_{hk0} = \frac{\sin \beta(T)}{\sin \beta} \left[ \frac{(h/a)^2 + (k \sin \beta/b)^2}{(h/a)\left(1 + \Delta a/a\right) + (k \sin \beta(T)/b)\left(1 + \Delta b/b\right)} - 1 \right].
$$

(5.22)

Equation (5.22) calculates $\Delta L/L$ along $[hk0]$ given $\Delta a/a$, $\Delta b/b$, $\beta(T)$. On the other hand, if we measure $(\Delta L/L)_{hk0}$, $\Delta a/a$, and $\Delta b/b$, we could use Equation (5.22) to calculate $\beta(T)$. The solution is

$$
\frac{1}{\sin^2 \beta(T)} = \left( \frac{1 + \Delta a/a}{1 + (\Delta L/L)_{hk0}} \right)^2 \left[ \frac{1}{\sin^2 \beta} + \left( \frac{k a}{h b} \right)^2 \right] - \left( \frac{1 + \Delta a/a}{1 + \Delta b/b} \right)^2 \left( \frac{k a}{h b} \right)^2.
$$

(5.23)

When $\beta(T)$ is weakly temperature-dependent, $\Delta V/V$ reduces to the same form as the orthorhombic case as seen in Table 5. Sometimes a temperature-independent $\beta$
is simply assumed for convenience,[142] but the procedure outlined above allows one to accurately determine $\beta(T)$ and $\Delta V/V$ from thermal expansion measurements.

**Effect of Single-Crystal Misorientation on $\Delta V/V$**

Progress in dilatometer-cell designs and the stability of capacitance bridges now allow resolution of thermal-expansion length changes on the sub-Angstrom level in samples with dimensions on the order of millimeters. With such outstanding resolution, systematic errors in sample orientation overshadow many other experimental errors. Despite its relevance, the error resulting from sample misorientation has, to our knowledge, never been addressed in the literature. We describe a procedure to estimate this uncertainty for small or large degrees of misorientation.

It is common to report the accuracy of the orientation of a polished surface as being within $1^\circ$, but even a difference of 1-2$^\circ$ results in a finite error in the measured $\Delta L/L$ that depends on inherent thermal expansion anisotropy. For example, a measurement along [9 2 1] might yield $\Delta L/L$ reasonably similar to $\Delta a/a$, but it includes components of $\Delta b/b$ and $\Delta c/c$ which causes $\Delta L/L$ to deviate from $\Delta a/a$. This deviation could be significant if $\Delta b/b$ and/or $\Delta c/c$ are large compared to $\Delta a/a$.

The possibility of error originating from non-ideal orientation exists in all Bravais lattices except cubic, which represents a special case. For a cubic system, the form of $\Delta L/L$ is

$$
\left( \frac{\Delta L}{L} \right)_{hkl} = \frac{\Delta a}{a},
$$

(5.24)
as calculated in Equation (B.4) for thermal expansion along any crystallographic direction [hkl]. Thus, for a cubic sample, there is no such thing as misorientation in the context of thermal expansion. A measurement along any arbitrary direction results in the appropriate thermal expansion result that would have been obtained had we measured precisely along any lattice parameter.

For non-cubic Bravais lattices, the possibility of misorientation errors must be considered. If we hope to measure thermal expansion along [hkl], but actually measure along [h'k'l'], the error \( \epsilon \) is calculated

\[
\epsilon = \frac{|(\Delta L/L)_{hkl} - (\Delta L/L)_{h'k'l'}|}{(\Delta L/L)_{hkl}} = 1 - \frac{(\Delta L/L)_{h'k'l'}}{(\Delta L/L)_{hkl}}.
\]

This result is general. To proceed further, we must consider specific cases. We start with a tetragonal lattice wherein we intend to measure \( \Delta a/a \), but measure along [hkl] \( \sim [1 0 0] \) instead. Using Equations (B.4) and (5.25), the misorientation error \( \epsilon \) is

\[
\epsilon_{\text{Tet}} = \frac{1}{\Delta a/a} \left( \sqrt{\left(\frac{(h/a)^2 + (k/a)^2 + (l/c)^2}{(1+\Delta a/a)^2 + (1+\Delta c/c)^2}\right)} - 1 \right).
\]

Before proceeding any further, we note that if thermal expansion is measured along [hk0] in a tetragonal system, \( \epsilon_{\text{Tet}} = 0 \) for all temperatures. Therefore, measurement along any direction within the (hk0) plane yields the same result one would obtain if they measured precisely along \( \langle 100 \rangle \). To fully appreciate Equation (5.26), it is illuminating to consider \( \text{La}_2\text{NiO}_{4.04} \) as an example. Misorientation error \( \epsilon(T) \) for \( \text{La}_2\text{NiO}_{4.04} \) is displayed in Figure 26(a) and (b) as a function of temperature for a
Figure 26. (a) Misorientation error $\epsilon(T)$ for $\text{La}_2\text{NiO}_{4.04}$ for a variety of measured crystallographic directions assuming the intended measurement direction is [1 0 0] (each data set is labeled with the measured direction and the angle between it and [1 0 0]), (b) $\epsilon(T)$ for measured crystallographic directions with small misorientations with respect to [1 0 0], and (c) experimental $\Delta L/L$ data for $\text{La}_2\text{NiO}_{4.04}$ along $a$ and $c$. 
variety of crystallographic directions assuming the intended measurement direction was along [1 0 0]. In addition to explicitly labeling the misoriented crystallographic directions, we have labeled the angle between [1 0 0] and the respective direction. We expect $\epsilon = 0$ at 300 K and this is observed, however the origins of the jump in $\epsilon$ below 300 K is currently unknown. Perhaps it is an artifact of the data density of $\Delta a/a$ and $\Delta c/c$ used to calculate $\epsilon$. However, we are able to acquire an intuitive feel for the magnitude of error which results from a given misorientation. $\text{La}_2\text{NiO}_{4.04}$ is an extreme example with large anisotropy ($((\Delta c/c(5 \text{ K})) / (\Delta a/a(5 \text{ K})) \sim 20$) as the experimental data in Figure 26(c) reveal. Therefore, we can state with some confidence that, for most tetragonal systems, orienting a measured crystallographic direction to within $1^\circ$ leads to a maximum error of $\epsilon \sim 1\%$.

Orientation of samples with low crystal symmetry should be performed as precisely as possible because misorientation error is a relevant effect. This is especially true when calculating $\Delta V/V$ from multiple $\Delta L/L$ measurements, each with its own finite $\epsilon$. 
THERMODYNAMIC SCALING RELATIONS

There are typically multiple relationships between thermodynamic parameters because every parameter can be calculated from a derivative of the thermodynamic free energy with respect to a different parameter. It is therefore possible to transition between parameters using Maxwell relations and Legendre transforms. We restrict our focus to the relationship between heat capacity and thermal expansion in the vicinity of a phase transition. The existence of such a scaling relationship allows us to justify studying critical behavior, which has been defined in terms of heat capacity, with thermal expansion instead. This concept is so crucial to the justification of studying critical behavior with thermal expansion that it merits its own chapter.

We have already discussed an expression connecting thermal expansion and heat capacity in the previous chapter (see Equation (5.8)). However, applying this relation is impractical because there is no independent method to obtain $\gamma$ and it is usually difficult to find $\chi_T$ data in the literature. So instead of concerning ourselves with Equation (5.8), we briefly consider scaling relations from classical thermodynamics such as the Clausius-Clapeyron and Ehrenfest relations. These relations are also unsuitable for our purpose, so we concentrate on a generalization of Ehrenfest’s relation due to Pippard. It is this relation which justifies the study of critical behavior with thermal expansion.
Classically, there are two scaling relations which couple heat capacity and thermal expansion at a phase transition: the Clausius-Clapeyron relation is appropriate for first-order transitions and the Ehrenfest relation is suitable for continuous transitions. The Clausius-Clapeyron relation, as it is typically expressed, does not directly connect heat capacity and thermal expansion. Rather, it calculates the pressure derivative of $T_C$ from the observed molar entropic $\Delta s$ and volumetric $\Delta v$ jumps at $T_C$. However, $\Delta s$ can be expressed alternatively using the latent heat of the transition $Q = T_C \Delta s$ or in terms of heat capacity by integrating. The latter association is featured in our representation of the Clausius-Clapeyron relation

$$\frac{dT_C}{dP} = \frac{\Delta v}{\Delta s} = \Delta v \left[ \int_{T_C-\delta}^{T_C+\delta} \frac{C_P}{T} dT \right]^{-1}. \quad (6.1)$$

Equation (6.1) is inapplicable to our situation because any transition exhibiting critical behavior is continuous and there are no discontinuities in entropy or volume at $T_C$. In the case of a second-order phase transition (defined in the classical Ehrenfest sense that two derivatives of the thermodynamic free energy result in parameters exhibiting discontinuous jumps at $T_C$), a relation was derived by Ehrenfest,[10] which calculates the pressure derivative of $T_C$ with observed discontinuous jumps in heat capacity $\Delta C_P$ and coefficient of thermal expansion $\Delta \Omega$

$$\frac{dT_C}{dP} = \frac{T_C \Delta \Omega}{\Delta C_P}. \quad (6.2)$$
Ehrenfest’s relation directly scales $C_P$ with $\Omega$ at $T_C$ where $v$ is the molar volume in units of cubic meter per mole. But it falls short in two areas. First, discontinuous jumps in $C_P$ and $\Omega$ at $T_C$ are not observed in most continuous phase transitions, with the transition between superconductivity and the normal state in zero applied field being the only notable exception.[70] Instead, critical behavior is observed. The second shortcoming of Ehrenfest’s relation is that it is only valid at $T_C$, whereas critical behavior is observed in a narrow but finite temperature region around $T_C$. Therefore, we need a scaling relation which is valid for more than a single temperature.

It was not until Pippard published his scaling relation that these requirements were satisfied.[151] However, we stress that the important differences between the Ehrenfest and Pippard relations do not imply incompatibility. In fact, Ehrenfest’s relation is a special case of the more general Pippard relation as we later show.

**Pippard Relation**

The Pippard relation[151] is not discussed by many published sources, so we produce a derivation of it here. We begin by assuming that a thermodynamic system may be completely described by a molar free energy $f(T,P)$ so that shifts of temperature $dT$ and pressure $dP$ result in a molar entropy change $ds$ in the three-dimensional $s$-$T$-$P$ space, which is described by

$$
\begin{align*}
\left( \frac{\partial s}{\partial T} \right)_P dT + \left( \frac{\partial s}{\partial P} \right)_T dP.
\end{align*}
$$

(6.3)
We make use of a Maxwell relation \((\frac{\partial s}{\partial P})_T = - (\frac{\partial V}{\partial T})_P\) by substituting it into Equation (6.3). Then, by exploiting the definitions of volumetric coefficient of thermal expansion \(\Omega = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)\) and heat capacity \(C_P = T \left(\frac{\partial s}{\partial T}\right)_P\), and multiplying Equation (6.3) by \(T\), we obtain

\[ Tds = C_PdT - vT\Omega dP, \]

(6.4)

where \(v\) is the molar volume. This result is valid for all temperatures and pressures. However, we are only interested in the situation near a phase transition. Employing

---

**Figure 27.** A generic three-dimensional \(s(T, P)\) surface is displayed outlined in green. If a system has a pressure-dependence of \(T_C\) as depicted in the magenta curve \(T_C(P)\), we can project it onto the \(s(T, P)\) surface as shown by the red dotted curve. This parametric curve is \(s(T_C, P(T_C))\), and it can be projected onto the \((T, s)\) plane to define the blue dotted curve \(s(T_C)\).

---

the line of reasoning in Souza et al. [70], we consider \(T_C(P)\) which marks a phase-transition curve on the \((T, P)\) plane (see Figure 27). We assume that, within the
pressure range of interest, \( T_C(P) \) can be inverted into \( P(T_C) \). Then, in the immediate vicinity of the phase transition, the molar entropy, \( s(T_C, P(T_C)) \), abbreviated as \( s(T_C) \), marks a transition curve on the \((T, s)\) plane (the blue dotted curve in Figure 27). When we consider infinitesimal temperature shifts of \( \delta \) from \( T_C \): \((T_C + \delta, P(T_C))\) and \((T_C + \delta, s(T_C))\) on the \((T, P)\) and \((T, s)\) planes respectively, we move an infinitesimal amount parallel to the transition curve, the amount of which is governed by Equation (6.4). With this in mind, and solving for \( C_P \), we obtain[70]

\[
C_P = T \left( \frac{\partial s}{\partial T} \right)_C + vT\Omega \left( \frac{\partial P}{\partial T} \right)_C, \tag{6.5}
\]

where each partial derivative of the form \((\partial \xi/\partial T)_C\) denotes a partial derivative of the quantity \( \xi(T_C) \) with respect to \( T_C \).

Equation (6.5) is applicable to the region around \( T_C \) with increasing validity as \( T \to T_C^\pm \). Typically, \( v \) and \( \left( \frac{\partial P}{\partial T} \right)_C \) are temperature-independent in the critical temperature region so the second term in Equation (6.5) can be replaced by \( \lambda T\Omega \) where \( \lambda \equiv v/\left( \frac{\partial P}{\partial T} \right)_C \). The first term in Equation (6.5) is related to the slope of the blue dotted curve in Figure 27.[70] We define \( C_P^* \equiv C_P - a - bT \) so that the Pippard relation becomes

\[
C_P^* = \lambda T\Omega. \tag{6.6}
\]

Some contributions to \( C_P \) have a negligible impact on thermal expansion such as certain phonon modes, which may still be quasi-harmonic in the vicinity of \( T_C \). These contributions can be modeled by \( a + b'T \) sufficiently near \( T_C \). Thus, the linear background we subtract from \( C_P \) is \( a + \left[ b' + \left( \frac{\partial s}{\partial T} \right)_C \right] T \) and the term in brackets is redefined
as $b$. We emphasize again that Equation (6.6) is valid only in a narrow temperature range about $T_C$. Its most important implication is that the singularities in $C_P^*$ and $\lambda T \Omega$ scale with the same critical exponent $\alpha$, so either can be used with equal justification to study critical behavior. The Pippard relation has been successfully applied to several magnetic phase transitions such as those in $\alpha$-Mn (see Chapter 10), $\text{Na}_x\text{CoO}_2$,[$71$] $\text{CaMn}_2\text{O}_4$,[$141$] $\text{Bi}_2\text{CuO}_4$,[$93$] $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$,[$70$] $\text{CaMnO}_3$,[$149$] and $\text{LaMnO}_3$.[$149$] Furthermore, given the scaling parameter $\lambda$, it is possible to calculate $dT_C/dP$ and compare it with direct experimental measurements. This comparison has always resulted in excellent agreement.[70, 71, 149]

**Uniqueness of Scaling Parameters**

The procedure of scaling $C_P^*$ with $\lambda T \Omega$ requires us to optimize the values of a set of scaling parameters $\{a, b, \lambda\}$, each with its own physical meaning. To provide confidence regarding the uniqueness of the set of parameter values which lead to $C_P^* = \lambda T \Omega$, we first assume there exist two distinct sets of scaling parameters $\{a_1, b_1, \lambda_1\}$ and $\{a_2, b_2, \lambda_2\}$ which individually satisfy the Pippard relation. This assumption implies that

$$C_P(T) - a_1 - b_1 T = \lambda_1 T \Omega(T)$$

$$C_P(T) - a_2 - b_2 T = \lambda_2 T \Omega(T).$$

Subtracting the two expressions in Equation (6.7) and collecting terms yields

$$(a_2 - a_1) + (b_2 - b_1) T = (\lambda_1 - \lambda_2) T \Omega(T).$$

(6.8)
By solving for $\Omega(T)$, we obtain the generic form of $\Omega(T)$ for which uniqueness of the scaling parameters is not required

$$\Omega(T) = \zeta_1 + \frac{\zeta_2}{T}, \quad (6.9)$$

where $\zeta_1$ and $\zeta_2$ are constants. If we measured $\Omega(T)$ with the form in Equation (6.9), there could be two distinct sets of scaling parameters, which are constrained to obey

$$(b_2 - b_1) = \zeta_1 (\lambda_1 - \lambda_2)$$

$$(a_2 - a_1) = \zeta_2 (\lambda_1 - \lambda_2). \quad (6.10)$$

The two simplest cases of Equation (6.9) are: $\zeta_1 = 0$ and $\zeta_2 \neq 0$, and $\zeta_1 \neq 0$ and $\zeta_2 = 0$. In the former case, we would conclude that $(a_2 - a_1) = \zeta_2 (\lambda_1 - \lambda_2)$ while $b_2 = b_1$, and in the latter case, $(b_2 - b_1) = \zeta_1 (\lambda_1 - \lambda_2)$ and $a_2 = a_1$. In either case, one or more scaling parameters is not unique. However, $\Omega$ is expected to exhibit a power-law behavior in the vicinity of $T_C$, which does not even remotely resemble Equation (6.9). Therefore, we conclude that $a_1 = a_2$, $b_1 = b_2$, and $\lambda_1 = \lambda_2$ and that the set of parameters which result in $C_P^* = \lambda \Omega T$ is unique.

**Equivalence to Ehrenfest Relation**

The Ehrenfest relation is a special case of the more general Pippard relation, and it is relatively simple to demonstrate how we can obtain the former from the latter. We begin with the Pippard relation where we assume $f(T)$ is a smooth and differentiable function which is subtracted from $C_P$. Typically we use $f(T) \equiv a - bT$, but for this analysis, we keep it general. The Pippard relation is

$$C_P(T) - f(T) = \lambda T \Omega(T). \quad (6.11)$$
We evaluate Equation (6.11) at temperatures slightly above \((T_C + \delta)\) and below \((T_C - \delta)\) \(T_C\) where \(\delta\) is small compared to \(T_C\)

\[
C_P(T_C + \delta) - f(T_C + \delta) = \lambda[T_C + \delta]\Omega(T_C + \delta)
\]

\[
C_P(T_C - \delta) - f(T_C - \delta) = \lambda[T_C - \delta]\Omega(T_C - \delta).
\] (6.12)

If we subtract the two expressions, the \(- f(T_C + \delta) + f(T_C - \delta)\) term vanishes as \(\delta \to 0\) and we obtain

\[
C_P(T_C + \delta) - C_P(T_C - \delta) = \lambda\{[T_C + \delta]\Omega(T_C + \delta) - [T_C - \delta]\Omega(T_C - \delta)\},
\] (6.13)

which, in the limit \(\delta \to 0\), is

\[
\Delta C_P(T_C) = \lambda T_C \Delta \Omega(T_C),
\] (6.14)

where we define

\[
\Delta C_P(T_C) \equiv \lim_{\delta \to 0} [C_P(T_C + \delta) - C_P(T_C - \delta)]
\] (6.15a)

\[
\Delta \Omega(T_C) \equiv \lim_{\delta \to 0} [\Omega(T_C + \delta) - \Omega(T_C - \delta)].
\] (6.15b)

Obviously, taking the limit of small \(\delta\) isolates the discontinuous jumps in heat capacity and coefficient of thermal expansion that are used for the Ehrenfest relation. If there are no jumps, then Equation (6.14) reduces to the result \(0 = 0\). Recalling the definition of \(\lambda = v / \left(\frac{\partial P}{\partial T}\right)_C\), we see Equation (6.14) is equivalent to the Ehrenfest relation (Equation (6.2)). The implication of this equivalency is that the Pippard relation can be applied to any continuous phase transition, including those which are generally studied with the Ehrenfest relation. This hypothesis has been tested
and confirmed by scaling heat capacity and thermal expansion in the vicinity of the superconducting transition in elemental niobium.[152]
THE STUDY OF CRITICAL PHENOMENA WITH THERMAL EXPANSION

All the pieces that have been developed over the last several chapters are now ready to be assembled. In Chapter 1, we introduced a general procedure which has been used to study the critical behavior exhibited by heat capacity. The Pippard relation, discussed in Chapter 6, asymptotically scales thermal expansion and heat capacity. This scaling justifies the study of critical behavior in thermal-expansion data. Therefore, the foundations of a strategy to study critical behavior are already laid and can be built upon with thermal expansion in mind. But before we consider strategies, we identify potential advantages and disadvantages of studying critical behavior with thermal expansion. Advantages and disadvantages are typically relative by nature, so we quantify them by comparing thermal expansion with heat capacity.

Advantages of Using Thermal Expansion

The primary advantage of using thermal-expansion measurements to study critical behavior originates from the thermal treatment of a sample during measurements. When we measure thermal expansion, there are small vertical and horizontal temperature gradients across the sample. Therefore, each datum is the average of a negligible distribution of thermal expansions (the infinitesimal volume of sample associated with each temperature in the thermal gradient has its own thermal expansion) and is associated with some average temperature of the gradient $T_{AV}$. The thermometers in
our experiment are deliberately placed at a position in the vertical and horizontal thermal gradients which is equivalent to the sample’s position. Therefore, the thermometers should measure $T_A$. As the measurement proceeds, the temperature of the sample slowly increases (0.2 K/min), and the magnitude of the vertical thermal gradient (the difference between the highest and lowest temperatures in the sample) slowly decreases. Thermal exchange is facilitated by the helium exchange gas, which surrounds the sample and is able to conduct heat to all of its surfaces. This results in a slow, uniform warming of the sample as the measurement progresses. We contrast this with the measurement of heat capacity by the thermal-relaxation technique as described in Chapter 4. A sample, which starts in thermodynamic equilibrium with a temperature reservoir at $T_b$, is subjected to a heat pulse from a resistive heater. The temperature of the sample increases from $T_b$ to $T_b + \Delta T$ over a time on the order of a few minutes or less and a maximum vertical thermal gradient of $\Delta T$ is established in the sample (though it is typically smaller than $\Delta T$). $C_P$ is extracted from the relaxation curve after the heat pulse is shut off and the sample temperature is allowed to relax towards $T_b$ over a longer time interval than it took to warm. The measurement assumes the sample cools uniformly over its entire volume during this process, but heat exchange is facilitated only through the sample’s interface with the platform on which it sits so that the sample is unable to cool uniformly and measurement quality suffers. Therefore, the warming and cooling of the sample is homogeneous and slow.
with thermal expansion, while in heat-capacity measurements it is inhomogeneous and fast. The quality of data can reflect these circumstances.

The second important advantage we gain by studying thermal-expansion data is that, for a crystal with non-cubic symmetry, measurements along a few distinct crystallographic directions are typically anisotropic. Superficially, it is difficult to see how this might be considered an advantage. After all, it is $\lambda \Omega T$ which scales with $C^*_P$, and $\Omega$ is completely insensitive to intrinsic thermal-expansion anisotropy. However, the same critical behavior exhibited by $\lambda \Omega T$ is also present in $\lambda_i \mu_i T$ along each of the distinct principle crystallographic axes. In general $\lambda_i \neq \lambda$, but the precise physical interpretation of $\lambda_i$ is unclear. Some might argue that the $\lambda_i$ are proportional to uniaxial pressure derivatives of $T_C$. However, we have found that scaling of $\lambda_i \mu_i T$ with $C^*_P$ is typically not very good. In any case, we need not worry about an interpretation for $\lambda_i$ because we could assign it any arbitrary constant without influencing the study of the inherent critical behavior in $\lambda_i \mu_i T$. We are unaware of any theoretical arguments for why the critical behavior is the same along each principal crystallographic axis, but it was first empirically observed in the hydrated manganese salts where the exponent was the same along all three lattice-parameter directions of the monoclinic structure. More recently, the same observation has been made in Bi$_2$CuO$_4$ where $\alpha$ is characteristic of the three-dimensional Ising model along $a$ and $c$ of its tetragonal structure. The concept makes good intuitive sense...
because, logically, there are only three possibilities: identical critical behavior is observed along all principle crystallographic axes, different critical behavior is observed along each principle crystallographic axis, or no critical behavior is observed along any principle crystallographic axis. Since we know the behavior of the sum of all principle crystallographic directions exhibits critical behavior, the latter two possibilities seem unreasonable. Fortunately, anisotropic thermal expansion provides multiple, independent $\Delta L/L$ data sets with which to study critical behavior instead of a single one as is the case with $\Delta V/V$ or $C_P$. By fitting multiple data sets, we can compare results against one another and be more confident about our analysis.

**Disadvantages of Using Thermal Expansion**

There are also a number of potential disadvantages worth considering that are consequences of using thermal-expansion measurements to study critical behavior. Certainly the most prominent disadvantage is an indirect effect of applying the Pippard relation (see Equation (6.6)), which is ironic because it is this same relation that justifies the use of thermal expansion for this purpose in the first place. The Pippard relation scales $C_P^*$ with $\lambda \Omega T$, therefore, we are required to numerically differentiate discrete thermal-expansion data to obtain $\Omega = d(\Delta V/V)/dT$. Two adverse complications arise when we differentiate discrete $\Delta V/V$ data. In general, the derivative of $f(T)$ data is calculated from the first term of the Taylor series expansion

$$f'(T) = \frac{f(T + \Delta T) - f(T)}{\Delta T} + O(\Delta T),$$

(7.1)
where $\Delta T$ is the data density (temperature step size between neighboring datum) and $O(\Delta T)$ represents the dominant leading term of the series: $-\frac{1}{2}f''(T)\Delta T - \frac{1}{6}f'''(T)(\Delta T)^2 - \ldots - \frac{1}{n!}f^{(n)}(T)(\Delta T)^{n-1} - \ldots$. Unfortunately, truncation of Equation (7.1) after the first term introduces an error[131] which can plague even smooth, well-behaved data sets. Since most data-analysis programs typically take a point-by-point derivative, truncation error is a common problem. Truncation error broadens the sharp, power-law anomalies which should be exhibited by $\lambda \Omega T$ and reduces their magnitude. This combination of effects conspires to conceal the true critical behavior by distorting the anomaly. The second important flaw which influences a derivative of discrete data concerns the propagation of statistical uncertainties. In our thermal-expansion experiments,[127] the uncertainty intrinsic to the measurement, $\delta V$, is generally quite low ($\delta V/(\Delta V/V)\sim 10^{-4}\%$ or less). However, the uncertainty of its derivative $\delta \Omega$ depends on both $\delta V$ and the uncertainty of the less resolved temperature measurement $\delta T$. Inspection of the first term in Equation (7.1) reveals that

$$\frac{\delta \Omega}{\Omega} = \sqrt{2} \frac{\delta T}{\Delta T},$$

(7.2)

if we ignore the contribution from $\delta V$ (which is much less prominent than $\delta T$). Reasonable experimental values for $\delta T$ and $\Delta T$ result in $\delta \Omega/\Omega \sim 0.1\text{-}1\%$ without any contribution from $\delta V$. Therefore, the relative noise level increases several orders of magnitude when we differentiate $\Delta V/V$ to obtain $\Omega T$. This increase in uncertainty,
which manifests itself as a lower signal to noise ratio, reduces the resolution with which we may extract salient critical parameters such as $\alpha$.

We have already stated that anisotropic thermal expansion in low-symmetry crystals can be exploited by fitting the thermal-expansion data ($\lambda_i \mu_i T$) along each principal crystallographic direction with suitable critical-behavior expressions. In this case, thermal-expansion anisotropy is an advantage. But anisotropic thermal expansion is a double-edged sword. To measure the thermal expansion of a single crystal along specific crystallographic directions, as is required for a system exhibiting anisotropic thermal expansion, a significant amount of sample preparation is necessary. The crystal must be precisely oriented so that the (1 0 0), (0 1 0), and (0 0 1) planes can be polished to within $\sim \pm 1^\circ$. The final result is a parallelepiped-shaped sample with six carefully prepared surfaces (three pairs of parallel surfaces), which are each perpendicular to one of the crystal’s lattice-parameter directions. This work has taken as long as an entire week for some samples. Furthermore, it is often not enough to prepare a well-oriented parallelepiped bar; the sample must also have sufficiently-large dimensions. The length of the sample along each measurement direction should be as long as possible (preferably 1-3 mm) to provide the best thermal-expansion signal. But sometimes a large percentage of the sample is lost in polishing if the principle crystallographic directions are oddly oriented with respect to the natural macroscopic topology of the crystal. For example, if the direction we polish is at a natural corner of the sample, then a lot of material must be polished away to obtain the necessary
surface area we require to measure thermal expansion. Unfortunately, some materials do not react well to significant amounts of polishing and cutting. They may crack, break, or cleave under the application of uniaxial pressure, and those which maintain their structural integrity throughout the process may still be strained as a result. This procedure contrasts sharply with the sample preparation necessary for a heat-capacity measurement wherein a sample of suitable mass has only one of its unoriented surfaces polished. The investment of time and energy necessary to prepare a low-symmetry crystal for a thermal-expansion measurement is certainly a disadvantage, though once completed, does not effect the quality of a critical-behavior study. Though it has not been experimentally confirmed, we expect that the critical behavior along an unoriented crystallographic direction will be identical to the volume behavior (and the behavior along principle crystallographic axes). Therefore, sample preparation need not necessarily be a time-consuming prerequisite, though it is far more satisfying to measure along the principle crystallographic axes than along an unknown direction.

A second unfortunate consequence of thermal-expansion anisotropy is that, to calculate $\Delta V/V$ so that $\Omega$ may be obtained, we must add two or more discrete $\Delta L/L$ data sets whose temperature data do not match. One way to add them is to select a data set and interpolate the other data sets at its temperatures. But interpolating data points in the vicinity of a sharp kink in $\Delta L/L$ introduces a modest error which is amplified when we take a derivative. Instead, it is common to fit the $\Delta L/L$ data
piecewise with a suitable polynomial function (such as Chebyshev polynomials),[128] but this can lead to other problems. For example, it is nearly impossible to create seamless joints at the boundaries between fitted regions such that the derivative $\mu$ does not exhibit some artificially introduced anomaly. Furthermore, even if it were possible to obtain perfect $\Delta L/L$ data sets, each with identical temperature data, misorientation errors in the individual data sets are also added and could be significant for $\Delta V/V$. Fortunately, these points are only disadvantages if the critical behavior of $\lambda\Omega T$ is studied. If we utilize the observation that critical behavior is the same along each $\lambda_i\mu_i T$, these problems are avoided entirely.

The final potential disadvantage of using thermal expansion to study critical behavior is a consequence of the way thermal expansion is measured. Most dilatometer designs, including the one used in this work (see Figure 24) apply uniaxial pressure to the sample so that there is some tension to move the capacitor plates closer together when the sample shrinks. This pressure could induce a finite strain in the sample and strain is known to effect critical behavior.[153] Fortunately, the applied uniaxial pressure is quite modest and it is not expected to be problematic for most systems.

The flexural spring constant of two quartz springs is[154]

$$k_{\text{eff}} = \frac{Ew}{2} \left( \frac{t}{l} \right)^3,$$

(7.3)

where $E$ is the bulk modulus of quartz, and $w$, $l$, and $t$ are the dimensions of a quartz spring. We call the spring constant $k_{\text{eff}}$, because we have multiplied the spring constant in Reference [154] (for a single quartz spring) by a factor of two to account
for the identical quartz springs being in parallel. The force applied to the sample is \( F = k_{\text{eff}}d \) where \( d \) is the gap between capacitor plates. Using average quartz spring dimensions of \( 14.0 \text{ mm} \times 11.9 \text{ mm} \times 0.12 \text{ mm} \), and the modulus for quartz \( E = 7.87 \times 10^{10} \text{ N/m} \), we calculate \( k_{\text{eff}} = 565 \text{ N} \). For a typical capacitance gap of \( 100 \mu\text{m} \), the pressure on a sample with a typical \( 1 \text{ mm}^2 \) cross-sectional area is about \( 56.5 \text{ kPa} \). For most materials, pressures need to be of order \( 0.1 \text{ GPa} \) before tangible effects are observed. However, any material which is particularly susceptible to pressure may feel some subtle influence from this uniaxial pressure.

**Strategies for Data Analysis**

Now that we have considered the advantages and disadvantages of applying thermal-expansion measurements to the study of critical behavior, we describe strategies to perform such an analysis. Any valid strategy requires a suitable critical expression to fit experimental data. In Chapter 1, we introduced critical expressions for \( C_P \) (see Equations (1.23) and (1.24)). When the Pippard relation holds, critical expressions for \( C_P \) become expressions for \( \lambda \Omega T \) (or \( \lambda_i \mu_i T \)). The linear background in \( C_P^* \) can be incorporated into the analytic background of the expressions. Therefore when \( \alpha \) is non-zero,

\[
\lambda \Omega T \simeq \frac{A_\pm}{\alpha} |t|^{-\alpha} \left[ 1 + E_\pm |t|^\kappa \right] + B + Dt, \quad (7.4)
\]

and when \( \alpha = 0 \), critical behavior is described by

\[
\lambda \Omega T \simeq -A_\pm \log |t| + B + Dt. \quad (7.5)
\]
We discuss three strategies to study critical behavior with thermal-expansion data including the graphical method, the $\lambda\Omega T$ least-squares method, and the $\Delta V/V$ least-squares method. The first two methods use Equation (7.4) or (7.5), while the latter method uses a critical expression for $\Delta V/V$ which we derive in this chapter.

**Graphical Method**

A simple graphical procedure to study critical behavior with thermal-expansion data was initially described\[70\] by Souza et al. and was used in a series of subsequent publications\[71, 141, 149\] by the Neumeier group. The procedure begins by assuming that $E_{\pm} = 0$ (no confluent singularity) so that the thermal-expansion data are fit with

$$\lambda\Omega T \simeq \frac{A_{\pm}}{\alpha} |t|^{-\alpha} + B + Dt. \quad (7.6)$$

The critical exponent $\alpha$ may be positive or negative (or zero, but that possibility is ignored for this analysis). We consider each case separately and define a positive-definite exponent $\alpha' \equiv |\alpha|$. Inserting $\alpha'$ into our critical expression, we obtain two cases

$$\lambda\Omega T \simeq \frac{A_{\pm}}{\alpha'} |t|^{-\alpha'} + B + Dt \quad \alpha > 0 \quad (7.7a)$$

$$\lambda\Omega T \simeq \frac{A_{\pm}}{-\alpha'} |t|^{\alpha'} + B + Dt \quad \alpha < 0. \quad (7.7b)$$
If we rearrange these expressions by subtracting the analytic background from both sides and taking a logarithm, the resulting expressions are

$$\log (\lambda \Omega T - B - Dt) \simeq -\alpha' \log |t| + \log \left( \frac{A_\pm}{\alpha'} \right) \quad \alpha > 0 \quad (7.8a)$$

$$\log (-\lambda \Omega T + B + Dt) \simeq \alpha' \log |t| + \log \left( \frac{A_\pm}{\alpha'} \right) \quad \alpha < 0, \quad (7.8b)$$

where it is clear that a plot of the left-hand side against $\log |t|$ is linear. Of course, a linear relationship is only obtained when we input the proper values of $B$, $D$, and $T_C$ (implicit in $t$). In each case, the intercept of the lines are $\log \left( \frac{A_\pm}{\alpha'} \right)$ and the slope of the lines are the critical-exponents $\alpha'$. To implement this method, we first assume $\alpha$ is positive, and then plot the left hand side of Equation (7.8) against $\log |t|$, guessing and refining values for $B$, $D$, and $T_C$ until we obtain two lines (one for data on each side of $T_C$) which have maximized temperature ranges and identical slopes ($\alpha^- = \alpha^+$). The procedure is then repeated assuming that $\alpha$ is negative. The assumption (positive versus negative $\alpha$) which provides the best results (larger critical region over which a linear behavior is observed) is selected as the solution.

The graphical method has two advantages. First and foremost, it allows us to fit critical behavior by merely optimizing values for $B$, $D$, and $T_C$, while the values of $A_\pm$ and $\alpha$ are simply consequences of the others. However, we have not really removed those degrees of freedom, because they are implicit in the criteria we use to judge the best fit: large temperature region and equivalent slopes of each line. The second advantage of the graphical method is that it can be performed with a simple
graphing program. Despite these advantages, the graphical method is not very satisfying for several reasons. First, it relies on our imperfect ability to decide on the best solution by eye. This evaluation technique is sometimes referred to as “chi-by-eye”, and can be inaccurate and subjective. Furthermore, even if truly optimal best-fit parameters were obtained by the graphical method, it is difficult to systematically extract reasonable uncertainties for them. Finally, it is far too complicated to include all the terms in Equation (7.4) when employing the graphical method. For example, all published[70, 71, 141, 149] uses of the graphical method neglected to include the confluent singularity, even though it is widely recognized that corrections to scaling are increasingly important as the temperature gets further from $T_C$. These disadvantages tend to outweigh any advantages and it is best to use the graphical method as an approximation or when no other alternative is available.

**λΩT Least-Squares Method**

Not satisfied with several problematic issues related to the graphical method, we developed a non-linear, least-squares fitting program to analyze the critical behavior of $λΩT$ (or $λ_iμ_iT$). There are many canned routines and software packages that provide least-squares fitting capability, however, we were unable to utilize any of them because of the nature of our fitting function in Equation (7.4). Fit parameters $A_\pm$ and $E_\pm$ may assume different values on each side of $T_C$, while the other fit parameters are constrained to be the same. This means that most of the parameters are fitted by considering all data in the critical temperature region, while $A_\pm$ and $E_\pm$ are
optimized only with the data on their respective sides of $T_C$. Unfortunately, canned least-squares routines are unsuitable to perform fitting of such a model, so we wrote our own program. Obviously, our fitting function is non-linear, so we must use non-linear, least-squares refinement, whereby the minimization problem is approximated as linear (which has a closed-form solution) and is approached iteratively. In general, the procedure is as follows: Imagine we have a data set $\{x_i, y_i\}$ and we wish to fit it with a model $y(x; \vec{a})$ where $\vec{a}$ is a vector of parameter values in the model ($A_\pm$, $\alpha$, $T_C$, $E_\pm$, $B$, and $D$ in our case). The goal of least-squares fitting is to minimize the $\chi^2$ merit function

$$
\chi^2(\vec{a}) = \sum_{i=1}^{N} \left( \frac{y_i - y(x; \vec{a})}{\sigma_i} \right)^2,
$$

(7.9)

where $\chi^2$ is calculated as a sum over all $N$ data points and $\sigma_i$ is the standard uncertainty of $y_i$. The $\chi^2$ merit function is minimized by starting with an initial $\vec{a}_0$ and calculating a small correction $\delta \vec{a}$ such that $\vec{a} = \vec{a}_0 + \delta \vec{a}$ results in a lower $\chi^2$. This calculation is done iteratively, with a newly calculated $\delta \vec{a}$, until $\chi^2$ is minimized. The Levenberg-Marquardt algorithm[155, 156] is the most common algorithm used to do these calculations. It switches automatically between the inverse-Hessian and steepest-descent methods to calculate each $\delta \vec{a}$ correction depending on which works better in a given situation.[131]
The uncertainties of fit parameters are obtained as a by-product of the calculations to minimize $\chi^2$. In the Levenberg-Marquardt method, the Hessian matrix \[ \alpha_{kl} = \sum_{i=1}^{N} \frac{1}{\sigma_i} \left[ \frac{\partial y(x_i; \vec{a})}{\partial a_k} \frac{\partial y(x_i; \vec{a})}{\partial a_l} \right], \tag{7.10} \]
is calculated at every iteration and is used to obtain the next correction $\delta \vec{a}$. The standard covariance matrix $C_{jk}$ (not to be confused with elastic constants) is defined as the inverse of the Hessian matrix $(\alpha^{-1}_{jk})$. Once an optimal $\vec{a}$ has been obtained, $\alpha_{jk}$ is recalculated and the standard error associated with a fit parameter $a_j$ is $\sigma^2(a_j) = C_{jj} = \alpha_{jj}^{-1}$. Therefore, the square root of the diagonal elements of the formal covariance matrix are the standard errors (variances) of fit parameters, and the off-diagonal elements are the covariances between parameters.\[ \text{The mrqmin Levenberg-Marquardt algorithm presented in Reference [131] (programming language C) was adopted. This algorithm calls the gaussj and mrqcoef routines, which are also described in Reference [131]. These routines were translated from C and written in a mostly unmodified form using the Java language. We have written several versions of the program, which is completely self-contained and calls no instantiable classes. To fit experimental data with this algorithm, we adopted a fitting procedure based on the one described in Chapter 1. We begin with a suitable guess for $\vec{a}_0$ and assume $E_{\pm} = 0$. The data are fit in a small region around $T_C$, which is incrementally increased until the critical temperature range is maximized.}
while simultaneously maintaining a high-quality fit. Then we allow $E_{\pm} \neq 0$ and increase the temperature range until it is maximized. It is sometimes necessary to try several different guesses for $\vec{a}_0$ when the algorithm fails to produce a good fit. The most common failure mode of the algorithm is when the best-fit results are $\alpha \simeq 0$ and $A_\pm \simeq -B$ with very large, unphysical magnitudes. When this failure mode is observed, the initial guess $\vec{a}_0$ is typically too far away from the ideal $\vec{a}$ and the system is not robust enough to recover. Sometimes, even changing $\vec{a}_0$ is not enough, and we must choose a fit parameter (usually $\alpha$) to constrain.

**Critical Expression for $\Delta V/V$**

To this point, we have discussed the graphical and $\lambda \Omega T$ least-squares methods. There is a third strategy to study critical behavior in thermal expansion. As we previously mentioned, there are two potentially serious issues with numerically differentiating $\Delta V/V$ to obtain $\Omega$. Why not develop a critical expression for $\Delta V/V$ with which the experimental data may be directly fit then? In this section, we calculate a critical expression for $\Delta V/V$ for two reasons: to obtain a critical expression to fit experimental data and to quantitatively study the adverse effects on $\lambda \Omega T$ (or $\lambda_i \mu_i T$) caused by numerical differentiation.

Examination of the Pippard relation (see Equation (6.6)) reveals that we can calculate an expression for $\Delta V/V$ in the critical temperature region (where $C_p^{*}$ =
\[ \lambda \omega T \) by integrating
\[
\frac{\Delta V}{V} \simeq \frac{1}{\lambda} \int \frac{C_p^*}{T} dT.
\] (7.11)

As a corollary, we note that the critical expression for \( \Delta V/V \) must scale with an analogous expression for entropy \( \Delta S = \lambda \Delta V/V \) given the form of the integral in Equation (7.11). Since \( C_p^* = C_P - a - bT \), we are able to use Equation (1.23) for \( C_p^* \) in a mostly unmodified form except technically the analytic background is \( B' + D't \) where \( B' = B - (a + bT_C) \) and \( D' = D - bT_C \). Expanding Equation (1.23) into a more convenient form, the critical expression for \( C_p^* \) used in Equation (7.11) is
\[
C_p^* \simeq \frac{A_\pm}{\alpha} |t|^{-\alpha} + \frac{A_{\pm}E_{\pm}}{\alpha} |t|^{-\phi} + B' + D't,
\] (7.12)

where we define an exponent \( \phi \equiv \alpha - \chi \) for convenience.

We integrate Equation (7.11) from \( \epsilon \) to \( T \) using \( C_p^* \) as expressed in Equation (7.12). The integral diverges when \( \epsilon = 0 \) so \( \epsilon \) is kept finite. However, its specific value merely fixes the constant of integration \( G(\epsilon) \) which has no physical significance. \( \Delta V/V \) is dimensionless and is defined in terms of a normalized volume difference between two temperatures. Therefore, as is the case with entropy, an arbitrary constant may be added to \( \Delta V/V \) without altering the fundamental characteristics of its behavior and the particular value of \( \epsilon \) which determines \( G(\epsilon) \) is irrelevant. Integrating
Equation (7.11) from $\epsilon$ to $T$, a critical expression for $\Delta V/V$ is obtained

$$
\left( \frac{\Delta V}{V} \right)_\pm = \pm \frac{A_\pm}{\lambda \alpha} \frac{1}{1 - \alpha} \left| 1 - \frac{T}{T_C} \right|^{1-\alpha} \binom{2}{1-\alpha,1;2-\alpha;1-T/T_C} + G + HT + I \ln T.
$$

Equations (7.13)

The temperature-dependence of the anomaly retains the form of a power law but is augmented by a Gaussian hypergeometric function. The analytic background is comprised of terms $H = D'/\lambda T_C$ and $I = (B' - D')/\lambda$ in addition to the constant of integration $G$.

Equation (7.13) is exact, but it is not always convenient to work with an expression containing hypergeometric functions. Therefore, we exploit a series-expansion representation of the hypergeometric functions to develop a more practical expression for $\Delta V/V$. A hypergeometric function of the form

$$
\binom{2}{1-\zeta,1;2-\zeta;1-T/T_C},
$$

where $\zeta$ represents either $\alpha$ or $\phi$, may be expressed as

$$
\sum_{k=1}^{\infty} \frac{1}{k-\zeta} \left( 1 - \frac{T}{T_C} \right)^{k-1}.
$$

This series converges quickly, especially in the temperature region $10^{-4} \leq |1-T/T_C| \leq 10^{-1}$ where we apply it. To develop an understanding of how quickly convergence is achieved, we compared the magnitudes of the $k^{th}$ term in the series with the sum of the preceding $k-1$ terms as a function of $\zeta$ and temperature for $k = 2, 3, \ldots, 7$. The dependence on $\zeta$ is negligible, but convergence is noticeably slower the further the temperature is from $T_C$. For example, at $|1-T/T_C| = 10^{-1}$, the $k^{th}$ terms from two
to seven, respectively, are 5.2%, 0.34%, 2.5 × 10^{-2}\% , 2.0 × 10^{-3}\% , 1.7 × 10^{-4}\% , and 1.5 × 10^{-5}\% of the sum of the preceding \( k - 1 \) terms. The situation improves closer to \( T_C \) where, for \(|1 - T/T_C| = 10^{-3}\), the same terms are 5.2 × 10^{-2}\% , 3.5 × 10^{-5}\% , 2.7 × 10^{-8}\% , 2.2 × 10^{-11}\% , 1.8 × 10^{-14}\% , and 1.5 × 10^{-17}\% of the preceding sum. These results indicate that the series adequately converges after six or seven terms in the temperature region of interest.

After substituting the series expansion in Equation (7.14) into Equation (7.13) and simplifying, we arrive at the following expressions for \( \Delta V/V \)

\[
\left( \frac{\Delta V}{V} \right)_- = -\frac{A_-}{\lambda \alpha} \sum_{k=1}^{\infty} \frac{1}{k - \alpha} \left( 1 - \frac{T}{T_C} \right)^{k-\alpha}
- \frac{A_- E_-}{\lambda \alpha} \sum_{k=1}^{\infty} \frac{1}{k - \phi} \left( 1 - \frac{T}{T_C} \right)^{k-\phi}
+ G + HT + I \ln T \quad (7.15)
\]

\[
\left( \frac{\Delta V}{V} \right)_+ = \frac{A_+}{\lambda \alpha} \sum_{k=1}^{\infty} (-1)^{k+1} \frac{1}{k - \alpha} \left( \frac{T}{T_C} - 1 \right)^{k-\alpha}
+ \frac{A_+ E_+}{\lambda \alpha} \sum_{k=1}^{\infty} (-1)^{k+1} \frac{1}{k - \phi} \left( \frac{T}{T_C} - 1 \right)^{k-\phi}
+ G + HT + I \ln T. \quad (7.16)
\]

These expressions are typically more suitable to fitting experimental \( \Delta V/V \) data than Equation (7.13). Our least-squares algorithm is unable to recognize a hypergeometric function, so the series expansions are necessary in our case. \( \Delta V/V \) and entropy \( (\Delta S = \lambda \Delta V/V) \) are constrained by thermodynamics to be continuous across \( T_C \) in a continuous phase transition. It is therefore an important check to make sure Equations
(7.15) and (7.16) meet this requirement. In the limit \( T \to T_C^\pm \), \((\Delta V/V)_\pm\) is single-valued \((G + HT_C + I \ln T_C)\) for most values of \( \alpha \). The absence of a discontinuity at \( T_C \) is consistent with expectations. However, if \( \alpha = 1.0 \), \((\Delta V/V)_\pm\) diverges at all temperatures, and when \( \alpha > 1.0 \), \((\Delta V/V)_\pm\) diverges as \( T \to T_C^\pm \). The breakdown of Equations (7.15) and (7.16) indicates that the application of the Pippard relation (Equation (6.6)) is inappropriate for the \( \alpha \geq 1.0 \) case. This conclusion is consistent with a similar analysis conducted in Chapter 1. The implication of this result is that the transition may no longer be considered continuous for \( \alpha \geq 1.0 \) and the physics is properly described by the Clausius-Clapeyron relation instead of Pippard’s.

Equations (7.15) and (7.16) are valid for \(-\infty \leq \alpha < 1.0\) with one exception. Systems exhibiting critical behavior described by the two-dimensional Ising universality class,[46] for example, have \( \alpha = 0 \) and the proper critical expression for \( C_P \) diverges logarithmically[68] as \( T \to T_C^\pm \)

\[
C_P^\alpha \simeq -A_\pm \log |t| + B' + D't. \tag{7.17}
\]

Just as when \( \alpha \neq 0 \), we use Equation (7.17) to calculate a critical expression for \( \Delta V/V \) via Equation (7.11). Integrating from zero to \( T \), \( \Delta V/V \) is

\[
\left( \frac{\Delta V}{V} \right)_- = \frac{A_-}{\lambda} \text{Li}_2 \left( \frac{T}{T_C} \right) + G + HT + I \ln T \tag{7.18}
\]

\[
\left( \frac{\Delta V}{V} \right)_+ = \frac{A_- \pi^2}{6} - \frac{A_+}{\lambda} \log \left( \frac{T}{T_C} - 1 \right) \log \left( \frac{T}{T_C} \right) - \frac{A_+}{\lambda} \text{Li}_2 \left( 1 - \frac{T}{T_C} \right) + G + HT + I \ln T, \tag{7.19}
\]
where the temperature-dependence of critical behavior includes both logarithm and polylogarithm functions. The constant $G$ is not from the integration, but has been added to account for any vertical shift in $\Delta V/V$ data. Again, $G$ has no physical significance. When applying this expression for $\Delta V/V$, it is impractical to deal with polylogarithm functions, much like it was with hypergeometric functions when $\alpha \neq 0$. Therefore, we utilize a series expansion representation for the polylogarithm functions

$$\text{Li}_2(z) = \sum_{k=1}^{\infty} \frac{z^k}{k^2}.$$  \hspace{1cm} (7.20)

When we check Equations (7.18) and (7.19) for continuity across $T_C$, we find $(\Delta V/V)_{\pm} = (A_\pm/\lambda)(\pi^2/6) + G + HT_C + I \ln T_C$ at $T_C$. This calculation was performed with the series expansion and makes use of the result $\text{Li}_2(1) = \pi^2/6$. Thus, this expression for $\Delta V/V$ also satisfies continuity across $T_C$.

**Detriments of Differentiation**

We next use the critical expression calculated for $\Delta V/V$ to study the effect of numerical differentiation on the anomaly in $\lambda \Omega T$. This analysis is then used to emphasize the comparative merits of fitting $\Delta V/V$ data instead. We evaluate the potential benefits of fitting $\Delta V/V$ data by comparing least-squares fits of $\Delta V/V$ with analogous fits of $\lambda \Omega T$ using the appropriate respective critical expressions. The focus of our comparison is on the uncertainty of best-fit parameter values and the size of the critical temperature region over which the fit is good. These two criteria are manifestations of the effect of the relative magnitudes of $\delta \Omega$ and $\delta V$ and the truncation
error, respectively. To implement a direct, clear comparison, we have chosen to use simulated data, which models the critical behavior of a real transition. This is done both to remove distractions related to measurement and sample quality and so that the fits of $\Delta V/V$ and $\lambda \Omega T$ may be compared not only with one another, but to the known character of the simulated model.

$\Delta V/V$ data, displayed in Figure 28, were generated with Mathematica 5.2 to model the critical behavior of the classic Heisenberg ferromagnet EuO using Equation (7.13) with parameter values taken from Reference [69]: $\alpha = -0.10$, $T_C = 69.332$, $A_-/\alpha = -29.070$, $A_+/\alpha = -43.90$, $B' = 69.0$, and $D' = 32.0$. The confluent singularity was not included in our generated data ($E_- = E_+ = 0$) and we have set $\lambda = 1.0 \text{ J mol}^{-1} \text{ K}^{-1}$, $B = B'$, and $D = D'$ for convenience. These choices were made to simplify the analysis, and have no influence on the results of our evaluation. Steps were taken to simulate a real measurement by generating $\Delta V/V$ data with data density $\Delta T = 10 \text{ mK}$ and including experimental noise. Gaussian noise was modeled using a random number generator so that a realistic $\delta V$ resulted. An estimate of $\delta V = 2.6781 \times 10^{-5}$ was made by calculating the standard deviation of the residuals (see upper inset of Figure 28) of the data set generated with noise subtracted by an analogous one without noise. We differentiated $\Delta V/V$ and multiplied by temperature to obtain $\Omega T$, which is also displayed in Figure 28. After subtracting $\Omega T$ from $C_p^* (C_p^* = \Omega T)$, generated without noise from Equation (1.23), we calculated the standard deviation of the residuals (see lower inset of Figure 28) to estimate $T \delta \Omega = \ldots$
$1.4926 \times 10^{-1}$. It is apparent that $\delta V \ll T \delta \Omega$ in this example, and a quick survey of other generated and experimental data revealed that $\delta V$ is typically smaller than $T \delta \Omega$ by 3-4 orders of magnitude.

Figure 28. Generated $\Delta V/V$ data with density $\Delta T = 10$ mK modeling the ferromagnetic transition of EuO. $\lambda \Omega T$ is calculated from the derivative of $\Delta V/V$ (note that $\lambda = 1.0$ J mol$^{-1}$ K$^{-1}$) and plotted for comparison. The insets depict the residuals from the difference of each data set with a noiseless analogue. The uncertainty of each data set is calculated from the standard deviation of the residuals.

We fit the $\Delta V/V$ and $\Omega T$ data using our Levenberg-Marquardt least-squares program. To make relevant comparisons, we fit each data set over the same temperature range from 62.40 to 69.31 K below $T_C$ and 69.34 to 76.27 K above $T_C$. This corresponds to a log $|t|$ temperature range from -1 to $\sim$3.75. We note that $T_C$ was not a variable parameter, but rather, was fixed at 69.332 K. Fitting $\Omega T$ data with Equation (7.4) is straight-forward, however, fitting $\Delta V/V$ requires a decision regarding
the number of terms to use in the series expansions of Equations (7.15) and (7.16).

To demonstrate the influence this choice has on the results, we truncated the series after \( k = 1, 2, 3, \ldots, 6 \) terms and compared the fit results in Table 6 with the true values (denoted in Table 6 by \( k = \infty \)). It is clear that inclusion of one or two terms is insufficient to obtain reasonably-accurate fit parameters, however, use of three or more terms results in increasingly-accurate best-fit parameters. As we have previously noted, the series-expansion approximation for the hypergeometric function gets worse as we move away from \( T_C \). Reduction of the temperature range over which the data is fit would allow us to truncate the series after a few terms while retaining accuracy. However, experimental critical regions for magnetic systems are typically\(^{[72]} \ -4 \leq \log |t| \leq -1, \) so in the interest of capturing the entire critical region, it is prudent to include at least six terms in the series.

Table 6. Least-squares best-fit values for \( \Delta V/V \) parameters in Equations (7.15) and (7.16) with \( k \) terms in the series expansion compared to the true values which one would obtain with \( k = \infty \).

<table>
<thead>
<tr>
<th></th>
<th>( k = \infty )</th>
<th>( k = 1 )</th>
<th>( k = 2 )</th>
<th>( k = 3 )</th>
<th>( k = 4 )</th>
<th>( k = 5 )</th>
<th>( k = 6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>-0.10</td>
<td>-0.07157(4)</td>
<td>-0.12061(3)</td>
<td>-0.10033(4)</td>
<td>-0.10019(4)</td>
<td>-0.10001(4)</td>
<td>-0.10000(4)</td>
</tr>
<tr>
<td>( A_-/\alpha )</td>
<td>-29.070</td>
<td>-36.06(2)</td>
<td>-25.426(6)</td>
<td>-28.96(1)</td>
<td>-29.03(1)</td>
<td>-29.07(1)</td>
<td>-29.07(1)</td>
</tr>
<tr>
<td>( A_+/\alpha )</td>
<td>-43.90</td>
<td>-49.39(1)</td>
<td>-41.642(4)</td>
<td>-43.832(7)</td>
<td>-43.870(7)</td>
<td>-43.900(7)</td>
<td>-43.900(7)</td>
</tr>
<tr>
<td>( I )</td>
<td>37.0</td>
<td>11.914(5)</td>
<td>30.79(1)</td>
<td>36.60(1)</td>
<td>36.93(2)</td>
<td>37.00(2)</td>
<td>37.00(2)</td>
</tr>
<tr>
<td>( H )</td>
<td>0.46155</td>
<td>0.9349(2)</td>
<td>0.49707(8)</td>
<td>0.46601(8)</td>
<td>0.46190(9)</td>
<td>0.46159(9)</td>
<td>0.46156(9)</td>
</tr>
<tr>
<td>( G )</td>
<td>0.0</td>
<td>73.52(3)</td>
<td>23.88(4)</td>
<td>1.39(6)</td>
<td>0.26(6)</td>
<td>0.01(6)</td>
<td>0.00(6)</td>
</tr>
</tbody>
</table>
Best-fit parameters for $\Omega T$ and $\Delta V/V$ (using $k = 6$) are compared in Table 7 with one another and the true values. The accuracy and resolution of the $\Delta V/V$ fit parameters are much better than their $\Omega T$ counterparts. The better accuracy is a result of the adverse influence of truncation error on $\Omega T$ while the better resolution is a consequence of $\delta V \ll T\delta \Omega$. Obviously, it is desirable to maximize the resolution and accuracy of best-fit parameters and it appears fitting $\Delta V/V$ data is one way to accomplish this. The differences in Table 7 may seem insignificant, but we stress that some of these parameters have inherent physical meaning. For example, the critical exponent $\alpha$ and the ratio of the singularity amplitudes $A_+/A_-$, indicate the transition’s universality class. As resolution decreases, we could envision an extreme case where a best-fit value for $\alpha$ had an uncertainty large enough to encompass more than one universality class. In such a case, there could be a significant advantage to fitting $\Delta V/V$ instead of $\lambda \Omega T$. A study by Guttmann on generated data sets with

<table>
<thead>
<tr>
<th>True Value</th>
<th>$\lambda \Omega T$</th>
<th>$\Delta V/V$ ($k = 6$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>-0.10</td>
<td>-0.099(2)</td>
</tr>
<tr>
<td>$A_-/\alpha$</td>
<td>-29.070</td>
<td>-29.3(4)</td>
</tr>
<tr>
<td>$A_+/\alpha$</td>
<td>-43.90</td>
<td>-44.1(3)</td>
</tr>
<tr>
<td>$B'$</td>
<td>69.0</td>
<td>69.2(4)</td>
</tr>
<tr>
<td>$D'$</td>
<td>32.0</td>
<td>31.8(3)</td>
</tr>
<tr>
<td>$B' - D'$</td>
<td>37.0</td>
<td>37.4(5)*</td>
</tr>
<tr>
<td>$D'/T_C$</td>
<td>0.46155</td>
<td>0.459(5)*</td>
</tr>
</tbody>
</table>
a variety of noise levels found that, to obtain reliable and meaningful fits of critical fit parameters (especially $\alpha$), the maximum permissible uncertainty is 5% (signal to noise ratio of 20:1).[153] If $\lambda \Omega T$ contains anywhere near this level of noise, the only reasonable approach, short of obtaining better data, is to fit $\Delta V/V$ data instead.

We focus next on the manifestation of truncation error in $\Omega T$. To study this, we generated $\Delta V/V$ data, using the same parameters from EuO as before, but without noise and for a variety of data densities. A normalized data density $\Delta T/T_C$ is defined to make our analysis more general. In Figure 29(a), we have plotted $\lambda \Omega T$ ($\lambda = 1.0 \text{ J mol}^{-1} \text{ K}^{-1}$) as differentiated from generated $\Delta V/V$ data. As $\Delta T/T_C$ increases, the transition region around $T_C$ experiences significant broadening and a reduction in its magnitude compared to the result we would get if we could take an exact derivative, uninfluenced by truncation error (obtained in the limit $\Delta T/T_C \to 0$). In practice, we calculate the $\Delta T/T_C = 0$ behavior with $C_P^*$ via Equation (1.23).

It is instructive to demonstrate the scope of the influence of truncation error by plotting the temperature at which deviation from $C_P^*$ occurs, in terms of $\log |t|_{\text{min}}$ against $\log (\Delta T/T_C)$ (see Figure 29(b)). To obtain this plot, we plotted $\log(\lambda \Omega T)$ as a function of $\log |t|$ for each data density $\Delta T/T_C$ (not shown) and identified the temperatures (defined as $\log |t|_{\text{min}}$) where deviations of 0.05%, 0.5%, 1%, and 4% from $C_P^*$ occur. Of course, the deviations appear at slightly different temperatures on each side of $T_C$, so $\log |t|_{\text{min}}$ is the average of the two with error bars reflecting the standard deviation. The deviations lie in a band denoted by dashed lines in
Figure 29. (a) $\lambda\Omega T$ ($\lambda = 1.0$ J mol$^{-1}$ K$^{-1}$) as differentiated from $\Delta V/V$ data, generated without noise and for a variety of data densities ($\Delta T/T_C$) to model the critical behavior of EuO. Lines are a guide to the eye. As $\Delta T/T_C$ increases, the anomaly becomes broader and its magnitude is reduced compared to simulated $C_P^*$ (black line), which is uninfluenced by truncation error. (b) Temperature log $|t|_{\text{min}}$ where deviations of 0.05% (side-ways triangles), 0.5% (circles), 1% (squares), and 4% (triangles) of $\lambda\Omega T$ from $C_P^*$ occur as a function of data density. The error bars reflect the standard deviation of the average of the deviation on both sides of $T_C$. Most deviation temperatures reside within a band denoted by dashed lines. (c) Deviation log $|t|_{\text{min}}$ from fitted critical behavior as a function of log ($\Delta T/T_C$) for several published studies involving $\lambda\Omega T$. Most of the deviations reside within the truncation-error influence band and are collinear. The central region, bounded by diagonal red lines, indicates the regions where critical behavior is expected to be observed in a magnetic system.
Figure 29(b). The critical behavior of a typical magnetic system is distorted for \( \log |t| \leq -4 \) by modest sample defects,\([72]\) so for \( \lambda \Omega T \) data to display unaltered critical behavior to \( |t| \approx 10^{-4} \), \( \log (\Delta T/T_C) \) must be at least -3.25, but preferably around -5.0. Most experiments use insufficient data densities to avoid truncation error. To emphasize this point, we have examined published studies\([67, 70, 71, 93, 141, 149]\) involving \( \lambda \Omega T \) and plotted the deviation from fitted critical behavior (as defined previously) as a function of \( \log (\Delta T/T_C) \) in Figure 29(c). Not only do the deviations reside within the band defined in Figure 29(b), most of them are collinear. This observation is convincing evidence that the limiting factor for most of these studies was the detrimental influence of truncation error. The studies on \( \text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3 \), \( \text{LaMnO}_3 \), and \( \text{CaMnO}_3 \) do not appear to follow this trend, because they measured polycrystalline samples\([70, 149]\) and their critical behavior was limited by sample-related issues before the influence of truncation error was observable. The critical region is confined to temperatures where the coherence length is smaller than the dimensions of magnetic domains, the latter of which are drastically limited by the grain size in a polycrystal.\([27]\) The implication of Figure 29 is that, with the exception of polycrystalline samples, the size of the critical region is increased if we minimize or remove the influence of truncation error.

From the perspective of optimizing resolution and accuracy of best-fit parameters and maximizing the temperature range over which critical behavior is free of
artificially-imposed distortion, there can be significant benefits to fitting thermal-expansion data directly with the critical expressions for $\Delta V/V$. This conclusion in no way repudiates previous work which studied critical behavior using the graphical and $\lambda \Omega T$ least-squares methods.[67, 70, 71, 93, 141, 149] It merely cautions that such an analysis may not always be optimal and, if attempted, requires care. For example, fitting $\Delta V/V$ piecewise with some polynomial in the region around $T_C$ may avoid truncation-error problems by allowing exact differentiation of the polynomial, but subtle details in the data are lost in the process. Furthermore, it is far simpler to fit $\Delta V/V$ once with a single function over the entire critical temperature range than performing multiple piecewise fits. It may also be tempting to measure thermal expansion with as high a data density as possible to circumnavigate the influence of truncation error. However, an unfortunate paradox emerges because the uncertainty of the derivative, ignoring $\delta V$, is $\delta \Omega/\Omega = \sqrt{2} \delta T/\Delta T$. So as $\Delta T \to \delta T$, $T \delta \Omega$ rapidly grows leading to increased noise and decreased resolution of best-fit parameters. Therefore, the finite experimental value of $\delta T$ creates a lower limit for $\Delta T$. If we consider both truncation error and uncertainty issues simultaneously, we might discover a compromise. From our analysis in Figure 29(b), we have determined that a data density of $\Delta T/T_C \sim 10^{-4}$ would minimize truncation error to a sufficient degree. If $\delta \Omega/\Omega$ is to have a relatively modest value of 0.1%, then the required temperature resolution is at least $\delta T/T_C \sim 1.4 \times 10^{-7}$. For reasonable values of $T_C$, this requires $\delta T \sim 10^{-7}$-10$^{-5}$ K. This resolution is pushing the boundaries of current resistive
thermometry ($10^{-7}$ K), but is easily attainable from SQUID-based high-resolution thermometry ($10^{-9}$ K).[157] However, $\delta\Omega/\Omega \sim 0.1\%$ is still much higher than typical values of $\delta V/(\Delta V/V)$. Therefore, it appears to be sensible in many circumstances to fit $\Delta V/V$ instead of $\lambda\Omega T$. Our experimental setup is nominally capable of $10^{-4}$ K temperature resolution (at low temperature), so if we use $\Delta T/T_C \sim 10^{-4}$, then $\delta\Omega/\Omega = \sqrt{2}/T_C$ which is of order 0.1-1.0\% depending on $T_C$. We can decrease $\delta\Omega/\Omega$ only by increasing $\Delta T/T_C$ (decreasing data density).

Earlier this chapter, we explained how the critical behavior (as characterized by particularly-salient parameters) exhibited in each $\lambda_i\mu_i T$ data set is the same as that exhibited by $\lambda\Omega T$. This observation also holds for $\lambda_i(\Delta L/L)$, and $\lambda\Delta V/V$. Therefore, Equation (7.13) (or Equations (7.15) and (7.16)) can be used to fit $\Delta L/L$ along any crystallographic direction with the same justification used to fit $\Delta V/V$. However, we caution that, though fitting thermal expansion directly appears to be optimal from our idealized example, it is typically more difficult than fitting $\lambda\Omega T$ when working with real data. $G$ is an additional parameter that comes with fitting $\Delta V/V$ which has been observed to correlate strongly with $\alpha$. In those cases, there can be many possible solutions with very different best-fit parameters but similar $\chi^2$ values. Sifting through these solutions in order to select the best one can be time-consuming and difficult. So while fitting $\Delta V/V$ does allow us to avoid detrimental effects from numerical differentiation, there is a cost associated with this advantage. In general, more care is required when fitting $\Delta V/V$ (or $\Delta L/L$).
Now that several strategies to study critical behavior with thermal expansion have been considered, we are ready to test them on real systems. CaMn$_2$O$_4$ exhibits a textbook antiferromagnetic transition and therefore provides an excellent test case to demonstrate/evaluate our ability to study critical behavior with thermal expansion. We then attempt to settle a long-standing question of whether Bi$_2$CuO$_4$ exhibits easy-axis or easy-plane anisotropy by studying its critical behavior in the vicinity of $T_N$. Finally, the limitations of studying critical behavior with a polycrystalline sample are demonstrated when we investigate the antiferromagnetic transition of $\alpha$-Mn. This latter system has extremely complicated crystal and magnetic structures and we examine the possibility that its transition belongs to the $n \geq 4$ universality classes described in Chapter 1.
CaMn$_2$O$_4$: A SIMPLE ANTIFERROMAGNETIC TEST SYSTEM

Introduction

Initial studies of CaMn$_2$O$_4$ were published shortly after its discovery in 1963 in Morocco as a naturally occurring mineral.[158] The material is commonly referred to by its mineral name, marokite, which originates from the name of its country of origin. Early work on CaMn$_2$O$_4$ demonstrated that it assumes an orthorhombic crystal structure described by space group[159] $Pbcm$ and exhibits antiferromagnetic ordering of Mn-moments below 225 K.[160] Following these preliminary investigations, there is a large temporal gap in the literature, ending in 2001, when CaMn$_2$O$_4$ was studied as an impurity phase in the solid-state synthesis of manganese oxides exhibiting colossal magnetoresistance.[161] CaMn$_2$O$_4$ has since enjoyed some renewed interest, however, most studies have been limited to reporting on aspects of its magnetic ordering[161, 162, 163] and crystal structure.[161, 162, 164]

Compounds with chemical formula $AB_2O_4$ frequently crystallize in the cubic spinel structure with space group $Fd3m$ or a tetragonally-distorted spinel structure with space group $I4_1/amd$. This is true of several manganese-oxide compounds: NMn$_2$O$_4$ with N = Ni, Cu, Mn, Zn, Cd, Mg, and Li.[165, 166] The crystal structure of CaMn$_2$O$_4$, which contrasts with these cases, is displayed in Figure 30 as generated by Java Structure Viewer.[167] It is primarily constructed from a complex network of
MnO$_6$ octahedra. We formulate a convenient description of this network by considering zig-zag layers of edge-sharing octahedra running parallel to $b$, which are coupled along $c$ by vertex-sharing of apical oxygen sites. All MnO$_6$ octahedra are oriented with one of two tilted orientations with respect to the $c$ axis and, while all octahedra display the same tilt orientation within each layer, successive zig-zag layers alternate between the two. Tunnels along $a$, between the zig-zag layers, are occupied by Ca$^{2+}$ ions. In stoichiometric CaMn$_2$O$_4$, all manganese ions are nominally high-spin Mn$^{3+}$
(3d$^4$; $t_{2g}^3e_g^1$). This electronic configuration is known to result in highly Jahn-Teller distorted MnO$_6$ octahedra. Neutron-diffraction studies observe 26\% elongation of the axial Mn-O bond distances relative to equatorial in the octahedra.[161] The magnitude of this distortion certainly prohibits assumption of a cubic spinel structure for CaMn$_2$O$_4$, but does not directly prevent the stabilization of a tetragonally-distorted spinel structure. However, it seems the large Ca$^{2+}$ ions do inhibit tetragonal symmetry. The A-site in the spinel structure is located in a position which forms AO$_4$ tetrahedra. Comparison of the ionic radii of all divalent ions occupying a tetrahedral site reveals that Ca$^{2+}$ has the largest ionic radius of any with only Pb$^{2+}$ and Hg$^{2+}$ being slightly smaller.[168] Most other divalent ions occupying the A-site of compounds which do crystallize in the spinel structure, have ionic radii 50-70\% as large as Ca$^{2+}$ (1.00 Å).[168] The structure of CaMn$_2$O$_4$ is stabilized when Ca$^{2+}$ incorporates itself into eightfold coordination with CaO$_8$ polyhedra instead of CaO$_4$ tetrahedra.[161, 162] Many cubic spinel compounds exhibit a structural phase transition under pressure to one of three related orthorhombic structures - those of CaMn$_2$O$_4$ (Pbcm), CaFe$_2$O$_4$ (Pnma), and CaTi$_2$O$_4$ (Cmcm).[165] This observation may imply that the chemical pressure exerted on the CaMn$_2$O$_4$ structure by Ca$^{2+}$ ions is similar to the effect hydrostatic pressure has on cubic spinel compounds. It is the combination of distorted MnO$_6$ octahedra and large Ca$^{2+}$ ions which results in a unique crystal structure for CaMn$_2$O$_4$, generally referred to as the marokite structure.[162]
CaMn$_2$O$_4$ exhibits a simple, textbook antiferromagnetic phase transition, which makes it an ideal candidate to test the strategies developed in Chapter 7 for studying critical behavior with thermal expansion. Furthermore, its orthorhombic crystal structure provides an opportunity to study critical behavior along three independent crystallographic axes (in addition to the volume behavior). This chapter is divided into three parts. We discuss the crystal growth of CaMn$_2$O$_4$ first. Most of our discussion on material synthesis is adapted from B. D. White, C. A. M. dos Santos, J. A. Souza, K. J. McClellan, and J. J. Neumeier, J. Cryst. Growth 310, 3325-3330 (2008) (Copyright 2008 by Elsevier B.V.). Then we examine the physical properties of this model Jahn-Teller system. Most physical properties of CaMn$_2$O$_4$ were unknown prior to the growth of the first large single crystals and were first measured by White et al. in Reference [141]. Finally, the critical behavior of CaMn$_2$O$_4$ is studied with the graphical ($\lambda \Omega T$) and least-squares methods (both $\lambda_i \mu_i T$ and $\lambda_i (\Delta L/L)_i$ along each principal crystallographic axis). The majority of our treatment of the physical properties of CaMn$_2$O$_4$ and some of the critical-behavior analysis is adapted from B. D. White, J. A. Souza, C. Chiorescu, J. J. Neumeier, and J. L. Cohn, Phys. Rev. B 79, 104427 (2009) (Copyright 2009 by the American Physical Society).
Crystal Growth and Characterization

Growth of CaMn$_2$O$_4$

The first successful growth of large (centimeter-size) single crystals of CaMn$_2$O$_4$ was reported by White et al. in Reference [91]. Prior to the crystals of White, the largest CaMn$_2$O$_4$ crystals were grown using a hydrothermal synthesis technique,[164, 169] yielding crystalline needles 10 µm in length[169] and needle-shaped crystals with sub-millimeter dimensions.[164] Immediately following publication of Reference [91], Fukabori et al. published their work on the growth of CaMn$_2$O$_4$ in a molten flux of CaCl$_2$.[170] However, the maximum dimensions of their crystals were 0.7 × 0.5 × 0.3 mm$^3$, which is certainly not an improvement in size. The quality of their crystals was not reported so it is impossible to make a comparison on that basis. The largest single crystals of CaMn$_2$O$_4$ currently available are made from the floating-zone method and we describe their synthesis and quality herein.

A detailed oxygen isobaric section of the ternary phase diagram for the Ca-Mn-O system at 0.2 atmosphere O$_2$ pressure was published by Horowitz and Longo.[171] Careful consideration of this phase diagram reveals that CaMn$_2$O$_4$ melts congruently and is therefore an ideal candidate for single-crystal growth by the floating-zone method. Furthermore, CaMn$_2$O$_4$ is the only congruently-melting ternary phase in the Ca-Mn-O system.[171]

The powder used in polycrystalline rod production was prepared by solid-state reactions in which MnO$_2$ (99.9%) and CaCO$_3$ (99.99%) were weighed to produce 20
g of powder with molar ratio Mn:Ca = 7:3. Once weighed, the powder was milled in a planetary ball mill for one hour at 200 rpm before firing in air at 1100° C for 20 hours. The powder was reground in an agate mortar and re-milled for one hour at 200 rpm between an additional reaction at 1200° C and three subsequent reactions at 1250° C, each for 20 hours in air. Al₂O₃ crucibles were used in each reaction of the powder. Polycrystalline rods were formed by pressing the powder inside Al₂O₃ tubes, as described in Chapter 2. A final reaction at 1280° C for 20 hours was used to anneal the rods. Reactions at 1315° C were found to bond the rod to the Al₂O₃ tube. Approximately 23.8 cm rod length was produced with 20 g of powder providing ∼ 12 mm of rod per gram of powder.


Growths were conducted in a mixture of O₂ and air. Both feed and seed rods were composed of the same chemical composition (CaMn₂O₄ with 3.33% excess manganese oxide). Rotational rates of 15 rpm for both upper and lower shafts were found to provide a stable, homogenous molten zone and advantageous liquid-solid interface,
and a growth rate of 5 mm/hour was adopted. This rate is slow enough to allow single-
grain crystallization while being fast enough to reduce the amount of manganese-oxide
volatilization from the melt.[172] The lamp power was kept near 340 watts (using 1000
watt lamps) throughout all growths. Crystals as large as \(\sim 5\) cm long were grown
with these parameters. One of our crystal boules is displayed in Figure 31. A

Figure 32. Cleavage plane in CaMn\(_2\)O\(_4\) single crystal. The white spots on the top
surface of the sample are reflections from cleaved surfaces within small fractures
caused by cutting the boule with a coarse diamond-wheel saw blade. Reprinted from
B. D. White, C. A. M. dos Santos, J. A. Souza, K. J. McClellan, and J. J. Neumeier,

section of single crystal, cut from a previous growth, was used as the seed for the
crystal and is visible between the 0 and 1 cm lines. Starting from a polycrystalline
seed rod, a single crystal is typically achieved within 1 to 2 cm of growth. The cross-
sectional shape of the single crystal is nearly elliptical with major axis 5 mm and
minor axis 4.2 mm. The surface of the crystals is highly reflective and black and the
crystals cleave easily as depicted in Figure 32. The planes revealed by cleaving in the
photograph are \(\{1\,0\,0\}\) as confirmed by back-reflection Laue diffraction. The crystal
structure[161, 162, 164] of CaMn$_2$O$_4$ suggests the {0 0 1} family of planes may also be revealed by cleaving. This was also observed.

**Characterization of Crystals**

The single-phase nature of the crystals was confirmed by powder x-ray diffraction (see Figure 33). Multiple patterns were taken for powder samples of the crystal and compared with theoretical patterns for CaMn$_2$O$_4$ generated by PowderCell.[106] All Bragg reflections were indexed to an orthorhombic unit cell with space group $Pbcm$ and room-temperature lattice parameters: $a = 3.1554\ \text{Å}$, $b = 9.9977\ \text{Å}$, $c = 9.6843\ \text{Å}$. The lattice parameters are in excellent agreement with recently reported structural refinements on both polycrystalline[161, 162] and single-crystalline[164, 169] samples. Further characterization with x-rays was done by collecting Laue patterns at multiple positions along the boule (in an identical orientation) to ensure the single-crystalline nature of the entire boule. The size and morphology of Laue spots was indicative of the high quality of the crystal. Absent from photographs were characteristics of low-angle grain boundaries or strain. A representative photograph featuring the Laue pattern for (1 0 0) is juxtaposed in Figure 34(a) with a calculation of the (1 0 0) pattern as generated by LauePatternSim.java (discussed in Chapter 3) in Figure 34(b).

Figure 34. (a) (1 0 0) back-reflection Laue pattern from cleaved surface of CaMn$_2$O$_4$ crystal, and (b) simulated Laue pattern from LauePatternSim.java for the same orientation. Reprinted from B. D. White, C. A. M. dos Santos, J. A. Souza, K. J. McClellan, and J. J. Neumeier, J. Cryst. Growth 310, 3325-3330 (2008). Copyright 2008 by Elsevier B.V.
Magnetization measurements provide an additional probe of phase purity in our single crystals. For example, unsuccessful attempts to grow CaMn$_2$O$_4$ from stoichiometric rods produced boules which exhibited a broad feature in their temperature-dependent magnetization between 20 - 100 K. This feature, which is displayed in Figure 35(a), is indicative of the presence of CaMnO$_3$ as a minor impurity phase. This suspicion is confirmed by low-angle Bragg reflections in powder x-ray diffraction patterns (not shown) which can unambiguously be identified with CaMnO$_3$. However, those reflections are so subtle that they would have been missed without knowing to look for them as a result of the magnetization measurement. The inset of Figure 35(a) displays a magnetization measurement for CaMnO$_3$ for comparison; although CaMnO$_3$ is antiferromagnetic, local ferromagnetism and canting of the manganese magnetic moments[173, 174] leads to a ferromagnetic signal and the broad peak below 130 K. This feature is obviously present in the magnetization of the sample grown from stoichiometric polycrystalline rods. The impurity may be explained by unavoidable manganese volatilization driving the chemistry of the melt towards the calcium-rich portion of the phase diagram and out of the single-phase region where only CaMn$_2$O$_4$ exists. If this is the case, it appears from the phase diagram in Reference [171] that the impurity phase should be Ca$_4$Mn$_3$O$_{10}$ rather than CaMnO$_3$. However, we must remember that the regions and boundaries in question have not been rigorously tested. This implies that the phase diagram requires some modification to incorporate these new observations. In addition to containing an impurity
phase, growths from stoichiometric rods produce boules of generally low quality with cracks and fractures. However, when the polycrystalline rods are manufactured with a 7:3 ratio of manganese to calcium (inclusion of excess manganese oxide), it was found that high-quality crystals with dense, un-fractured boules and without any magnetic signature due to CaMnO$_3$ could be grown. The magnetization along the $a$ axis of a crystal grown from rods with excess manganese oxide is shown in Figure 35(b). The sharp nature of the antiferromagnetic transition around $T_N \sim 217$ K and the absence of any feature attributable to CaMnO$_3$ both indicate the high quality of the crystal.

![Figure 35.](image)

Energy-dispersive x-ray spectrometry measurements were conducted with a scanning electron microscope. Multiple scans were conducted on several crystals and
polycrystalline rods to study possible aluminum contamination originating from diffusion during reactions of the powder and pressed rods in alumina crucibles and tubes, respectively. These scans were able to detect a maximum of 0.7% aluminum content (0.7% of atoms in the measured region were aluminum) in the polycrystalline rods, though typically contamination was well below levels of 0.5%. Measurements of the crystal boules failed to resolve any aluminum peaks from the background suggesting that the aluminum impurities were unable to enter the CaMn$_2$O$_4$ crystal structure. This is not surprising given the 17% difference in ionic radius between high spin Mn$^{3+}$ and Al$^{3+}$. Even Fe$^{3+}$ with ionic radius identical to Mn$^{3+}$ is unable to substitute itself into CaMn$_2$O$_4$ and form the solid solution CaMn$_{2-x}$Fe$_x$O$_4$ with low $x$. Interstitial substitution by aluminum is also highly unlikely considering the dense crystal structure of CaMn$_2$O$_4$. The only plausible way for the aluminum impurities to enter the growing crystal seems to be in the form of inclusions. However, neither energy-dispersive x-ray spectrometry nor powder x-ray diffraction managed to detect any traces of an inclusion phase and electron microscopy was unable to image any inclusion-phase regions either.

The phase diagram presented in Reference [171] suggests that CaMn$_2$O$_4$ forms as a solid solution, rich in manganese, when the composition is not precisely onstoichiometry. Therefore, we might expect crystals with a slightly manganese-rich chemistry because our growths begin with 3.33% excess manganese oxide. However, we also expect at least $\sim$1.5% of the excess manganese oxide will volatilize from the
melt as was measured by Velázquez et al. for a different manganese-oxide phase which was also grown at 5 mm/hour. Manganese-oxide volatility was observed in our growths in the form of a thin layer of powder on the interior of the quartz tube enclosing the growth chamber. The grown crystals are composed of stoichiometric CaMn$_2$O$_4$ to within the uncertainty of energy-dispersive x-ray spectrometry measurements, which indicate the average ratio of manganese to calcium is 2.0(2). Taken together, these observations suggest that if the grown single crystals are somewhat off-stoichiometry, it is at maximum on the order of 1%.

Iodometric titration of powder from ground crystals was used to determine the oxygen content of our samples. The technique precisely determines the sample’s average Mn-valence (Mn$^{\sigma+}$), or equivalently, the ratio of Mn$^{3+}$ to Mn$^{4+}$ in the sample. We write the chemical formula as Ca[Mn$^{3+}_{(1-\alpha)}$Mn$^{4+}_{\alpha}$]$\delta$O$_4$$^{\delta+}$. We must be careful not to confuse this $\alpha$ with the critical-exponent $\alpha$ discussed later in this chapter. Then, by assuming exact oxidation states for the other ions (O$^{2-}$ and Ca$^{2+}$) and imposing charge neutrality, $\delta$ and $\alpha$ are related by $\alpha = \delta$. Therefore, excess oxygen ($\delta > 0$) is indicative of the presence of Mn$^{4+}$ in the sample. After six titrations, we determined our crystals had oxygen content $\delta = 0.012(6)$, which corresponds to an average manganese valence of $\sigma = 3.012(6)$. 
Physical Properties

Knowledge regarding the physical properties of CaMn$_2$O$_4$ was advanced considerably by White et al. in Reference [141]. All physical-property studies available previous to Reference [141] used either synthetic polycrystalline samples[161, 162, 165] or the natural mineral in polycrystalline form.[176] The measurement of anisotropic or strain-sensitive physical properties is severely limited in these cases, a problem which was only alleviated after a reproducible method to grow large single crystals of high quality was discovered.[91] A comprehensive discussion of the physical properties of CaMn$_2$O$_4$, adapted from Reference [141], is presented herein before its critical behavior is considered.

Magnetic Susceptibility

Antiferromagnetic order below $T_N = 220$ K was previously observed in both magnetization[161, 162] and neutron diffraction[160, 161, 162]. As the temperature is lowered through $T_N$, the symmetry of the magnetic superstructure requires a doubling of the $a$ axis of the chemical unit cell. The magnetic unit cell[161, 162] is described by the $\Gamma_2$ irreducible representation of the space group $Pbca$.[162] Neutron-diffraction studies of the magnetic structure observed that the antiferromagnetic sublattices anti-align along the $a$ axis with negligible canting along the $b$ and $c$
axes.[161, 162] Jahn-Teller distortion of the MnO₆ octahedra creates six unique Mn-O bond lengths.[161, 162, 164] As a result, there are six distinct superexchange-interaction strengths between neighboring Mn³⁺ ions, facilitated through the oxygen ions their MnO₆ octahedra share. Whangbo et al. studied these superexchange interactions in detail, calculating a spin-exchange parameter $J = J_{AFM} + J_{FM}$ for each superexchange pathway using spin-dimer analysis.[163] They concluded with confidence that four interactions were antiferromagnetic. The remaining two were observed to be weakly antiferromagnetic from their calculations, though they noted that neutron-diffraction experiments[161] suggest a weakly-ferromagnetic interaction is possible.

After zero-field cooling, the magnetic susceptibility $\chi$ was measured between 10 and 350 K in a 2000 Oe applied field. The results are displayed in Figure 36(a). The behavior of $\chi$ along each axis is best described within three temperature regions. For $T \gg T_N$, CaMn₂O₄ exhibits Curie-Weiss paramagnetism.[161, 162] Antiferromagnetic ordering is observed along each axis just below 220 K; however, the anomaly along $a$ is much more distinct than along $b$ and $c$ (consistent with the previous identification of $a$ as the magnetic easy axis).[161, 162] The true value of $T_N$ is somewhat difficult to extract from $\chi$. In lieu of a better method, we identify the temperature of the peak in $d\chi_a/dT$ as the Néel temperature ($T_N = 217.3(3)$ K). This is shown in the inset of Figure 36(a). For $T < T_N$, $\chi$ exhibits the textbook characteristics of antiferromagnetic order within an anisotropic magnetic structure until $\sim 75$ K when an upturn is
observed. This same upturn has been previously reported in polycrystalline samples where explanations have invoked scenarios where either spin canting[162] or a minor, Mn-based magnetic impurity phase[161, 162] was responsible. Our results support the latter position.

Figure 36. (a) Magnetic susceptibility $\chi$ measured along all three principle crystallographic axes in an applied field of 2000 Oe. The inset reveals the peak at $T_N$ in $d\chi_a/dT$. (b) Curie-Weiss fit to the low-temperature upturn in $\chi_a$ (line) is plotted with $\chi_a$ (open circles). The inset displays $\chi_a$ after the low-temperature Curie-Weiss behavior is subtracted. Reprinted in adapted form from B. D. White, J. A. Souza, C. Chiorescu, J. J. Neumeier, and J. L. Cohn, Phys. Rev. B 79, 104427 (2009). Copyright 2009 by the American Physical Society.

Proper analysis of the Curie-Weiss behavior of CaMn$_2$O$_4$ requires subtraction of temperature-independent diamagnetism $\chi_D$. The diamagnetic contribution is $\chi_D = -7.610 \times 10^{-5}$ emu mol$^{-1}$ Oe$^{-1}$ as calculated from tabulated[177] ionic values. Conduction electron contributions leading to Pauli paramagnetism $\chi_P$ can be completely
neglected because CaMn$_2$O$_4$ is electrically insulating. After subtracting non-Curie-Weiss contributions from $\chi$, we fit the data to the Curie-Weiss law

$$\chi_{\text{CW}} = \frac{C}{T - \Theta_{\text{CW}}},$$

(8.1)

where $C$ is the Curie constant $C = (Np^2\mu_B^2)/3k_B$, $p^2 = g^2J(J+1)$, and $\Theta_{\text{CW}}$ is the Curie-Weiss temperature. We assumed the Landé $g$-factor is 2.0 and that the orbital angular momentum is quenched by the oxygen crystal field[161, 162] so that $J = S$. Curie-Weiss fits below 400 K result in unreasonable values for $S$ (expected to be 2.0 given the Mn$^{3+}$ high-spin electronic state), which are inconsistent with the chemical characterization of our samples.[91] Magnetic susceptibility (not shown) was subsequently measured for a randomly-oriented sample between 300 and 500 K to fit at higher temperature. It is evident that above 420 K, deviations from Curie-Weiss behavior, likely due to short-range magnetic order, become insignificant. Between 420 and 500 K, the fit is optimized by $C = 6.896(5)$ emu K mol$^{-1}$ Oe$^{-1}$ and $\Theta_{\text{CW}} = -376.8(6)$ K. If we assume there are exactly two Mn ions per CaMn$_2$O$_4$ unit (good to within about 1%)[91] then each contributes an average spin $S = 2.174$ which is about 9% higher than expected. The most plausible explanation for this is that there is an additional contribution to $\chi$ which must be subtracted to isolate Curie-Weiss behavior. For example, we had no way to account for Van Vleck paramagnetic contributions in our analysis. The negative value of $\Theta_{\text{CW}}$ is consistent with long-range antiferromagnetic order.
The upturn in $\chi$ below 75 K in Figure 36(a) is reminiscent of paramagnetism. It appears to be isotropic which removes spin canting as a possible explanation. If we assume the upturn is paramagnetic in origin and properly account for $\chi_D$, $\chi$ is composed of contributions associated with antiferromagnetic ordering $\chi_{AFM}$ and a simple paramagnetic background $\chi_{CW}$ below $T_N$. CaMn$_2$O$_4$ displays typical $\chi_{AFM}$ behavior wherein $\chi$ approaches zero along $a$ (easy axis) and is weakly temperature-dependent (almost constant) along $b$ and $c$. We cannot reliably subtract $\chi_{AFM}$ from $\chi$, but are able to fit the upturn with the Curie-Weiss law between 10 and 17 K where $\chi_{AFM}$ is roughly zero along $a$ and approximately constant along $b$ and $c$. The fit along the $a$-axis upturn can be seen in Figure 36(b). Curie-Weiss fits to the upturns provide values for $\Theta_{CW}$: 8.17 K, 12.10 K, and 13.56 K along $a$, $b$, and $c$, respectively. We consider only $\Theta_{CW}$ here because we have derived a relationship between $\Theta_{CW}$ values, optimized along different directions $i$ and $j$, by assuming $\chi = \chi_{CW} + \chi_{AFM}$

$$\Theta_{CW,i} = \frac{C'_i - C'_j}{\chi_{AFM}^i} + T \left(1 - \frac{\chi_{AFM}^i}{\chi_{AFM}^j}\right) + \Theta_{CW,j} \frac{\chi_{AFM}^j}{\chi_{AFM}^i}.$$

(8.2)

$C'_i$ is the Curie constant extracted from data which includes the contribution from $\chi_{AFM}^i$. If the underlying nature of the upturn in CaMn$_2$O$_4$ is truly paramagnetic, the Curie-Weiss fits to them should provide $\Theta_{CW}$ values related by Equation (8.2). In the special case where $\chi_{AFM}^i \approx \chi_{AFM}^j$, as is true along $b$ and $c$ (see Figure 36(a)), Equation (8.2) simplifies to

$$\Theta_{CW,i} = \frac{C'_i - C'_j}{\chi_{AFM}^i} + \Theta_{CW,j}.$$

(8.3)
Using this simplified form, we estimate that the difference between $\Theta_{CW,b}$ and $\Theta_{CW,c}$ should be approximately 2.95 K; the actual difference is found to be 1.5 K. The discrepancy is surely related to our assumption that the antiferromagnetic susceptibility contributions along $b$ and $c$ are identical.

After establishing the nature of the upturn as paramagnetic, we next identify which ions are responsible. We expect a negligibly low level of impurities to exist in the samples themselves as was demonstrated by several chemical characterization methods.[91] Therefore, the paramagnetic ions are necessarily identified as manganese ions. Oxygen non-stoichiometry in the samples leads directly to the formation of small amounts of Mn$^{4+}$ or Mn$^{2+}$ depending on whether excess oxygen has been absorbed or the samples are oxygen deficient, respectively. Measurements of the average manganese valence in crystals using iodometric titration have shown an average of $\sim 1\%$ of all manganese ions were in the Mn$^{4+}$ oxidation state.[91] The most accurate estimate of the true Curie constant associated with the paramagnetic upturn (without the influence of $\chi_{AFM}$) comes from the $a$-axis data where $\chi_{AFM}$ is the smallest. Yet, $C'_a = 0.27122 \text{ emu K mol}^{-1} \text{ Oe}^{-1}$ implies that 7% of manganese ions would have to be Mn$^{4+}$, which is inconsistent with our titration results. Of course, iodometric titration is not sensitive to the difference between a Mn$^{3+}$-Mn$^{3+}$ pair and a Mn$^{4+}$-Mn$^{2+}$ pair. Hundley and Neumeier have previously suggested that accounting for charge disproportionation in La$_{1-x}$Ca$_x$MnO$_3$ (2Mn$^{3+}$ $\rightarrow$ Mn$^{2+}$ + Mn$^{4+}$) is necessary to explain its temperature-dependent thermoelectric power.[178] They claimed that in the $x =$
0 case (all Mn$^{3+}$), 70-80% of all Mn$^{3+}$ disproportionates by the time the sample is heated to 1000 - 1300 K. Only 4% of Mn$^{3+}$ ions would need to disproportionate (and be quenched in that state at low temperature) to result in the paramagnetic upturn we observe in CaMn$_2$O$_4$. More likely, however, is that samples become oxygen deficient over time as a function of annealing or conducting measurements at temperatures exceeding 300 K, and eventually Mn$^{2+}$ sites evolve. 3% of manganese ions being in the Mn$^{2+}$ state would account for the paramagnetic upturn at low temperature.

**Transport Properties**

The room-temperature electrical resistivity of CaMn$_2$O$_4$, as measured by an electrometer along two axes, reveals insulating behavior: $\rho_a = 2.70 \times 10^8$ Ω cm and $\rho_c = 2.14 \times 10^8$ Ω cm. Repeated measurements along the $b$ axis were unsuccessful, with resistivity values in excess of $10^{12}$ Ω; though it is believed this is related to contact resistance problems rather than anisotropy. In order to better understand these results without the aid of band-structure calculations or spectroscopy measurements, we compare them with resistivity values for related materials. We are able to immediately contrast CaMn$_2$O$_4$ with CaMnO$_3$, Ca$_2$MnO$_4$, Ca$_3$Mn$_2$O$_7$, Ca$_4$Mn$_3$O$_{10}$, which belong to a Ruddlesden-Popper series of structurally-related phases. Their resistivity values at room temperature are 12.3, $1.1 \times 10^4$, $1.3 \times 10^3$, and $8.32 \times 10^2$ Ω cm, respectively as determined with polycrystalline samples.[179] Though measurements of single-crystalline CaMnO$_3$ yield slightly lower resistivity on the order of 1 Ω cm.[180] Insulating layers of CaO planes isolate the connectivity of MnO$_6$ octahedra along $c$ in
Ca$_2$MnO$_4$, Ca$_3$Mn$_2$O$_7$, and Ca$_4$Mn$_3$O$_{10}$, accounting for their relatively large resistivity. However, high resistivity values in CaMn$_2$O$_4$ cannot be ascribed to insulating CaO planes and no MnO$_6$ octahedra are isolated in its crystal structure (see Figure 30). The crystal structure of CaMnO$_3$ also contains no insulating CaO planes, enjoying instead an unbroken octahedral network along all three crystallographic axes. This explains its predictably lower resistivity when compared with Ca$_2$MnO$_4$, Ca$_3$Mn$_2$O$_7$, and Ca$_4$Mn$_3$O$_{10}$.

The definitive distinction between CaMn$_2$O$_4$ and the other calcium-manganese-oxide phases is that it is composed entirely of Mn$^{3+}$ ions rather than Mn$^{4+}$, which results in highly Jahn-Teller distorted MnO$_6$ octahedra. It is therefore more instructional to consider the behaviors of other compounds containing Jahn-Teller distorted octahedra. The most well-studied material fitting this description is LaMnO$_3$, generally considered to be a Mott insulator with room-temperature electrical resistivity between $10^3$ and $10^5$ $\Omega$ cm depending on the reference[181, 182] (it is highly sensitive to oxygen non-stoichiometry). Studies of LaMnO$_3$ in the vicinity of the Jahn-Teller transition at $T_{JT}$ have demonstrated a significant resistivity decrease above $T_{JT}$ when the distortion of the MnO$_6$ octahedra is relieved.[181, 182, 183] In fact, optical conductivity measurements[184] reveal the opening of a gap below $T_{JT}$ in the electronic structure of LaMnO$_3$ - a gap whose existence is predicted by band-structure calculations.[185] The onset of Jahn-Teller distortion lifts the degeneracy of the $e_g$ levels opening a gap between the half-filled $d_{3z^2-r^2}$ and empty $d_{x^2-y^2}$ orbitals. It is
reasonable that an energy gap originating from the Jahn-Teller distortion could also
be responsible for insulating behavior in CaMn$_2$O$_4$. The magnitude of distortion in
CaMn$_2$O$_4$ is much larger than in LaMnO$_3$ according to neutron refinements[161, 186]
at 300 K (26% versus 10% increase of elongated bond lengths versus equatorial bonds).
Insulating behavior is also observed in MgMn$_2$O$_4$ with resistivity $4 \times 10^5$ Ω cm.[187]
MgMn$_2$O$_4$ is quite similar to CaMn$_2$O$_4$ in that Jahn-Teller distortion forces its crystal
structure to deviate from the ideal cubic spinel structure to lower symmetry (in this
case a tetragonal structure). Though there are more, these two examples indicate
a probable correlation between Jahn-Teller distortion and an electrically insulating
ground state. If the size of the band gap scales at all with the magnitude of distortion,
the high resistivity values of CaMn$_2$O$_4$ are completely consistent with that picture.

The thermal conductivity $\kappa$ along each principle crystallographic axis is shown in
Figure 37. The sharp maxima near 20 K are typical signatures of lattice conduction
in crystalline insulators having modest imperfections. Any spin-wave contribution is
likely negligible in comparison to that of the lattice except at the very lowest tempera-
tures ($T < 1$ K). The Debye-Calloway model[188] was found to provide an excellent
description of the data for $T \leq 125$ K (see the lower inset of Figure 37). A sum of re-
laxation rates representing phonon scattering by other phonons (Umklapp processes),
sheet-like faults, and point-like defects, was employed with forms, $A_1\omega^2T e^{(-\Theta_D/4T)},$
$A_2\omega^2$, and $A_3\omega^4$, respectively ($\omega = vq$ is the phonon frequency). A sound velocity $v = 2800$ m/s ($\Theta_D = 384$ K) provided the best fit to $\kappa$ for all orientations, indicating
relatively isotropic elastic properties. Parameter values in the ranges $A_1 = (1.8-2.1) \times 10^{-17}$ s/K, $A_2 = (1.6-2.1) \times 10^{-17}$ s, and $A_3 = (3-8) \times 10^{-44}$ s$^3$, were employed for the $b$- and $c$-axis data; defect terms ($A_2$ and $A_3$) 2-4 times larger were required to model the $a$-axis data. Whether this difference can be attributed to magnetism or is simply a consequence of a higher defect concentration in the $a$-axis specimen will require further measurements to determine. Antiferromagnetic domain boundaries are a likely source of strain that can scatter heat-carrying acoustic phonons, and it is possible that such scattering is enhanced for heat flow along the magnetic easy axis. The phonon mean-free paths at 10 K, inferred from values of $\kappa$ and the specific heat $\ell = 3\kappa/C_P \approx 10-20 \mu$m, are for all specimens substantially smaller than the minimum crystal dimension (0.5-0.7 mm). This indicates, consistent with the model fitting, that boundary scattering was negligible.

At higher temperatures, the slope-change anomalies in $\kappa$ at $T_N$ (see upper inset of Figure 37) are typical of magnetostrictive effects that modify the phonon dispersion and/or scattering. The slope change occurs at $T_N = 218.0(5)$ K, in rough agreement with the result from magnetization ($T_N = 217.3(3)$ K). The temperature dependence of $\kappa$ in the paramagnetic phase is considerably weaker than the $\kappa \sim 1/T^n$ ($n \sim 1-2$) behavior typical of anharmonic decay. Similarly-weak temperature dependencies of $\kappa$ are found in the paramagnetic phases of antiferromagnetic materials such as MnO,[61] CaMnO$_3$,[189, 190] and YMnO$_3$,[191] and have been attributed to phonon scattering by nanoscale strain generated by spin fluctuations.
Figure 37. Thermal conductivity $\kappa$ measured along each principal crystallographic axis. The upper inset shows an anomaly in $\kappa$ at $T_N$ resulting from magnetostrictive effects that modify the phonon dispersion (lines are a guide to the eye). The lower inset displays low-temperature fits (solid line through data) to $\kappa$ along $b$ using the Debye-Calloway model. Reprinted from B. D. White, J. A. Souza, C. Chiorescu, J. J. Neumeier, and J. L. Cohn, Phys. Rev. B 79, 104427 (2009). Copyright 2009 by the American Physical Society.

Heat Capacity

Heat capacity at constant pressure $C_P$ is displayed in Figure 38. An anomaly is clearly present at $T_N = 217.39(6)$ K. At low temperature, we fit the data with a function of the form $C_P = \gamma T + (\beta_{latt} + \beta_{AFM})T^3$. Terms of other orders including $T^{-2}$, $T^2$, and $T^5$ characterizing contributions from the nuclear moment of $^{55}$Mn, long-wavelength spin-wave excitations, and higher-order lattice terms, respectively,[192] were neglected because they did not improve the fit. The linear term accounts for the electronic contribution and is characterized by the Sommerfeld parameter $\gamma$ while the cubic term describes contributions from the lattice and antiferromagnetic spin
excitations,[192] and is characterized by \( \beta_{Tot} = \beta_{latt} + \beta_{AFM} \). Of course, if a spin gap is present in the magnon dispersion, \( \beta_{AFM} = 0 \) in the temperature range where \( \beta_{Tot} \) is extracted. The fit was carried out by plotting \( C_P/T \) against \( T^2 \) and fitting a linear region below 42 K. It was optimized with \( \gamma = 0 \) J mol\(^{-1}\) K\(^{-2}\) (a negligible value is not surprising in light of its electrically-insulating behavior) and \( \beta_{Tot} = 1.367 \times 10^{-4} \) J mol\(^{-1}\) K\(^{-4}\). The Debye temperature was estimated \( \Theta_D = 463(4) \) K. However, \( \Theta_D \) is proportional to \( \beta_{latt}^{-1/3} \), and because there is no method to decouple \( \beta_{latt} \) from \( \beta_{Tot} \) if \( \beta_{AFM} \neq 0 \), our estimate might be slightly lower than the true value depending on whether the magnon dispersion in CaMn\(_2\)O\(_4\) is gapless or not.

![Figure 38. Heat capacity at constant pressure (left abscissa with filled circles) and entropy (right abscissa with open circles). Reprinted from B. D. White, J. A. Souza, C. Chiorescu, J. J. Neumeier, and J. L. Cohn, Phys. Rev. B 79, 104427 (2009). Copyright 2009 by the American Physical Society.](image-url)
$C_P$ is about 145 J mol$^{-1}$ K$^{-1}$ at the highest measured temperature (305 K) and continues to trend upward as shown in Figure 38. At high temperature ($T \gg \Theta_D$), $C_P$ should asymptotically approach $21R \approx 174.6$ J mol$^{-1}$ K$^{-1}$ as predicted by the classical law of Dulong-Petit for a crystal with seven atoms per formula unit, though the asymptotic value may be smaller due to the contribution of lighter oxygen atoms.

The molar entropy $S$ was calculated with

$$S = \int \frac{C_P}{T}dT,$$

while constraining the integration constant so that $S \to 0$ as $T \to 0$. It is displayed in Figure 38 with $C_P$. The total molar entropy change from 2 to 305 K was 151.5(5) J mol$^{-1}$ K$^{-1}$. The magnetic entropy contribution $S_{Mag}$ associated with the transition can be extracted from the calculated entropy by subtracting from $S$ an entropy background (representing all non-magnetic contributions), calculated with a polynomial fit of $S$ between 80-305 K excluding the region immediately around the anomaly at $T_N$.\[70\] The change in entropy due to antiferromagnetic order was found to be $\Delta S_{Mag} = 1.19(3)$ J mol$^{-1}$ K$^{-1}$. We can compare this with the somewhat naïve calculation of $N$ spins/mol, randomly oriented with $S_{Mag} = 2R\ln 2$, which transition to a perfectly ordered state with $S_{Mag} = 0$ ($\Delta S_{Mag} = 11.53$ J mol$^{-1}$ K$^{-1}$). The large disparity between experiment and model is attributed to the unintentional inclusion of magnetic entropy contributions to the subtracted entropy background. The observation of magnetic fluctuations leading to departure from Curie-Weiss behavior up to 200 K above $T_N$ suggests short-range order exists well above the temperature range we considered.
when extracting $S_{Mag}$. These observations indicate the necessity of expanding the temperature range far beyond the vicinity of the singularity to properly extract $S_{Mag}$ (we constrained $S_{Mag}$ to the boundaries of the anomaly). This task is inhibited by the non-trivial difficulty of reliably subtracting other entropy contributions in those regions where the magnetic contribution is by no means obvious.

Thermal Expansion

Figure 39. (a) Linear thermal expansion ($\Delta L/L$) along all three principle crystallo-
graphic axes. The inset displays $\Delta L/L$ along the $c$ axis in better detail to reveal the striking nature of the anomaly at $T_N$. (b) The coefficients of linear thermal expansion ($\mu = d(\Delta L/L)/dT$) are displayed to highlight the anomaly in each direction at $T_N$. The inset displays the coefficient along the $c$ axis with the dashed line running along zero to highlight the two temperature ranges where thermal expansion is negative. Reprinted in adapted form from B. D. White, J. A. Souza, C. Chiorescu, J. J. Neumeier, and J. L. Cohn, Phys. Rev. B 79, 104427 (2009). Copyright 2009 by the American Physical Society.

Linear thermal expansion $\Delta L/L$, normalized to room-temperature length, is plotted in Figure 39(a) revealing anisotropic behavior comparable to compounds with layered crystal structures like Na$_2$CoO$_2$ and YBa$_2$Cu$_3$O$_{7-\delta}$ wherein a strong anisotropy
exists between inter- and intra-layer $\Delta L/L$. The transition at $T_N$ is clearly visible as kinks in $\Delta L/L$, most pronounced along $b$ and $c$. All three principle axes contract with decreasing temperature throughout the measured temperature range except along $c$, where an expansion takes place just below $T_N$ and again below 25 K before contracting at 8 K. The inset of Figure 39(a) highlights the complex detail of $\Delta L/L$ along the $c$ axis. Negative thermal expansion at low temperature may be associated with thermal population of anomalous phonon modes and is common in layered systems. Comparison reveals the behavior along $a$ and $b$ (interlayer) is qualitatively similar with a few subtle differences. Above 200 K, the $a$ axis experiences the largest relative contraction of the three principle crystallographic axes, but the onset of magnetic order at $T_N$ results in a higher rate of contraction with decreasing temperature along $b$, while modifying the contraction rate along $a$ comparatively little. This contraction-rate disparity below $T_N$ results in more relative contraction along $b$ than $a$ below 200 K. The $c$-axis contraction is much smaller than the other two axes. A similar anisotropy is often observed in layered materials, suggesting the “layers” in the $a$-$b$ plane might share similar phonon dispersion characteristics. However, the quasi-two-dimensional nature of the crystal structure does not result in two-dimensional magnetic behavior because superexchange calculations suggest the inter-layer coupling between MnO$_6$ zig-zag chains is as strong as the intra-layer coupling. Refinements of lattice parameters from powder neutron diffraction report relative reductions of 0.38%, 0.43%, and 0.060% between 300 K and 20 K along
Our direct measurements of $\Delta L/L$ provide consistent results in the same temperature range: 0.358%, 0.379%, and 0.059% along $a$, $b$, and $c$, respectively. The slight difference is attributed to a combination of uncertainty in the neutron-diffraction refinements and a minor admixture of contributions from the $c$ axis in our measurements along $a$ and $b$, the result of which reduces the total relative contraction along those axes.

Results for $\mu$ (point by point derivatives of our $\Delta L/L$ data with no fitting or smoothing) are displayed in Figure 39(b). There are a few general features about this data that merit some attention. Antiferromagnetic ordering at $T_N$ results in strains along $a$ and $b$, which are opposite in direction to the strain along $c$. Similar opposing strains[71, 193] are observed at $T_N$ in $\text{Na}_x\text{CoO}_2$ and $T_c$ in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Second, each $\mu_i \to 0$ as temperature approaches zero. This is required by the third law of thermodynamics given the definition: $\mu L \equiv -(\partial S/\partial P)_T$. Finally, each $\mu_i$ increases rapidly with increasing temperature around 25 K. This is especially apparent along $a$ and $b$. $C_P$ increases at the same temperature (see Figure 38), suggesting this behavior designates the onset of strong phonon activity. Consequently, we observe the anharmonic peak in $\kappa$ (displayed in Figure 37) at about the same temperature.

**Analysis of Critical Behavior**

The critical behavior of CaMn$_2$O$_4$, like most properties, was not studied prior to the work of White *et al.* in Reference [141]. The analysis therein utilized the graphical
method to study critical behavior exhibited by $\lambda\Omega T$, resulting in critical-exponent $\alpha = 0.082(7)$. A summary of that study is presented, however, we revisit the issue of critical behavior in CaMn$_2$O$_4$ by fitting $\lambda_i\mu_i T$ and $\lambda_i(\Delta L/L)_i$ along all three principal crystallographic axes with the least-squares method. We then compare the results of each analysis. This is an excellent opportunity to test whether the critical behavior is the same along each principal crystallographic axis as has been observed in other antiferromagnetic systems.[67]

To study the critical behavior of CaMn$_2$O$_4$ with the graphical method, we first invoke the Pippard relation (Equation (6.6)) to scale $C_P^*$ and $\lambda\Omega T$. $\Delta V/V$ was obtained by fitting $\Delta L/L$ along each principle crystallographic direction with Chebyshev polynomials and then generating data sets with common temperatures and summing them. The overlap between $C_P^*$ and $\lambda\Omega T$ for CaMn$_2$O$_4$ is optimized by $\lambda = 8.9(3) \times 10^3$ J mol$^{-1}$ K$^{-1}$. As can be seen in Figure 40(a), the quality of the overlap is excellent over a wide temperature range, which is a requirement for continuous phase transitions.[70] As was discussed in Chapter 6, the pressure derivative of $T_N$ may be expressed $dT_N/dP = v/\lambda$. The molar volume of CaMn$_2$O$_4$ at 218 K was calculated $v = 4.587(7) \times 10^{-5}$ m$^3$ mol$^{-1}$ using our results for $\Delta V/V = \Delta a/a + \Delta b/b + \Delta c/c$ and lattice parameters measured[161] at 300 K. The pressure derivative is calculated $dT_N/dP = 5.2(2)$ K/GPa. Unfortunately, we are unable to compare this result with
any direct measurement. The only published study of CaMn$_2$O$_4$ under pressure investigated a pressure-induced structural phase transition at 35 GPa, but did not consider the antiferromagnetic transition.[165]

![Figure 40. (a) Overlap between $C_P^*$ (red triangles) and $\lambda T\Omega$ (closed circles) in the critical temperature region around $T_N$. (b) Critical behavior above and below $T_N$ as characterized by linear fits of thermal expansion data on a log-log plot. Reprinted in adapted form from B. D. White, J. A. Souza, C. Chiorescu, J. J. Neumeier, and J. L. Cohn, Phys. Rev. B 79, 104427 (2009). Copyright 2009 by the American Physical Society.]

Once $C_P^*$ and $\lambda T\Omega$ are scaled, we are able to employ the graphical method (as described in Chapter 7) to study the critical behavior of $\lambda T\Omega$. We plotted $\log(\lambda T\Omega - B_\pm - Dt)$ and $\log(-\lambda T\Omega + B + Dt)$, suitable for $\alpha > 0$ and $\alpha < 0$, respectively, against $\log|t|$. The constraint $B_- = B_+$ was relaxed for $\alpha > 0$, but applied for $\alpha < 0$. Values for $B_\pm$, $D$, and $T_N$ were systematically refined in each case until the linear fittable range was optimized above and below $T_N$ with the additional constraint that $\alpha_+ = \alpha_-$ within experimental uncertainty. We were unable to obtain a suitable result for
\( \alpha < 0 \) (finite singularity). However, assumption of a divergent transition with \( \alpha > 0 \) yielded significantly better results. The data and fit are displayed in Figure 40(b) for

\( D = 140(5) \text{ J mol}^{-1} \text{ K}^{-1}, B_+ = 2.0(5) \text{ J mol}^{-1} \text{ K}^{-1}, B_- = 6.0(5) \text{ J mol}^{-1} \text{ K}^{-1}, \) and

\( T_N = 217.5(1) \text{ K}. \) These parameters result in critical exponents \( \alpha_+ = 0.085(7) \) and \( \alpha_- = 0.078(3). \) The critical exponent associated with the antiferromagnetic transition in CaMn\(_2\)O\(_4\) is obtained by averaging \( \alpha_+ \) and \( \alpha_- \). The result is \( \alpha = 0.082(7). \) This value of \( \alpha \) is close to the prediction for the three-dimensional Ising model (see Figure 6). Critical behavior, as evidenced by the linear regions in Figure 40(b), covers two decades of the reduced temperature. This is good, but it is troubling that the best fit required \( B_- \neq B_+ \). If corrections to scaling are included, a suitable fit should be possible which constrains \( B_- = B_+ \). We next study the critical behavior of \( \lambda_i \mu_i T \) with least-squares fitting, which allows us to easily include the confluent singularity terms.

The critical behavior of CaMn\(_2\)O\(_4\) was also studied with the Levenberg-Marquardt least-squares algorithm. We fit \( \lambda_i \mu_i T \) along \( a, b, \) and \( c \) with the critical expression in Equation (7.4). The salient critical parameters in the fit are completely independent of the value of \( \lambda_i, \) therefore, we selected simple values \( \lambda_a = \lambda_b = -\lambda_c = 1 \times 10^4 \text{ J mol}^{-1} \text{ K}^{-1} \) (rounded up from \( \lambda = 8.9(3) \times 10^3 \text{ J mol}^{-1} \text{ K}^{-1} \)). \( \lambda_c \) is negative so that the anomaly in \( \mu_c T \) has the same sign as the other two anomalies. We obtained excellent fits which are displayed in Figure 41(a)-(c) by fitting between 200 and 240 K. The
Figure 41. (a) $\lambda_a \mu_a T$ data with $\lambda_a = 1 \times 10^4$ and least-squares fit (red line). (b) $\lambda_b \mu_b T$ data with $\lambda_b = 1 \times 10^4$ and least-squares fit (red line). (c) $\lambda_c \mu_c T$ data with $\lambda_c = -1 \times 10^4$ and least-squares fit (red line). (d) Normalized $\chi^2$ values ($(\chi^2 - \chi^2_{\alpha=0.1})/\chi^2_{\alpha=0.1}$) displayed as a function of $\alpha$ for all three principle axes. The minima indicate best-fit values for $\alpha$ along each axis.
values for the best-fit parameters are tabulated in Table 8. To obtain the uncertainties of best-fit parameters, we incorporated the uncertainties of each data set into the fitting algorithm. The uncertainties of $\lambda_i \mu_i T$ were obtained by calculating the standard deviation of the residuals when we subtracted our optimized least-squares fit from the data. This procedure yielded $\sigma_a = 0.05535 \text{ J mol}^{-1} \text{ K}^{-1}$, $\sigma_b = 0.34459 \text{ J mol}^{-1} \text{ K}^{-1}$, and $\sigma_c = 0.06749 \text{ J mol}^{-1} \text{ K}^{-1}$. The diagonal entries of the formal covariance matrix, which supply the uncertainties for all best-fit parameters, incorporate these $\sigma_i$ values. Inspection of the entries in Table 8 reveals several important results. Most importantly, the values of $\alpha$ and $A_+/-A_-$ are roughly identical for all three principle crystallographic axes. These two quantities are characteristic of the universality class to which the transition belongs, so we are able to conclude that the analysis along all three directions is self-consistent. To emphasize just how similar $\alpha$ is along each axis, we performed several least-squares fits wherein $\alpha$ was fixed at a constant value near 0.1 ($\alpha$ was not a fitted parameter) and observed the effect on the $\chi^2$ merit function. A normalized $(\chi^2 - \chi^2_{\alpha=0.1})/\chi^2_{\alpha=0.1}$ is plotted in Figure 41(d) as a function of $\alpha$. The minima of the parabolas occur at about the same value of $\alpha$.

Table 8. Best-fit values for parameters in Equation (7.4) along $a$, $b$, and $c$.

<table>
<thead>
<tr>
<th>axis</th>
<th>$A_-$</th>
<th>$A_+/A_-$</th>
<th>$\alpha$</th>
<th>$E_-$</th>
<th>$E_+$</th>
<th>$B$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>1.03(5)</td>
<td>0.50(2)</td>
<td>0.098(2)</td>
<td>-0.93(4)</td>
<td>-1.25(8)</td>
<td>31.3(3)</td>
<td>52.5(7)</td>
</tr>
<tr>
<td>$b$</td>
<td>3.7(2)</td>
<td>0.52(4)</td>
<td>0.095(4)</td>
<td>-0.93(8)</td>
<td>-1.5(1)</td>
<td>19(2)</td>
<td>54(5)</td>
</tr>
<tr>
<td>$c$</td>
<td>0.76(5)</td>
<td>0.46(4)</td>
<td>0.095(6)</td>
<td>-1.08(7)</td>
<td>-1.5(2)</td>
<td>-11.6(5)</td>
<td>-20(1)</td>
</tr>
</tbody>
</table>
for each principle crystallographic direction. Furthermore, the values $\alpha \simeq 0.0958(7)$ and $A_+/A_- \simeq 0.50(3)$, obtained by averaging the three results, are consistent with predictions for the three-dimensional Ising universality class ($0.106 \leq \alpha \leq 0.125$ and $A_+/A_- = 0.52(1)$).[66, 194]

It is clear from Figures 40 and 41 that our fit in the critical region terminates by $|t|_{\text{min}} \sim 10^{-3}$. To penetrate the critical region to the $|t| = 10^{-4}$ boundary, the quality of the sample must be high and data must be measured with sufficient density. Therefore, either our sample is of insufficient quality or detrimental effects from numerical differentiation have obscured the last decade in $|t|$ from us due to measuring with insufficient data density. The placement of CaMn$_2$O$_4$ in Figure 29(c) is compelling evidence that truncation error is limiting the size of the critical region. To potentially increase the critical temperature region, we fit $\lambda_i(\Delta L/L)_i$ along each principle crystallographic axis with Equations (7.15) and (7.16) using six terms ($k = 6$) in the series expansion. We used the same values for $\lambda_i$ that were used in the critical-behavior analysis of $\lambda_i \mu_i T$ to allow comparison between best-fit values. It is far more challenging to fit $\lambda_i(\Delta L/L)_i$ than it is to fit $\lambda_i \mu_i T$. Strong correlations between fitting parameters, especially $G$ and $\alpha$, often lead to unphysical solutions or the inability for the algorithm to converge to any solution at all. For this reason, we chose to fix $\alpha$ near values obtained in the fitting of $\lambda_i \mu_i T$. This is fine because we are not searching for independent solutions, but rather hoping to extend the critical temperature range. The data and best fits are displayed in Figure 42 and appear
Figure 42. (a) $\lambda_a \Delta a/a$ data with $\lambda_a = 1 \times 10^4$ and least-squares fit (red line). (b) $\lambda_b \Delta b/b$ data with $\lambda_b = 1 \times 10^4$ and least-squares fit (red line). (c) $\lambda_c \Delta c/c$ with $\lambda_c = -1 \times 10^4$ and least-squares fit (red line). (d) $\lambda_b \Delta b/b$ data and fit displayed closer to $T_N$.

to be fairly good. The best-fit parameters are summarized in Table 9. Comparison of best-fit parameters which exist in both Table 8 and Table 9 ($A_-,$ $A_+/A_-, E_-$, and $E_+$) demonstrate that the optimized fits for $\lambda_i \mu_i T$ and $\lambda_i (\Delta L/L)_i$ are quite similar. This was our expectation. We are also able to compare $I$ with $B - D$ and $H$ with $D/T_N$ and find these are also quite similar. However, the point of fitting $\lambda_i (\Delta L/L)_i$ was to determine whether we could increase the critical region closer to $T_N$. The region around $T_N$ in $\lambda_b \Delta b/b$ is displayed in Figure 42(d). It appears that the fit
remains good at data points measured closest to \( T_N \) (\(|t| = 1.66 \times 10^{-4}\)). Therefore, it appears as though the critical region does extend to \(|t| \sim 10^{-4}\).

Table 9. Best-fit values for parameters in Equations (7.15) and (7.16) along \( a, b, \) and \( c \). Parameters followed by * were fixed at these values in the fits.

<table>
<thead>
<tr>
<th>axis</th>
<th>( A_- )</th>
<th>( A_+/A_- )</th>
<th>( \alpha )</th>
<th>( E_- )</th>
<th>( E_+ )</th>
<th>( I )</th>
<th>( H )</th>
<th>( G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>0.99(5)</td>
<td>0.470(9)</td>
<td>0.100*</td>
<td>-1.06(3)</td>
<td>-1.52(8)</td>
<td>-20.0(8)</td>
<td>0.239(4)</td>
<td>41(3)</td>
</tr>
<tr>
<td>( b )</td>
<td>3.8(2)</td>
<td>0.507(6)</td>
<td>0.095*</td>
<td>-0.97(2)</td>
<td>-1.29(5)</td>
<td>-27(2)</td>
<td>0.21(1)</td>
<td>89(8)</td>
</tr>
<tr>
<td>( c )</td>
<td>0.82(4)</td>
<td>0.50(1)</td>
<td>0.095*</td>
<td>-0.93(4)</td>
<td>-1.1(1)</td>
<td>7.7(9)</td>
<td>-0.093(4)</td>
<td>-17(4)</td>
</tr>
</tbody>
</table>

By applying the least-squares method to \( \lambda_i \mu_i T \) and \( \lambda_i (\Delta L/L)_i \), we were able to demonstrate the equivalence of the critical behavior fitted for data along each principle crystallographic axis. This gives us more confidence in our results, which are consistent for three independent data sets. Classification of CaMn\(_2\)O\(_4\) as a three-dimensional Ising antiferromagnet is unsurprising given what is known about the nature of its magnetic order. The study on its superexchange pathways\(^{163}\) demonstrated that magnetic interactions were definitely three-dimensional. Furthermore, its magnetic moments anti-align along [1 0 0] with almost no canting.\(^{161, 162}\) This is consistent with the typical Ising-model picture of spins modeled as one-dimensional sticks, which are constrained to be collinear with a non-degenerate crystallographic easy axis. Furthermore, by conducting our analysis based on strategies described in Chapter 7 and arriving at reasonable conclusions, we have convincingly demonstrated the validity of applying thermal-expansion data to the study of critical behavior.
Bi$_2$CuO$_4$: EASY-AXIS OR EASY-PLANE ANTIFERROMAGNET?

**Introduction**

Despite a total absence of superconductivity, Bi$_2$CuO$_4$ received considerable attention during the cuprate physics boom following the discovery of high-temperature superconductivity. Interest was driven by its unique crystal structure and the consequences thereof. One might expect Bi$_2$CuO$_4$ to be isostructural with La$_2$CuO$_4$, especially given nearly identical ionic radii for Bi$^{3+}$ and La$^{3+}$ with eightfold coordination.[195, 196] However, strongly covalent Bi-O bonds reduce the coordination of Bi to six while the strongly ionic nature of La-O bonds allow for ninefold coordination.[196] Definitive early x-ray diffraction work[197] revealed a tetragonal unit cell with space group $P4/nnc$. This result has been unambiguously confirmed by neutron-diffraction[196, 198, 199, 200, 201] and Raman infrared-reflectivity[202] experiments. The crystal structure, which is displayed in Figure 43(a) and (b) (as generated by JAVA STRUCTURE VIEWER[167]), is unique among the generally two-dimensional, layered cuprates. It is constructed from isolated CuO$_4$ plaquettes which form staggered, collinear “chains” along $c$, connected by BiO$_4$ units,[203, 204] with a twist angle[201] of $33.3^\circ$ between adjacent plaquettes. The isolated nature of CuO$_4$ plaquettes has led some to refer to Bi$_2$CuO$_4$ as a “zero-dimensional” compound. For example, a study of the intensity of Cu 2$p_{5/2}$ core level x-ray photoemission spectra demonstrated
that CuO$_4$ plaquettes result in a low-dimensional behavior that is fundamentally different from those arising from CuO$_3$ chains (one-dimensional) and CuO$_2$ planes (two-dimensional).[205]

Figure 43. (a) Isolated CuO$_4$ plaquettes form collinear chains along c, which are connected by BiO$_4$ units, and (b) Looking down along the chains. Reprinted in adapted form from B. D. White, W. M. Pätzold, and J. J. Neumeier, Phys. Rev. B 82, 094439 (2010). Copyright 2010 by the American Physical Society.

Like other cuprates, the $S = \frac{1}{2}$, Cu$^{2+}$ moments of Bi$_2$CuO$_4$ undergo antiferromagnetic order as observed around 43 K in neutron-diffraction,[196, 199, 200, 201] antiferromagnetic-resonance,[196] and magnetic-susceptibility experiments.[196, 200, 206] Four distinct Cu-O-Bi-O-Cu superexchange paths have been identified, which are responsible for magnetic order,[196, 201, 204, 207, 208] however, there remain disagreements about the orientation of the ordered moments.[203] Tetragonal antiferromagnets with anisotropic exchange are said to exhibit easy-axis anisotropy
when their sublattices are polarized parallel to $c$ and easy-plane anisotropy when they are polarized perpendicular to $c$. The reason for this distinction is simple. In a tetragonal crystal structure, the $c$ direction is a unique crystallographic direction (no other directions are related to it by symmetry operations), while on the other hand, there are two equivalent crystallographic $a$ directions. If the moments prefer to anti-align along $c$, this direction is energetically favorable and is called the easy axis. However, if the magnetic moments prefer to polarize perpendicular to $c$, there are at least two distinct crystallographic directions, related by symmetry operations, along which anti-alignment is energetically-favorable. These energetically-degenerate crystallographic directions lie in the plane perpendicular to [0 0 1]; referred to as the easy plane. In the case of Bi$_2$CuO$_4$, it is known that magnetic moments order ferromagnetically within the chains running along $c$, and that neighboring chains are coupled antiferromagnetically. However, despite numerous attempts to settle the matter, there is still disagreement about whether the magnetic moments order parallel (easy-axis anisotropy)[201, 203, 207, 209] or perpendicular (easy-plane anisotropy)[198, 204, 210, 211] to the chains. One way to resolve this issue is to identify the universality class to which the antiferromagnetic phase transition in Bi$_2$CuO$_4$ belongs. Easy-axis anisotropy is associated with the Ising model and easy-plane anisotropy is associated with the XY model. In this chapter, we discuss the growth and characterization of Bi$_2$CuO$_4$ crystals first before addressing its heat capacity and
thermal expansion. Then, the critical behavior of Bi$_2$CuO$_4$ is studied with the least-squares method (both $\lambda_i \mu_i T$ and $\lambda_i (\Delta L/L)_i$ along each principle crystallographic axis). Best-fit values for $\alpha$ and $A_+/A_-$ correlate well with predictions for the three-dimensional Ising model, indicating Bi$_2$CuO$_4$ is an easy-axis antiferromagnet. The majority of this chapter is adapted from B. D. White, W. M. Pätzold, and J. J. Neumeier, Phys. Rev. B 82, 094439 (2010) (Copyright 2010 by the American Physical Society).

Crystal Growth and Characterization

Single-crystalline Bi$_2$CuO$_4$ was grown by the floating-zone method. Polycrystalline rods containing 1% CuO excess were synthesized from oxide powders Bi$_2$O$_3$ (99.99%) and CuO (99.995%). The powder was reacted in air at 600°, 650°, 700°, and 725° C for 24 hours each, between which it was subjected to grinding by mortar and pestle and planetary ball milling for two hours at 200 rpm. Polycrystalline rods were pressed by hand in quartz tubes by a procedure described in Chapter 2. Quartz was used instead of alumina tubes due to their less reactive interface with the rods. The pressed rods were reacted a final time at 750° C for 24 hours.

Growth parameters were selected to replicate conditions for the floating-zone growth of Bi$_2$CuO$_4$ as published in Reference [212]. Crystal growth was conducted in air (1 atm) with a 10 mm/hr growth rate and 30 rpm counter-rotation. The surface tension of molten Bi$_2$CuO$_4$ is too low to maintain a stable molten zone throughout the
course of a long, slow growth, which explains previous use[212] of a rather fast growth rate. We found that a 5 mm/hr growth speed yielded higher quality crystalline boules than those grown at 10 mm/hr, though growing at lower speeds required constant adjustments to the molten zone. All grown boules had an affinity for cleaving to reveal the (0 0 l) plane and seemed to grow approximately along [1 0 2].

Figure 44. Powder x-ray diffraction pattern for Bi$_2$CuO$_4$ single crystals (black line) compared with calculated pattern generated from PowderCell (red line).

Phase purity of single crystals was confirmed with powder x-ray diffraction as displayed in Figure 44. No superfluous Bragg reflections due to an impurity phase were observed when we compared our diffraction pattern with a calculated pattern, generated with PowderCell.[106] Laue-diffraction patterns revealed some evidence of low-angle grain boundaries, however, these defects appeared to be relatively modest. No evidence of intrinsic strain was observed in the shape and quality of Laue spots.
We were unable to determine $\delta$ in the chemical formula $\text{Bi}_2\text{CuO}_{4+\delta}$. Iodometric titration, described in Chapter 3, fails when a material is composed of more than one constituent element which may assume multiple oxidation states. $\text{Bi}_2\text{CuO}_4$ should nominally contain only $\text{Bi}^{+3}$ and $\text{Cu}^{+2}$, but small amounts of both $\text{Bi}^{+5}$ and $\text{Cu}^{+1}$ may also exist within the crystal.

**Thermodynamic Properties**

Figure 45. (a) Linear thermal expansion $\Delta L/L$ along $a$ and $c$. The insets display the behavior along both axes in the vicinity of the antiferromagnetic phase transition ($T_N$ denoted by arrow). (b) Linear coefficient of thermal expansion along $a$ and $c$. Reprinted in adapted form from B. D. White, W. M. Pätzold, and J. J. Neumeier, Phys. Rev. B 82, 094439 (2010). Copyright 2010 by the American Physical Society.

Linear thermal expansion $\Delta L/L$ along $a$ and $c$ is displayed in Figure 45(a). The coefficient of thermal expansion $\mu$, obtained from point-by-point differentiation of $\Delta L/L$ without prior processing or smoothing, is displayed in Figure 45(b). Ignoring the effect of antiferromagnetic order on $\Delta L/L$ and $\mu$ around 43 K, anisotropy is the
most obvious characteristic of the data. Tetragonal Bi$_2$CuO$_4$ belongs to the class of axial crystal structures which always exhibit two unique thermal expansion coefficients $\mu_\parallel$ and $\mu_\perp$ taken to be along $c$ and $a$, respectively. Theoretical calculations of each are discussed in Chapter 5 (see Equation (5.11)). The ratio of $\mu_\parallel$ and $\mu_\perp$,[139, 140]

$$\frac{\mu_\parallel}{\mu_\perp} = \frac{(C_{11} + C_{12}) \gamma_\parallel - 2C_{13}\gamma_\perp}{C_{33}\gamma_\perp - C_{13}\gamma_\parallel}, \quad (9.1)$$

is an excellent measure of anisotropy. $\mu_\parallel/\mu_\perp$ is a function of elastic constants $C_{ij}$ and the weighted mean Grüneisen parameters $\gamma_\parallel$ and $\gamma_\perp$, which are averaged over individual Grüneisen parameters $\gamma_{\parallel,k}$ and $\gamma_{\perp,k}$ (for the $k^{\text{th}}$ phonon mode) and weighted by the heat-capacity contribution $C_k$ of that mode. A crystal described by space group $P4/ncc$ ($D_{4h}^8$) has six independent elastic constants.[213] Equation (9.1) contains four of them omitting only $C_{44}$ and $C_{66}$ because they result in rotation of the crystal. Examination of Equation (9.1) suggests that the observed anisotropic thermal expansion arises from the interplay of thermal stress coefficients (proportional to $\gamma$) and elastic constants.[140] Unfortunately, we cannot compare the results of Equation (9.1) with our data because the elastic constants of Bi$_2$CuO$_4$ have not been measured. Instead, we compare the observed anisotropy to other sources. For example, neutron-diffraction experiments show a reduction of the lattice parameters between 290 and 1.5 K of 0.0588(2)% and 0.393(2)% along $a$ and $c$, respectively.[201] These are consistent with our measurements of $\Delta L/L$ which show reductions of 0.07(2)% and 0.371(1)% between 300 and 5 K along those same directions. These values were calculated from averaging three measurements of $\Delta a/a$ and two measurements of
$\Delta c/c$. We are also able to consider that refinements of thermal parameters from neutron diffraction exhibit an anisotropy wherein the amplitude of thermal motion of Bi, Cu, and O ions is $\sim$3-4 times larger along $c$ than along $a$.\[199, 201] This implies that the lattice is stiffer along $a$ than along $c$, which is also in agreement with our measurements.

The heat capacity of Bi$_2$CuO$_4$ is displayed in Figure 46. Our results are consistent with previous publication of $C_P$ data for this system.\[214, 215] At low temperature, the data was successfully described by $C_P = \beta T^3$ (see upper inset of Figure 46), where $\beta = \beta_{\text{Ph}} + \beta_{\text{AFM}}$ represents, in general, a combination of phonon and antiferromagnetic spin-wave contributions to $C_P$.\[192] Attempts to extract a linear temperature term representing electronic degrees of freedom were predictably unsuccessful given the compound’s insulating ground state (2 eV band gap).\[216] Neutron-diffraction studies of spin-wave dispersion in Bi$_2$CuO$_4$ demonstrate the existence of a 2.1 meV $\simeq$ 24.4 K energy gap of the lowest energy spin-wave branch at the zone center.\[198] Therefore, our low-temperature fit of $C_P$ (2 - 13.5 K) is expected to be free of any spin-wave contribution and is dominated by phonons ($\beta = \beta_{\text{Ph}}$). The Debye temperature of Bi$_2$CuO$_4$ is a function of $\beta_{\text{Ph}}$ and is calculated $\Theta_D \simeq 108$ K from our optimized $\beta = 1.56 \times 10^{-3}$ J mol$^{-1}$ K$^{-4}$. At high temperature ($T \gg \Theta_D$), $C_P$ asymptotically approaches $21R \simeq 174.6$ J mol$^{-1}$ K$^{-1}$, which is denoted by a dashed line in Figure 46. This asymptotic value is predicted by the classic law of Dulong-Petit for a compound with seven ions per formula unit.
Figure 46. Heat capacity of Bi$_2$CuO$_4$. Note that the line in the main figure is not a fit but is rather a guide to the eye. The upper inset highlights the $T^3$ dependence of $C_P$ at low temperature by fitting a line through a plot of $C_P/T$ against $T^2$. The lower inset highlights the anomaly around $T_N$. Reprinted from B. D. White, W. M. Pätzold, and J. J. Neumeier, Phys. Rev. B 82, 094439 (2010). Copyright 2010 by the American Physical Society.

In the vicinity of $T_N$, anomalies corresponding to antiferromagnetic ordering of Cu$^{2+}$ spins are observed in $\Delta L/L$ and $\mu$ along each principal crystallographic axis (Figures 45(a) and (b)) and in $C_P$ (Figure 46). In the case of $\Delta L/L$, the anomalies are characterized by an abrupt change in slope and are highlighted in the upper and lower insets of Figure 45(a). The minimum along $a$ indicates the onset of negative thermal expansion and should not be confused with $T_N$. Lambda-like anomalies are observed in $\mu$ and $C_P$ in Figures 45(b) and 46, respectively. The anomalies in $\mu$ exhibit a commonly-observed anisotropy wherein the peaks have opposite sign.[71, 141] We study the critical behavior exhibited in these anomalies next.
The critical behavior of Bi$_2$CuO$_4$ was first addressed by White et al. in Reference [93] as a way to settle the question of whether easy-axis or easy-plane anisotropy was exhibited. In that study, $\lambda_i \mu_i T$ data were studied along the $a$ and $c$ axes using a least-squares method. We review that work first before building upon it by fitting $\lambda_i \langle \Delta L/L \rangle_i$ with Equations (7.15) and (7.16) to maximize the size of the critical temperature range.

The first step in our study is to invoke the Pippard relation (Equation (6.6)) to scale $C_P^*$ and $\lambda \Omega T$. For Bi$_2$CuO$_4$, satisfactory scaling (not shown) is achieved with $\lambda = -3.96(4) \times 10^4 \text{ J mol}^{-1} \text{ K}^{-1}$. Satisfaction of Pippard scaling allows us to conclude that the transition is continuous, and provides justification to study critical behavior with thermal expansion. From our optimized value of $\lambda$, we calculate $dT_N/dP = -1.59(2) \text{ K/GPa}$ where we have used molar volume $v= 6.30 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$. Unfortunately, there are no direct measurements of $dT_N/dP$ for Bi$_2$CuO$_4$ with which we can compare this calculation, but our value is on the same order of magnitude as other antiferromagnets.[71, 141] Recall that 5.2(2) K/GPa was the pressure derivative of CaMn$_2$O$_4$ in the previous chapter. The next logical step after scaling $C_P^*$ with $\lambda \Omega T$ would be to study the critical behavior exhibited by $\lambda \Omega T$. However, instead of studying the volume critical behavior, we study critical behavior along the two principle crystallographic axes ($\lambda_a \mu_a T$ and $\lambda_c \mu_c T$). Since we established
that the salient critical parameters are identical for $\lambda_i\mu_i T$ along each lattice-parameter direction and in $\lambda \Omega T$ in the last chapter, it is advantageous to study two independent data sets from which we can extract information about critical behavior.

We employed our Levenberg-Marquardt algorithm to fit each $\lambda_i\mu_i T$ data set around $T_N$ with the critical expression in Equation (7.4). Values of $\lambda_a = -1.0 \times 10^5$ and $\lambda_c = 1.0 \times 10^4$ were chosen purely for convenience and have no physical significance. We see from Equation (7.4) that we can multiply through by a constant without influencing fit parameters except for $A_\pm, B,$ and $D$ (no influence on $\alpha$ and $A_+/A_-$ for example). When we wish to compare best-fit parameters from the fits along each axis which are sensitive to the scaling constant, we could simply multiply each by an appropriate constant so that $\lambda_a = \lambda_c$. The experimental uncertainty of our $\lambda_i\mu_i T$ data was estimated from the standard deviation of the residuals (which exhibit reasonably Gaussian characteristics) of a sixth-order Chebyshev polynomial fit to the data in the critical temperature region. This uncertainty was inserted into the $\chi^2$ minimization function, from whence it propagates into the best-fit parameter uncertainties.

We performed an identical procedure for fitting the critical expression (Equation (7.4)) to our $\lambda_i\mu_i T$ data along each axis. This procedure began by ignoring corrections to scaling and considering instead a simple case where we constrain $E_- = E_+ = 0$. This constraint limits the temperature range over which the data may be fit well, but allows us to get an initial estimate of the critical temperature region. We obtained
this estimate by adjusting the fitted temperature range until it was maximized while simultaneously producing an acceptable fit to the data. We then allowed $E_-$ and $E_+$ to be different from zero, which increases the fittable temperature range. In order to account for all possibilities, we considered two cases: application of the constraint $E_- = E_+$ and relaxing that constraint so that $E_- \neq E_+$.

The resulting fits for the three cases along both axes are displayed in Table 10. The first thing we observe is that $\alpha$ and $A_+/A_-$ are similar in all six fits, which implies that the critical behavior along the two principal crystallographic directions is the same (in agreement with our observations from CaMn$_2$O$_4$ in the previous chapter). Some of the parameters in Table 10 have no uncertainty listed. We observed strong correlations between $A_\pm$ and $B$, which resulted in large covariances between them and absurdly large calculated uncertainties. In those cases, we chose to fix $B$ at its best-fit value and refit the data over the remaining parameters. This procedure results in much lower uncertainties which certainly underestimate the true uncertainty, but nonetheless are more reasonable. Negative values for the analytic background terms ($B$ and $D$) in many of the fits may appear unphysical. Certainly, when fitting the critical behavior of $C_P$, the analytic background parameters must be positive. However, if we examine the scaling relation $C_P = \lambda \Omega T + a + bT$ (see the definition of $C_P^*$ leading to Equation (6.6)), we see that we should consider the analytic background of $\lambda \Omega T = 2 (\lambda/\lambda_a) \lambda_a \mu_a T + (\lambda/\lambda_c) \lambda_c \mu_c T$ and then add $a + bT$ to it to yield the effective background associated with $C_P$. When we perform this calculation with our best-fit
values, the resulting linear background is perfectly consistent with expectations that
its slope and intercept be positive. There is no analogous expectation, however, for
the individual backgrounds of each $\lambda_i \mu_i T$ data set.

Table 10. Best-fit values for critical parameters in Equation (7.4) along $a$ and $c$
for various constraints on $E_+$ and $E_-$.  

<table>
<thead>
<tr>
<th>axis</th>
<th>constraint</th>
<th>$A_-$</th>
<th>$A_+/A_-$</th>
<th>$\alpha$</th>
<th>$E_-$</th>
<th>$E_+$</th>
<th>$B$</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>$E_- = E_+ = 0$</td>
<td>4.31(5)</td>
<td>0.737(6)</td>
<td>0.130(1)</td>
<td>0.0</td>
<td>0.0</td>
<td>-30.003</td>
<td>1.4(8)</td>
</tr>
<tr>
<td>$a$</td>
<td>$E_- = E_+ \neq 0$</td>
<td>3.8(2)</td>
<td>0.73(4)</td>
<td>0.096(3)</td>
<td>-0.34(2)</td>
<td>-0.34(2)</td>
<td>-29(1)</td>
<td>-0.5(5)</td>
</tr>
<tr>
<td>$a$</td>
<td>$E_- \neq E_+ \neq 0$</td>
<td>2.69(3)</td>
<td>0.693(4)</td>
<td>0.111(1)</td>
<td>-0.53(1)</td>
<td>-1.69(2)</td>
<td>-9.5168</td>
<td>24.3(5)</td>
</tr>
<tr>
<td>$c$</td>
<td>$E_- = E_+ = 0$</td>
<td>0.65(2)</td>
<td>0.77(1)</td>
<td>0.109(2)</td>
<td>0.0</td>
<td>0.0</td>
<td>-3.6610</td>
<td>8.6(2)</td>
</tr>
<tr>
<td>$c$</td>
<td>$E_- = E_+ \neq 0$</td>
<td>0.39(6)</td>
<td>0.6(1)</td>
<td>0.11(1)</td>
<td>-1.2(1)</td>
<td>-1.2(1)</td>
<td>0.7(4)</td>
<td>5.9(3)</td>
</tr>
<tr>
<td>$c$</td>
<td>$E_- \neq E_+ \neq 0$</td>
<td>0.556(6)</td>
<td>0.64(1)</td>
<td>0.111(5)</td>
<td>-0.75(1)</td>
<td>0.13(2)</td>
<td>-1.53(9)</td>
<td>2.7(1)</td>
</tr>
</tbody>
</table>

Noticeably absent from Table 10 are values for $T_N$. We found that allowing $T_N$
to vary as a fittable parameter led to our algorithm’s failure to converge to a least-
squares solution. So instead, we fixed $T_N$ at reasonable values and obtained a best-fit
solution for $T_N$ manually. We repeated this procedure for each fit in Table 10 finding
that the optimized $T_N$ values were 43.381(1) K. Therefore, we chose to simply fix $T_N$
= 43.381 K for each fit.

We display the critical-behavior fits (case where $E_- \neq E_+ \neq 0$) and our $\lambda_a \mu_a T$
and $\lambda_c \mu_c T$ data in Figure 47(a) and (b). Small oscillations in the measured data
around 45-50 K are a consequence of the dilatometer cell’s remarkable sensitivity to
modest 10 mK/min oscillations about our 0.2 K/min warming rate in that temper-
ature region. The fits in each case are good over a reduced temperature range of
Figure 47. (a) $\lambda_a \mu_a T$ data with $\lambda_a = -1 \times 10^5$ J mol$^{-1}$ K$^{-1}$ and critical-behavior fit (red line). (b) $\lambda_c \mu_c T$ data with $\lambda_c = 1 \times 10^4$ J mol$^{-1}$ K$^{-1}$ and fit (red line). The inset displays $\alpha$ from fits over maximized temperature ranges (results in Table 10) as well as some smaller temperature ranges, assuming a variety of constraints on $E_\pm$ for both $a$- and $c$-axis data. Reprinted in adapted form from B. D. White, W. M. Pätzold, and J. J. Neumeier, Phys. Rev. B 82, 094439 (2010). Copyright 2010 by the American Physical Society.

$\sim \log |t| = -0.75$ to $\sim \log |t| = -2.0$. A high-quality single crystal with a magnetic transition should exhibit a critical temperature range that begins by $\sim \log |t| = -1.0$ and ends close to $\log |t| = -4.0$, where even modest crystalline defects begin to influence critical behavior.[72] Our limited critical region is largely a consequence of numerically differentiating each $(\Delta L/L)_i$ to yield $\mu_i$,[217] as discussed in Chapter 7.

The best-fit values of $\alpha$ and $A_+/A_-$, as summarized in Table 10, are not only self-consistent with one another, they correlate fairly well with expected behavior for the three-dimensional Ising universality class. Unfortunately, there is not an exact solution for the Ising model in three spatial dimensions, however, a variety of techniques have been employed to yield approximate values for $\alpha$ and $A_+/A_-$. Pelissetto and
Vicari[194] summarize the results of numerous three-dimensional Ising-model studies including 21 which employ the high-temperature series-expansion technique, 24 using Monte-Carlo simulations, and 11 using low-temperature series expansions. If we average the results for each technique, we find $\alpha = 0.108(2), \alpha = 0.112(4)$, and $\alpha = 0.121(4)$, respectively, which provides a range of $0.106 \leq \alpha \leq 0.125$. The inset of Figure 47 displays the results for $\alpha$ from Table 10 (fit over maximized temperature ranges) along with other values obtained from fits over smaller temperature ranges and with various constraints on $E_\pm$. These values mostly fall within the range between 0.106 and 0.125. Furthermore, our values for $A_+/A_-$ from Table 10 are also most consistent with the three-dimensional Ising universality class. Expansions to second order in $\epsilon$ where $\epsilon = 4 - d$ and $d$ is the lattice dimensionality, lead to $A_+/A_-$ values[66] of $0.52(1), 1.03(1)$, and $1.52(2)$ for an order parameter with one, two, and three dimensions, respectively. These values assume a three-dimensional lattice ($\epsilon = 1$). Our least-squares fits give $A_+/A_- \sim 0.7$ which is closest to a one-dimensional order parameter (Ising model). Therefore, we can say that both $\alpha$ and $A_+/A_-$ correlate most closely with the three-dimensional Ising model.

We studied the critical behavior exhibited in $\lambda_i(\Delta L/L)_i$ data in an attempt to increase the size of the critical temperature region. We kept the same $\lambda_a$ and $\lambda_c$ values used in the fitting of $\lambda_i\mu_iT$ and, as in those fits, $T_N$ was fixed at 43.381 K. Difficulties were encountered when attempting to fit $\lambda_a\Delta a/a$ that were systematic of the strong correlations between $\alpha$ and $G$. To study the effect in detail, we fixed $G$
at various values and studied how the optimized $\chi^2$ behaved as a function of fixed $\alpha$ when fitting the temperature ranges 37-43.2 and 43.4-45 K. The results are displayed in Figure 48(a). As $G$ is incrementally increased 54% from 162.0 J mol$^{-1}$ K$^{-1}$ to 250.0 J mol$^{-1}$ K$^{-1}$ there is a mere change of 1.25% in minimum $\chi^2$. At the same time, optimized $\alpha$ values changes by 44% as a result of adjusting $G$. Therefore, a wide range of $G$ values result in a large range of $\alpha$ values with little difference in the $\chi^2$ merit function. This makes it difficult to obtain confidence in a best-fit value for $\alpha$. Minimized $\chi^2$ values for various fixed values of $\alpha$ ($G$ is a fittable parameter now), fit in the temperature ranges 37-42.5 and 43.7-49 K, are illustrated in Figure 48(b). $\chi^2$ has been plotted as a function of $\alpha$ in terms of percent change from the minimum $\chi^2$ calculated when $\alpha = 0.16$. Only a fraction of a percent separates a wide range of $\alpha$ values, but the minimum is close to $\alpha = 0.16$. The fit from the global minimum $\chi^2$ (where $\alpha$ and $G$ were free parameters) is plotted in Figure 48(c) along with $\lambda_a \Delta a/a$ data. The best-fit parameters are summarized in Table 11. The fit appears to be fairly good, especially over the expected maximum critical temperature range denoted by the black bar. Most importantly, the data nearest to $T_N$ are included in the region where the fit is good, which means we were successful in our attempt to increase the critical temperature region. We attribute the difference in fitting parameters from those obtained by fitting $\lambda_a \mu_a T$ to the very shallow character of optimized $\chi^2$ parabolas, which allows a wide range of values to provide an acceptable fit (minor differences in $\chi^2$ values). $\lambda_c \Delta c/c$ is plotted in Figure 48(d) along with its optimized fit
with fixed $\alpha = 0.10$. The best-fit parameters are also listed in Table 11. The critical region in this case was increased so that deviation from the critical expressions was not detected above the 0.1% level in the data points closest to $T_N$. Thus, the critical temperature region was extended to at least $\log |t|_{\text{min}} = -2.7(1)$, which is a significant improvement over the previous result of -2.0 from fitting $\lambda_c \mu_c T$.

Figure 48. (a) Optimized $\chi^2$ as a function of $\alpha$ when fitting $\lambda_a \Delta a/a$ for a variety of fixed $G$ values. (b) $\chi^2$ normalized to its minimum value at $\alpha = 0.16$ (expressed in percent change from $\chi^2_{\alpha=0.16}$) when fitting $\lambda_a \Delta a/a$ as a function of $\alpha$. (c) $\lambda_a \Delta a/a$ with $\lambda_a = -1 \times 10^5$ and best fit (red line). The critical region ($0.0 \leq |t| \leq 10^{-1}$) is explicitly indicated by the black bar. (d) $\lambda_c \Delta c/c$ with $\lambda_c = 1 \times 10^4$ and best fit (red line). The extent of the critical region is indicated by the black bar.
Table 11. Best-fit values for parameters in Equations (7.15) and (7.16) along \( a \) and \( c \). Values with * were held fixed as the other parameters were optimized.

<table>
<thead>
<tr>
<th>axis</th>
<th>( A_\perp )</th>
<th>( A_\perp/A_\parallel )</th>
<th>( \alpha )</th>
<th>( E_- )</th>
<th>( E_+ )</th>
<th>( I )</th>
<th>( H )</th>
<th>( G )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a )</td>
<td>1.7(2)</td>
<td>0.74(2)</td>
<td>0.1626*</td>
<td>-0.55(1)</td>
<td>-5.2(1)</td>
<td>-35(2)</td>
<td>0.95(3)</td>
<td>162(5)</td>
</tr>
<tr>
<td>( c )</td>
<td>0.24(5)</td>
<td>0.4(1)</td>
<td>0.10*</td>
<td>-1.7(3)</td>
<td>-4(1)</td>
<td>-3(1)</td>
<td>0.15(3)</td>
<td>-38(4)</td>
</tr>
</tbody>
</table>

Identification of Bi\(_2\)CuO\(_4\) as a three-dimensional Ising antiferromagnet distinguishes it from other 214-cuprates, which are generally classified among two-dimensional Heisenberg systems.\([35]\) More importantly, it suggests that Bi\(_2\)CuO\(_4\) is an easy-axis antiferromagnet with its magnetic moments polarized parallel to \( c \). This conclusion is consistent with theory\([203, 209]\) and two-magnon Raman\([207]\) studies. Torque-magnetometry\([210]\) and antiferromagnetic-resonance\([206, 211]\) experiments offer the strongest and most compelling support for the opposite conclusion (easy-plane anisotropy). Compared with these latter experiments, we feel our study of critical behavior is, perhaps, a more straightforward method to address the easy-axis versus easy-plane anisotropy question in Bi\(_2\)CuO\(_4\), because we arrived at our conclusion without invoking any prior assumptions about the details of its magnetic order. In any case, our result should help to settle the issue of magnetic anisotropy in Bi\(_2\)CuO\(_4\) as future studies investigate this question further. On a separate note, our analysis also provides a second successful example of studying critical behavior with thermal expansion.
Elemental manganese can assume one of four allotropic crystal structures including α-, β-, γ-, and δ-Mn, though only α-Mn and β-Mn are thermodynamically stable at room temperature and ambient pressure. Due to geometric frustration,[218] β-Mn is non-magnetic down to liquid-helium temperatures,[219] while α-Mn is known to undergo long-range antiferromagnetic order, as shown in early neutron-scattering experiments.[219, 220] The room-temperature crystal structure of α-Mn (cubic space group $I\bar{4}3m$) is surprisingly complicated, with 58 atoms per unit cell occupying four crystallographically-unique sites.[219, 221] It is depicted in Figure 49 as generated with JAVA STRUCTURE VIEWER.[167] The complexity of the crystal structure has been described as originating from an instability of the 3d electronic shell, which allows for the formation of self-intermetallic compounds between atoms with different electronic configurations.[222, 223] Given so complicated a crystal structure, it is not surprising that its non-collinear magnetic structure is similarly complex.[223, 224] (See the outstanding depiction of the magnetic structure in Reference [223]). Antiferromagnetism in α-Mn can be described with localized moments[224] (as opposed to antiferromagnetic chromium which has a spin-density wave and is an itinerant system) and its symmetry is well described by Shubnikov group[124] $P\bar{4}2c$ and principal
magnetic symmetry axis ⟨100⟩.[225] Guided by its observed tetragonal magnetic symmetry, it was found from careful refinement of neutron-diffraction data, that magnetic order in α-Mn induces[226] a lowering of the crystal structure’s symmetry to tetragonal $I42m$ (of which $P_{1}42c$ is a subgroup).[124] The tetragonal unit cell contains 58 Mn-atoms as well, but they now occupy six crystallographically-unique positions.[124] Tetragonal splitting of the lattice parameters was difficult to resolve because its magnitude, as embodied by the ratio $c/a$, is small. The ratio between refined[124] lattice parameters is estimated to be only $c/a \sim 0.9996$. We contrast this with a larger[227] but similar tetragonal distortion in antiferromagnetic CoO below $T_N$ where $c/a \sim 0.988$.

Figure 49. Complicated crystal structure of α-Mn at 300 K with 58 atoms occupying four distinct crystallographic sites in its cubic unit cell. MnI sites are red, MnII sites are blue, MnIII sites are yellow, and MnIV sites are green.
The observed symmetry lowering of the crystal structure of $\alpha$-Mn at $T_N$ is suggestive of a magnetostrictive-induced structural distortion, which accompanies magnetic order. Magnetoelastic coupling in cubic materials often leads to similar structural distortions.[227] Some transitions, such as those in MnO and FeO, are classified as first order as a consequence of their distortions, while others, such as CoO and NiO, remain second order despite them.[59] Claims of observed critical behavior[224, 228] and even attempts to extract critical exponents[229, 230] in the past have tacitly disclosed an assumption that the transition in $\alpha$-Mn is second order. While this was not a particularly poor assumption, being made before evidence of the structural distortion was published, the order of the phase transition must be clarified. Thermal-expansion and heat-capacity data offer evidence that the transition in $\alpha$-Mn should properly be classified as second order. The critical behavior exhibited by $\lambda\Omega T$ data is then studied. Assignment of a particular universality class to such a complex element with non-collinear antiferromagnetic structure holds intrinsic interest and motivates our critical-behavior study of $\alpha$-Mn. Our analysis demonstrates the limitations of using a polycrystalline sample to study critical behavior. Rounding of the data closest to $T_N$ impedes our ability to make any definite conclusions, but our results suggest that the transition may be classified as belonging to either the three-dimensional Heisenberg or three-dimensional $n = 4$ universality class.
All experiments were performed on commercially-available, polycrystalline α-Mn (99.95%). Chemical analysis of the samples provided by the manufacturer suggested parts per million impurity levels of 260, 45, 20, 10, 3, and 2 for S, C, Si, Fe, P, and Se, respectively. Powder x-ray diffraction patterns (not shown) exhibited Bragg reflections attributable only to the crystal structure of α-Mn. Measurements of single crystals would have been preferable, however, it is extremely difficult to grow sizeable, high-quality crystals of α-Mn. Single crystals of α-Mn have been grown by vapor deposition[221, 231] and cut from an arc-melted ingot.[124] However, the resolution of thermal-expansion measurements improves as sample length increases and the crystals yielded from the aforementioned techniques had maximum dimensions at least an order of magnitude smaller than the polycrystalline sample we measured (9397(2) µm at room temperature). The most comprehensive study of the growth of α-Mn crystals was reported by Yamada[232] who claimed to grow crystals 300-400 mg in weight with a vapor-transport technique. However, the crystals are of poor quality with many small-angle sub-grain structures. Despite this problem, it appears that growing from the vapor is the most appropriate method. Yamada explicitly articulated the unsuitability of growing α-Mn by conventional methods used to grow metallic elements such as the Bridgman or stress-anneal methods.[232] Our attempts to grow α-Mn crystals by the chemical vapor-transport method using TeCl$_4$ as a
transport agent failed because hydrated MnCl$_2$ crystals grew instead. Furthermore, attempts to exploit the high vapor pressure of manganese by growing crystals from the vapor in an evacuated, sealed quartz tube failed to yield crystals larger than a few $\mu$m. Therefore, we were forced to measure polycrystalline samples. In Chapter 1, we cautioned against studying critical behavior with samples of low quality because ideal critical behavior is obscured as the diverging correlation length approaches the length scale of magnetic domains. However, in the case of $\alpha$-Mn, it appears a polycrystalline sample is the only reasonable choice, and we proceed being mindful of the limitations it places on our experimental analysis.

**Thermodynamic Properties**

The thermal expansion of $\alpha$-Mn was previously reported using refined lattice parameters from x-ray[233] and neutron-diffraction[124] studies. However, the resolution provided by these diffraction techniques is at least four orders of magnitude less sensitive than our dilatometry measurements,[127] and the time-consuming process required to yield each datum tends to inhibit data sets with many points. These disadvantages necessarily preclude diffraction results from extensive physical analysis. For example, no study of the thermal-expansion coefficient could be initiated with such sparse data sets without resorting to interpolation. Nevertheless, our measurement of the thermal expansion of $\alpha$-Mn, as displayed in Figure 50(a), is entirely consistent with these earlier results.
The linear thermal expansion of $\alpha$-Mn was measured on a polycrystalline sample, and because we are unable to consider our thermal-expansion data as along a particular crystallographic direction, the physically relevant quantity is the volumetric thermal expansion. In the limit of a statistically-random distribution of grain orientations (zero preferential orientation), the volumetric thermal expansion is calculated by the Reuss method (see Chapter 5) $\Delta V/V = 3\Delta L/L$. This is displayed in Figure 50(a). The data has not been fit or smoothed and was corrected only for the thermal expansion of quartz and the empty-cell effect.\[127\] Clearly, there are three distinct temperature regions, marked by dissimilar behavior. The most prominent of these is a phase transition region at $T_N \pm 25$ K, with a typical lattice response at temperatures
above it, and a stiffening of the lattice with negative thermal expansion below it. We estimate \( T_N = 101.4(3) \) K from thermal expansion.

These regions are better visualized in the volumetric coefficient of thermal expansion \( \Omega \) as displayed in Figure 50(b). \( \Omega \) appears to asymptotically approach a constant value, as expected for \( T \gg \Theta_D \) where \( \Theta_D = 479(6) \) K for \( \alpha\text{-Mn} \).[228] At low temperature, starting inside the critical region about \( T_N \), \( \alpha\text{-Mn} \) exhibits negative thermal expansion as clearly displayed in the inset of Figure 50(b). The onset of negative thermal expansion occurs in the critical region slightly above \( T_N \) and is likely associated with magnetoelastic coupling. At the lowest temperatures, \( \Omega \) trends towards zero as required by the third law of thermodynamics. We note as an interesting aside that the behavior of the data below 70 K is reminiscent, both in character and magnitude, of the low temperature behavior of Invar (\( \text{Fe}_{65}\text{Ni}_{35} \)), which is a well-known low thermal-expansion material.[234]

Careful analysis of a phase transition of unknown order conventionally begins with the search for latent heat, phase coexistence, or thermal hysteresis which are all systematic of a first-order transition. We are able to look for hysteresis in thermal expansion, though our experimental setup is optimized to measure on warming. When measuring on cooling, we have slightly less temperature control, generally resulting in a thermal-lag effect. This effect arises mainly because the sample is not in direct contact with the thermometer and the thermal conductivity of the quartz dilatometer cell is poor. Therefore, the observed temperature difference of about 0.5 K between
Figure 51. Volumetric coefficient of thermal expansion $\Omega$ on warming (black data) and cooling (red data) exhibits what could be identified as weak hysteresis, but $\Delta T \leq 0.5 \text{ K}$ is smaller than the expected difference in absolute temperature measured on warming and cooling. Lines are guides to the eye. The inset shows $\Delta V/V$ in the immediate vicinity of $T_N$ where no volume discontinuity is observed.

warming and cooling curves, shown in Figure 51, is not significant and probably originates with the reversed thermal gradients experienced by the sample between warming and cooling. With this caveat in mind, we conclude that if there were truly thermal hysteresis, it is $< 0.5 \text{ K}$.

Given less than conclusive thermal-hysteresis results, we turn to an infrequently-utilized distinction between first- and second-order transitions. A first-order transition exhibits discontinuous entropy and volume at $T_N$. Naturally, the latent heat originates from the discontinuous entropy, but we can use our $\Delta V/V$ data directly to look for a volume discontinuity which would also indicate a first-order character. As is apparent in the inset of Figure 51, the volume is continuous across $T_N$ which is
consistent with a second-order nature. We note that this is also apparent by the lack of a large (ideally infinite), sharp feature in $\Omega$, which would be an easily-observable consequence of a discontinuity in $\Delta V/V$.

Figure 52. Heat capacity of $\alpha$-Mn with anomaly at $T_N$. The inset displays the Pippard scaling between $C_p^*$ (red triangles) and $\lambda \Omega T$ (black circles) for $\lambda = -375$ J mol$^{-1}$ K$^{-1}$.

Another useful technique to test whether a transition is continuous is to attempt to scale $C_p^*$ and $\lambda \Omega T$ using the Pippard relation (see Equation (6.6)). Heat capacity is displayed in Figure 52 with its anomaly at $T_N$ and asymptotic value at high temperature just a bit higher than the predicted value of $3R \simeq 24.942$ J mol$^{-1}$ K$^{-1}$ from the law of Dulong-Petit. Thermodynamically, the relevance of Pippard scaling is embodied in the Ehrenfest-like expression $dT_N/dP = v/\lambda$ where $v$ is the molar volume.[70] For $\alpha$-Mn, we calculate $v = 7.5(1) \times 10^{-6}$ m$^3$ mol$^{-1}$. Experimental measurements report[231] $dT_N/dP \simeq -20$ K GPa$^{-1}$ for $\alpha$-Mn. Given an experimentally
measured $dT_N/dP$ and our calculated value of $v$, the scaling parameter must be $\lambda \simeq -375 \text{ J mol}^{-1} \text{ K}^{-1}$. The uniqueness of scaling parameters, proved in Chapter 6, guarantees that if $\lambda \simeq -375 \text{ J mol}^{-1} \text{ K}^{-1}$ results in satisfactory scaling, it is the correct result. The inset of Figure 52 displays the scaling between $C_P^*$ and $\lambda \Omega T$ for $\lambda = -375 \text{ J mol}^{-1} \text{ K}^{-1}$. Clearly, the overlap is excellent over a wide temperature range. This is a requirement of second-order phase transitions.[70] Had we not known $dT_N/dP$ a priori, we could have correctly hypothesized its sign would be negative because of the opposite signs of the corresponding anomalies in $C_P$ and $\Omega$ at $T_N$ (See Figures 50 and 52).

The second-order character of the transition in $\alpha$-Mn is confirmed by the absence of a discontinuity in our $\Delta V/V$ data and the Pippard scaling in Figure 52. While this result is not unexpected, neither is it necessarily trivial. Structural distortions resulting from magnetoelastic strain (like in $\alpha$-Mn below $T_N$) can alter what might otherwise be a second-order magnetic transition as is the case with MnO and FeO.[59, 235] In general, we do expect some magnetostrictive strain to arise in conjunction with antiferromagnetic order if there is finite magnetoelastic coupling. This can be demonstrated in a simple calculation using Landau’s phenomenological theory of phase transitions. If we define a single-component antiferromagnetic order parameter $\eta$, and write the thermodynamic free energy including elastic- and magnetoelastic-strain contributions, we can minimize it with respect to strain to obtain the following
induced magnetostrictive strain[235]

\[
\epsilon_m = -\frac{D_1(T)\eta^2 + \ldots}{C_1(T) + G_1(T)\eta^2 + \ldots}.
\] (10.1)

Obviously, \(\epsilon_m\) is zero above \(T_N\) where \(\eta = 0\), but is non-zero to lowest order for \(T \leq T_N\) as long as magnetoelastic terms such as \(D_1(T)\) are non-zero (\(G_1(T)\) is a higher-order magnetoelastic term and \(C_1(T)\) is an elastic strain term). It has been argued that such a strain need not alter the fundamental nature of the phase transition. Fisher demonstrated that in many cases the introduction of a hidden variable, such as stress, would merely adjust the critical temperature and result in a renormalization of the critical exponents.[235, 236]

Magnetostriction \(\lambda_m \equiv \Delta L(H)/L\) was measured with a quartz dilatometer cell, the designs and utilization of which will be the subject of a future publication.[237] Measurements of \(\lambda_m\) (not shown) in the antiferromagnetic state of \(\alpha\)-Mn (measured at 80 K) are two orders of magnitude smaller[238] than \(\lambda_m\) for cubic antiferromagnetic monoxides CoO, MnO, and NiO. Though measurements of the latter materials were made on single-crystal samples, their pseudo-cubic structures in the antiferromagnetic state imply there is minimal \(\lambda_m\) anisotropy, and therefore, little problem comparing \(\lambda_m\) along a specific crystallographic direction with a polycrystal’s average \(\lambda_m\). The physical relationship between magnetostriction and magnetoelastic coupling suggests that magnetoelastic coupling in \(\alpha\)-Mn should therefore be smaller than in the aforementioned monoxides, which is consistent with the relative disparity of the observed
magnitude of structural distortions in these materials. Since CoO and NiO both exhibit second-order transitions, we conclude that the coupling in $\alpha$-Mn is probably not strong enough to drive a first-order transition.

**Analysis of Critical Behavior**

Observations of critical behavior in $\alpha$-Mn were previously reported in experiments measuring nuclear magnetic relaxation,[229] adiabatic compressibility,[228], reduced hyperfine fields,[230] and the temperature-dependent intensities of magnetic Bragg reflections from neutron diffraction.[224] However, only two studies attempting to extract critical exponents exist (both involve the order parameter exponent $\beta$). Experiments measuring nuclear magnetic relaxation[229] report $\beta = 1/3$ and measurements of the hyperfine fields[230] report $\beta = 0.34$ to 0.371 depending on the sample. These reports were not used to identify the universality class to which the antiferromagnetic transition in $\alpha$-Mn belong. However, looking at Figure 6, it appears these values of $\beta$ suggest the universality class should be identified with one of the three-dimensional $n = 2$, 3, or 4 universality classes.

Because we are measuring a polycrystalline sample, we are only able to study the critical behavior of $\lambda \Omega T$ data (as opposed to along specific crystallographic axes). However, it is likely that the thermal-expansion anisotropy between $\Delta a/a$ and $\Delta c/c$ in the tetragonal phase is small anyway. If this is true, the difference between $\mu_a T$ and $\mu_c T$ would be insufficient to really call them independent data sets, and the main
advantage of fitting along distinct crystallographic axes is blunted. The $T > T_N$ data, at least, are constrained to be identical because the structure is cubic there. Additionally, the behavior of our data in the temperature region nearest $T_N$ is expected to differ from ideal critical behavior because of the limited size of antiferromagnetic domains in our polycrystalline sample. As mentioned in Chapter 1, pure critical behavior is expected so long as the size of magnetic domains is larger than the correlation length $\xi$ which diverges as $T \to T_N$. However, $\xi$ reaches the size of magnetic domains much more quickly if they are constrained to be small by the sample. The broadening effect that results overshadows any truncation-error effects influencing the behavior of $\lambda \Omega T$. Therefore, there is no advantage to fitting the $\lambda \Delta V/V$ data and we are only able to consider $\lambda \Omega T$.

We use $\lambda = -375$ J mol$^{-1}$ K$^{-1}$ from our Pippard scaling and fit $\lambda \Omega T$ with Equation (7.4) using our least-squares algorithm. Uncertainty in our $\lambda \Omega T$ data of $\sigma = 2 \times 10^{-3}$ J mol$^{-1}$ K$^{-1}$ was used to obtain best-fit parameter uncertainties. The least-squares solution was obtained by fitting in the temperature ranges 64.1-99 K and 105-138.7 K and is displayed along with $\lambda \Omega T$ in Figure 53(a). The best-fit solution is unable to fit data any closer to $T_N$ than this as a result of the polycrystalline nature of the sample. While the fit looks fairly good, the best-fit value of $T_N = 103.9$ K is inconsistent with $T_N$ determined from magnetic susceptibility (not shown) and heat capacity (see Figure 52). Based on the character of the anomaly in $\lambda \Omega T$ near its maximum (see inset of Figure 53(b)), $T_N$ should lie between $101.2 \leq T_N \leq 102.0$ K. It
is known that the best-fit value of $T_N$ is often a few mK higher than the temperature of the anomaly’s maximum,[65] however, $\sim 2$ K higher is unacceptable. We next constrained $T_N$ to fixed values in the range 101.2-102.0 K and studied the behavior of $\chi^2$ at various fixed values of $\alpha$. The results of this analysis are summarized in Figure 53(b). Clearly, the global minimum $\chi^2$ value is achieved as $T_N$ increases, which is consistent with the observation that the fully-optimized solution obtained $T_N = 103.9$ K. However, we cannot accept the global-minimum solution and are forced to consider local-minima solutions instead, obtained with acceptable constraints. The best-fit values of $\alpha$, which result from our constraint of $T_N$ in Figure 53(b), are between $-0.16 \leq \alpha \leq -0.08$. Recalling that previous critical-behavior studies of exponent $\beta$ suggested the phase transition in $\alpha$-Mn belongs to one of the three-dimensional $n = 2$, 3, or 4 universality classes, we consider these universality classes case by case.

Interestingly, the global best-fit solution is consistent with the three-dimensional XY model ($n = 2$). When we compare predictions for this universality class ($\alpha = -0.007(6)$ and $A_+/A_- = 1.03(1))$[66, 239] with the parameters in Table 12, we see they are quite close. Recent work on the magnetic structure of $\alpha$-Mn lends support to this universality class. Hobbs et al. demonstrated that MnI, MnII, and MnIII sites form simple collinear magnetic structures, while the topological arrangement of MnIV sites is almost identical to that of a frustrated triangular antiferromagnet. The ground state of an ideal antiferromagnetic triangular lattice has magnetic moments oriented with a 120° angle between nearest neighbors which are constrained to lie in
Figure 53. (a) $\lambda \Omega T$ data and global best-fit solution (red line). The value of $\alpha$ matches the three-dimensional XY universality class, but the value of $T_N$ is a few degrees too high. (b) $\chi^2$ studied for fixed values of $T_N$ between 101.2 and 102.0 K. The local minima in parabolas at fixed $T_N$ reveal local best-fit values for $\alpha$. A portion of the left side of the global $\chi^2$ minimum parabola is indicated by the red line. The inset highlights $\lambda \Omega T$ data near its maximum in order to better visualize the range of probable values for $T_N$. (c) $\lambda \Omega T$ data and best-fit solution (red line) for fixed $\alpha = -0.16$ and $T_N = 101.2$ K. (d) $\lambda \Omega T$ data and best-fit solution (red line) for fixed $\alpha = -0.10$ and $T_N = 101.8$ K.
the plane of the triangle \((n = 2\) order parameter). The MnIV magnetic moments deviate only slightly from this arrangement with minor out of plane components and small magnitude differences.[223] However, while one could accept that the MnIV sites alone might fall into the three-dimensional XY universality class, it would be puzzling if the collinear antiferromagnetic arrangements of MnI, MnII, and MnIII sites did not alter or adjust the global critical behavior of the system. As it turns out, these speculations are inconsequential because the solution in Figure 53(a) is not possible as a consequence of \(T_N\) being far too high. The three-dimensional XY universality class is implied by the \(\beta = 1/3\) result reported in Reference [229], but we are able to definitively rule it out here.

Table 12. Best-fit values for parameters in Equation (7.4) organized by fit in Figure 53. Values with * were held fixed as the other parameters were optimized.

<table>
<thead>
<tr>
<th>Fit</th>
<th>(A_-)</th>
<th>(A_+/A_-)</th>
<th>(\alpha)</th>
<th>(E_-)</th>
<th>(E_+)</th>
<th>(B)</th>
<th>(D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>0.267(3)</td>
<td>1.057(5)</td>
<td>-0.007(3)</td>
<td>0.0482(3)</td>
<td>-0.0230(2)</td>
<td>38.0(1)</td>
<td>-2.673(9)</td>
</tr>
<tr>
<td>(c)</td>
<td>0.304(2)</td>
<td>2.59(2)</td>
<td>-0.16*</td>
<td>1.18(1)</td>
<td>-0.564(4)</td>
<td>1.612(8)</td>
<td>-3.27(2)</td>
</tr>
<tr>
<td>(d)</td>
<td>0.305(2)</td>
<td>1.82(1)</td>
<td>-0.10*</td>
<td>0.557(6)</td>
<td>-0.312(3)</td>
<td>2.72(1)</td>
<td>-2.73(1)</td>
</tr>
</tbody>
</table>

The optimized values of \(\alpha\) in our constrained \(T_N\) range in Figure 53(b) include both \(\alpha = -0.16\) and \(\alpha = -0.10\) which are close to predictions for the three-dimensional \(n = 4\) \((\alpha = -0.17)[240]\) and \(n = 3\) \((\alpha = -0.10)[2]\) universality classes, respectively. We first fixed \(\alpha = -0.16\) and obtained optimized values for the other parameters (best-fit solution and data plotted in Figure 53(c)). Then a similar procedure was followed by fixing \(\alpha = -0.10\) and its best-fit solution is plotted in Figure
53(d). These two fits appear worse than that of Figure 53(a), but \( T_N \) assumes an acceptable value in these cases. Optimized values for the parameters in these two fits are summarized in Table 12. We are unable to make a definitive statement regarding which fit is better, or to which universality class the antiferromagnetic phase transition in \( \alpha\)-Mn belongs. However, our results do suggest that the three-dimensional \( n = 3 \) (Heisenberg) and \( n = 4 \) universality classes are both possible.

We address the \( \alpha = -0.10 \) best-fit solution, plotted in Figure 53(d), first. Its critical exponent is consistent with the three-dimensional Heisenberg universality class \( (n = 3) \). In many ways, this make more sense than the \( n = 2 \) universality class because our intuition suggests that the order parameter of such a complicated magnetic structure would probably have to be at least three-dimensional. Comparison of our optimized value of \( A_+/A_- = 1.82 \) with the prediction for this universality class \( (A_+/A_- = 1.52(2)) \)[66] reveals our value is about 20% too high. However, this is not necessarily enough to exclude this universality class from consideration. Another relevant criterion to check is whether the best-fit parameter \( B = 2.72(1) \) J mol\(^{-1}\) K\(^{-1}\) is equal to \( \lambda \Omega T \) at \( T_N \), as it should be when \( \alpha < 0.0 \). In this case, \( B \) is probably a factor of \( \sim 5 \) too large. However, the rounding of the transition in the vicinity of \( T_N \) has a big impact on the value of \( \lambda \Omega T \) at \( T_N \) and so this discrepancy is also insufficient to exclude the possibility that this is the best solution. Taking these points together, the evidence suggests we cannot rule out the three-dimensional Heisenberg universality class for \( \alpha\)-Mn.
The best-fit solution with $\alpha = -0.16$, plotted in Figure 53(c), is comparable in quality to the solution with $\alpha = -0.10$. The predictions for the three-dimensional $n = 4$ universality class are less well established than those of the three-dimensional Heisenberg class, but are approximately $\alpha = -0.17$ and $A_+/A_- \simeq 1.7$ (though this latter parameter seems to be a low estimate). Comparison of our best-fit parameters in Table 12 with these values demonstrates strong similarities. Furthermore, the optimized value of $B$ is much closer to the value of $\lambda \Omega T$ at $T_N$ than was the case with the three-dimensional Heisenberg solution. When chemical and magnetic unit cells are identical, the ordering vector in the first Brillouin zone is $\vec{k} = (0, 0, 0)$. The ordering vector of $\alpha$-Mn is either $\vec{k} = (1, 0, 0)$ or $\vec{k} = \left( \frac{2\pi}{a} \right) (0, 0, 1)$ depending on the source,[224, 241] but each result implies that the magnetic and chemical unit cells are not coincident. This makes it possible for the transition of $\alpha$-Mn to belong to an $n \geq 4$ universality class. Furthermore, the space group of the paramagnetic phase of $\alpha$-Mn (cubic space group $I\bar{4}3m$) has point-group symmetry $T_d$ (achiral tetrahedral symmetry).[100] A maximum $n = 24$ is allowed for this point-group symmetry, though it is likely $n$ would be lower than 24 if a similar group-theory calculation was conducted for $\alpha$-Mn as detailed in other work.[41, 42, 43]. Mukamel et al. predicted many $n \geq 4$ systems, but almost all were later found to exhibit first-order transitions as a result of not having any stable fixed points in their renormalization-group $\epsilon$ expansions.[12] We have found only one paper that tentatively claimed to have measured a critical exponent $\alpha$ that correlated with an $n \geq 4$ universality class. However,
the results of Malmström and Geldart[58] on antiferromagnetic Dy ($\alpha = -0.20(5)$) were later refuted by evidence that the transition in Dy is first order.[52] Therefore, we tentatively suggest the best-fit solution plotted in Figure 53(c) is consistent with the three-dimensional $n = 4$ universality class, but that analysis of a single crystal would be required to conclude anything decisive.

The results of previous analysis[229, 230] of the critical exponent $\beta$ in $\alpha$-Mn suggested its transition belonged to one of three universality classes: the $d = 3$, $n = 2, 3, \text{or } 4$ universality classes. Since our analysis was conducted on a polycrystalline sample, our ability to probe the critical region was severely limited. However, we did obtain least-squares solutions matching the three-dimensional $n = 2, 3, \text{and } 4$ universality classes as well. Because $T_N$ was unphysical for the $n = 2$ solution, we excluded it from consideration. However, both the three-dimensional $n = 3$ and 4 universality classes seem to be valid possibilities, though it will take further analysis on a better sample of $\alpha$-Mn to decide between these two solutions. For now, it is sufficient to conclude that our analysis has narrowed the possibilities down to these two universality classes.
CONCLUSION AND FUTURE WORK

The history of applying thermal-expansion data to the study of critical behavior is remarkably limited. This seems to be a consequence of the relative infrequency with which thermal-expansion studies are conducted, and a deficit of information regarding the concept itself. Therefore, it was our objective to support the following thesis statement: *Analysis of high-resolution measurements of thermal expansion is a legitimate method to study critical phenomena in antiferromagnetic systems.* To support this thesis statement, we successfully studied the critical behavior exhibited by antiferromagnetic CaMn$_2$O$_4$, Bi$_2$CuO$_4$, and α-Mn with thermal expansion. Our criteria for demonstrating the legitimacy of the method were that these examples demonstrate critical behavior over sufficiently-large temperature ranges and that results correspond to theoretical predictions for universality classes. Antiferromagnetic systems were selected because they are not as susceptible as ferromagnetic materials to long-range dipole contributions which adjust the behavior in the vicinity of the phase transition away from ideal critical behavior predicted by theory.

The validity of studying critical behavior with thermal expansion relies heavily on the Pippard relation's ability to scale $\Omega T$ with $C_P$. Exploring this important scaling relation in more detail, we have proved the uniqueness of scaling parameters \( \{\lambda, a, b\} \) so that if a scaling solution is obtained, those scaling parameters are the only correct set. The equivalence of the Pippard and Ehrenfest relations has also been proved in
transitions exhibiting jump discontinuities in $C_P$ and $\Delta V/V$. This demonstrates that the Ehrenfest relation is actually a special case of the Pippard relation.

Single-crystalline test systems CaMn$_2$O$_4$ and Bi$_2$CuO$_4$ were grown by the floating-zone method and characterized by a variety of techniques. We studied the textbook antiferromagnetic transition of single-crystalline CaMn$_2$O$_4$ first and found that the critical behavior exhibited by $\lambda\Omega T$ and $\lambda_i\mu_i T$ along each principle axis of its orthorhombic crystal structure are fully consistent with predictions for the three-dimensional Ising universality class. Following this successful application of thermal expansion, we studied the critical behavior of single-crystalline Bi$_2$CuO$_4$ using the same strategies employed for CaMn$_2$O$_4$. Our results revealed the transition in Bi$_2$CuO$_4$ also belongs to the three-dimensional Ising universality class. This conclusion settled a long-standing question by suggesting Bi$_2$CuO$_4$ exhibits easy-axis anisotropy rather than easy-plane anisotropy and provided a second successful test case. Finally, the limitations of studying critical behavior with a polycrystalline sample were demonstrated when we investigated the antiferromagnetic transition of $\alpha$-Mn. We concluded that the transition in $\alpha$-Mn most likely belongs to either the three-dimensional Heisenberg or three-dimensional $n = 4$ universality class. A sample of higher quality will be necessary to provide definitive results necessary to decide between these two possibilities. Having conducted successful analysis on three examples, we feel justified in stating our primary conclusion: the application of thermal
expansion to study critical behavior in antiferromagnetic systems is a valid, useful technique.

As a result of our analysis, we are also able to offer several secondary conclusions. In CaMn$_2$O$_4$ and Bi$_2$CuO$_4$, the critical behavior exhibited along distinct crystallographic axes $\lambda_i\mu_i T$ was found to be equivalent to that exhibited by $\lambda\Omega T$. This behavior was mentioned once, though not demonstrated, in a published study.[67] We have not only demonstrated this behavior, we did so for two distinct materials. This result is one of the strongest advantages of studying critical behavior with thermal expansion because multiple, independent data sets may be considered. When each data set provides consistent results, we are given more confidence regarding the veracity of the results of critical-behavior fits than if we conducted analysis on only one set of data.

The most prominent disadvantage of studying critical behavior with thermal expansion is that the Pippard relation scales $C_P$ and $\Omega T$, which forces us to numerically differentiate $\Delta V/V$ to obtain $\Omega$. The detrimental effects of numerical differentiation were studied quantitatively with a critical expression for $\Delta V/V$ we calculated using the Pippard relation and critical expressions for $C_P$. We discovered that measuring thermal expansion with a sufficient data density is required to avoid problems with truncation error, but that temperature resolution constrains the data density. As data density (the temperature difference between neighboring data) approaches similar values as the intrinsic temperature resolution, the statistical uncertainty of $\Omega$
increases dramatically. This is problematic because the uncertainty of $\Omega T$ is used to calculate the uncertainties of best-fit parameters when fitting the data with critical expressions. Therefore, a balance must be reached between these competing effects.

Truncation error was determined to lead to reduced critical temperature ranges in the vicinity of $T_N$ in most critical-behavior studies of $\lambda \Omega T$. To circumnavigate this problem and demonstrate that the true critical temperature range is larger than it appears, we fitted CaMn$_2$O$_4$ and Bi$_2$CuO$_4$ thermal-expansion data ($\lambda_i(\Delta L/L)_i$ along each principal crystallographic axis) with our critical expression for $\Delta V/V$. In so doing, we demonstrated that the critical temperature region in those systems extended to the data points closest to $T_N$. For CaMn$_2$O$_4$, this extended the critical range to the $|t| \sim 10^{-4}$ boundary.

Taken together, these results offer a convincing endorsement of the application of thermal expansion to study critical behavior exhibited by antiferromagnetic phase transitions. The extension of this method and strategy to ferromagnetic systems is expected to be trivial. In the future, it would be interesting to conduct analysis of data from a single crystal of $\alpha$-Mn in order to conclusively determine the universality class to which its phase transition belongs. If it does belong to the three-dimensional $n = 4$ universality class, to our knowledge, it would be the first true observation of a second-order transition with an $n \geq 4$ order parameter which exhibits critical behavior. Furthermore, there are several antiferromagnetic systems with stable fixed points in their renormalization-group $\epsilon$ expansions that are also predicted to belong
to \( n \geq 4 \) universality classes. These include TbAu\(_2\), DyC\(_2\), and K\(_2\)IrCl\(_6\) and, to our knowledge, no critical-behavior studies of any of them have been conducted. It would be interesting to study one or more of these materials.
APPENDICES
APPENDIX A

LAUE DIFFRACTION-PATTERN SIMULATION CALCULATIONS
The calculation of the direct-space lattice-parameter vectors in the initial orientation of Figure 19 and referenced to \((O; \vec{x}, \vec{y}, \vec{z})\) is a simple exercise in vector algebra. The vector \(\vec{a}_1\) conserves its magnitude and maintains its direction in \((O; \vec{x}, \vec{y}, \vec{z})\) given the specified initial orientation. The vector \(\vec{a}_2\) is calculated by an elementary implementation of dot products.

\[
\vec{a}_2 = (\vec{a}_2 \cdot \hat{i})\hat{i} + (\vec{a}_2 \cdot \hat{j})\hat{j}
\]

\[
= (a_2 \cos \gamma)\hat{i} + \left(a_2 \cos \left(\frac{\pi}{2} - \gamma\right)\right)\hat{j}
\]

\[
= (a_2 \cos \gamma)\hat{i} + (a_2 \sin \gamma)\hat{j}
\]

(A.1)

Slightly more involved is the calculation of \(\vec{a}_3\), which has components in all three directions. It is convenient to adopt notation of the form

\[
\vec{a}_1 = a_1 \hat{i}
\]

\[
\vec{a}_2 = a_{2x} \hat{i} + a_{2y} \hat{j}
\]

\[
\vec{a}_3 = a_{3x} \hat{i} + a_{3y} \hat{j} + a_{3z} \hat{k},
\]

(A.2)

so we can solve for components of \(\vec{a}_3\) one at a time. The \(x\) component of \(\vec{a}_3\) is calculated with a dot product,

\[
\vec{a}_1 \cdot \vec{a}_3 = a_1 a_3 \cos \beta = a_1 a_{3x}
\]

\[
a_{3x} = a_3 \cos \beta,
\]

(A.3)
while the $y$ component of $\vec{a}_3$ is calculated with a dot product and substitution of the values for components $a_{2x}$, $a_{2y}$, and $a_{3x}$

$$\vec{a}_2 \cdot \vec{a}_3 = a_{2x}a_3 \cos \alpha = a_{2x}a_{3x} + a_{2y}a_{3y} = a_{2x}a_{3x} \cos \gamma + a_{2y}a_{3y} \sin \gamma$$

$$a_3 \cos \alpha = a_{3x} \cos \gamma + a_{3y} \sin \gamma = a_3 \cos \beta \cos \gamma + a_{3y} \sin \gamma$$

(A.4)

$$a_{3y} = a_3 \frac{\cos \alpha - \cos \gamma \cos \beta}{\sin \gamma}.$$  

The $z$ component of $\vec{a}_3$ is easily calculated by taking a dot product and substituting in the other two components of $\vec{a}_3$

$$\vec{a}_3 \cdot \vec{a}_3 = a_3^2 = a_{3x}^2 + a_{3y}^2 + a_{3z}^2$$

$$a_{3z} = \sqrt{a_3^2 - a_{3x}^2 - a_{3y}^2}$$

(A.5)

$$= \sqrt{a_3^2 - a_3^2 \cos^2 \beta - a_3^2 \left[ \frac{\cos \alpha - \cos \gamma \cos \beta}{\sin \gamma} \right]^2}$$

$$= a_3^2 \sqrt{\sin^2 \beta - \left[ \frac{\cos \alpha - \cos \gamma \cos \beta}{\sin \gamma} \right]^2}.$$  

All together, the direct-space lattice parameters, expressed relative to $(O; \vec{x}, \vec{y}, \vec{z})$ and given the initial orientation of Figure 19, have the following components which are functions of lattice-parameter magnitudes and crystallographic angles.

$$a_{2x} = a_2 \cos \gamma$$

$$a_{2y} = a_2 \sin \gamma$$

$$a_{3x} = a_3 \cos \beta$$

(A.6)

$$a_{3y} = a_{3y} = a_3 \frac{\cos \alpha - \cos \gamma \cos \beta}{\sin \gamma}$$

$$a_{3z} = a_3^2 \sqrt{\sin^2 \beta - \left[ \frac{\cos \alpha - \cos \gamma \cos \beta}{\sin \gamma} \right]^2}$$
Calculation of Vector Normal to Plane \((hkl)\) in Initial Orientation

Given suitable expressions for the direct-space lattice parameters, we can calculate a general expression for the vector normal to an arbitrary crystallographic plane \((hkl)\), assuming the initial orientation defined in Figure 19. To calculate the plane-normal vector, we utilize the reciprocal lattice, which has the useful property that the vector,

\[
\vec{n} = h\vec{b}_1 + k\vec{b}_2 + l\vec{b}_3, \quad \text{(A.7)}
\]

(a linear combination of reciprocal-lattice vectors) is perpendicular to crystallographic plane \((hkl)\). The reciprocal-lattice vectors \((\vec{b}_1, \vec{b}_2, \vec{b}_3)\), originally introduced by J. W. Gibbs,[242] are defined in terms of direct-space lattice vectors \((\vec{a}_1, \vec{a}_2, \vec{a}_3)\) by

\[
\begin{align*}
\vec{b}_1 &= \frac{\vec{a}_2 \times \vec{a}_3}{(\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3} \\
\vec{b}_2 &= \frac{\vec{a}_3 \times \vec{a}_1}{(\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3} \\
\vec{b}_3 &= \frac{\vec{a}_1 \times \vec{a}_2}{(\vec{a}_1 \times \vec{a}_2) \cdot \vec{a}_3}. \quad \text{(A.8)}
\end{align*}
\]

By substituting the definitions of the reciprocal-lattice vectors in Equation (A.8) into Equation (A.7) and ignoring the denominators, we get an expression for \(\vec{n}\) in terms of the direct-space lattice parameters

\[
\vec{n} = h\vec{a}_2 \times \vec{a}_3 + k\vec{a}_3 \times \vec{a}_1 + l\vec{a}_1 \times \vec{a}_2. \quad \text{(A.9)}
\]

We ignore the denominators because only the direction of the plane-normal vector and not its magnitude is important. Re-scaling the magnitudes of \(\vec{b}_i\) by dropping a common denominator has no influence over the direction of \(\vec{n}\). Finally, substitution
of \((\vec{a}_1, \vec{a}_2, \vec{a}_3)\) from Equation (A.6) into Equation (A.9) provides an expression for the plane-normal vector, perpendicular to crystallographic plane \((hkl)\), under the assumption that the crystal orientation is that of Figure 19. The components of \(\vec{n}\) are

\[
\begin{align*}
n_1 &= h a_{2y} a_{3z} \\
n_2 &= -h a_{2x} a_{3z} + k a_1 a_{3z} \\
n_3 &= h(a_{2x} a_{3y} - a_{2y} a_{3x}) - k a_1 a_{3y} + l a_1 a_{2y}.
\end{align*}
\]

Calculation of Laue-Spot Coordinates

Given expressions for the vectors representing diffracted x-ray beams from crystallographic planes \((hkl)\), \(\vec{c}'_{hkl}\), the next step is to calculate where the beams intersect the plane occupied by the film. The vector \(\vec{c}'_{hkl}\) originates from the crystal and intersects the film where the Laue spot is recorded. The vector \(\vec{D}\) originates from the crystal and intersects the film at the origin of the \((O', \vec{x}', \vec{y}')\) frame. Expressions for both vectors are known relative to the \((O, \vec{x}, \vec{y}, \vec{z})\) reference frame. They are \((c'_1, c'_2, c'_3)\) and \((D, 0, 0)\), respectively. A third vector, denoted \(\vec{p} = \vec{c}'_{hkl} - \vec{D}\), lies in the \(\vec{x}'-\vec{y}'\) plane when the magnitude of \(\vec{c}'_{hkl}\) is appropriately scaled. If we define the angle between \(\vec{c}'_{hkl}\) and \(\vec{D}\) to be \(\phi\), then

\[
\cos \phi = \frac{D c'_1}{D \sqrt{(c'_1)^2 + (c'_2)^2 + (c'_3)^2}} = \frac{c'_1}{\sqrt{(c'_1)^2 + (c'_2)^2 + (c'_3)^2}}.
\]
We need to scale $\vec{c}_{hkl}'$ so that $\vec{p}$ resides within the plane of the film. Using simple trigonometry, and substituting in the result of Equation (A.11), we calculate the magnitude of $\vec{c}_{hkl}'$ which results in the desired character of $\vec{p}$

$$\text{magnitude} = \frac{D}{\cos \phi} = \frac{D}{c'_1} \sqrt{(c'_1)^2 + (c'_2)^2 + (c'_3)^2}. \quad (A.12)$$

We must re-scale the magnitude of $\vec{c}_{hkl}'$ by a factor $D/c'_1$. The final step is to solve for the projection vector $\vec{p}$. This is a simple matter of subtracting $\vec{D}$ from the re-scaled vector $\vec{c}_{hkl}'$

$$\vec{p} = \frac{D}{c'_1}(c'_1, c'_2, c'_3) - (D, 0, 0)$$
$$= \left(0, \frac{D c'_2}{c'_1}, \frac{D c'_3}{c'_1}\right). \quad (A.13)$$

Of course, the vector we calculate is referenced to the $(O; \vec{x}, \vec{y}, \vec{z})$ reference frame. To mathematically map the vector's coordinates into the $(O'; \vec{x}', \vec{y}', \vec{z}')$ reference frame, $\vec{x}$ has no counterpart, but $\vec{y} \rightarrow \vec{x}'$, and $\vec{z} \rightarrow \vec{y}'$. The $x'$ and $y'$ coordinates of $\vec{p}$, after its transformation, are the coordinates of the Laue spot, referenced from the center of the film

$$\left(-D \frac{c'_2}{c'_1}, D \frac{c'_3}{c'_1}\right). \quad (A.14)$$
APPENDIX B

CALCULATION OF THERMAL EXPANSION ALONG AN ARBITRARY CRYSTALLOGRAPHIC DIRECTION
Table 13. Lattice spacing $d_{hkl}$ calculated for various Bravais lattices.

<table>
<thead>
<tr>
<th>Bravais Lattice</th>
<th>Lattice Spacing for Plane $(hkl)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cubic</td>
<td>$d_{hkl}^{-2} = h^2+k^2+l^2$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$d_{hkl}^{-2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$d_{hkl}^{-2} = \frac{4}{3} \left( \frac{h^2+kk+k^2}{a^2} \right) + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$d_{hkl}^{-2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$d_{hkl}^{-2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right)$</td>
</tr>
</tbody>
</table>

It is occasionally necessary to calculate the linear thermal expansion $(\Delta L/L)_{hkl}$ along arbitrary crystallographic direction $[hkl]$.\cite{142} We begin this calculation by expressing the distance $d_{hkl}$ between adjacent $(hkl)$ planes in terms of lattice parameters and crystallographic angles. They are published in many references such as Cullity and Stock,\cite{99} but are reproduced in Table 13 for all Bravais lattices except triclinic. We ignore the triclinic lattice due to the amount of tedious algebra involved and the low probability anyone would attempt to study the thermal expansion of a triclinic crystal in the first place. However, if one did wish to do this calculation, the procedure outlined below is general. The rhombohedral expression was also omitted in Table 13 because we assumed anybody studying a rhombohedral crystal would use the rhombohedral-hexagonal transformation to simplify the crystallography.\cite{99} In general, we calculate $(\Delta L/L)_{hkl}$ with

$$
\left( \frac{\Delta L}{L} \right)_{hkl} = \frac{d_{hkl}(T) - d_{hkl}(300)}{d_{hkl}(300)} = \frac{d_{hkl}(T)}{d_{hkl}(300)} - 1,
$$

where the expressions for $d_{hkl}$ are chosen from Table 13 corresponding to the relevant crystal structure. For example, if we wish to know the thermal expansion along $[hkl]$
in an orthorhombic crystal, we first write

$$\left( \frac{\Delta L}{L} \right)_{hkl} = \frac{d_{hkl}(T)}{d_{hkl}(300)} - 1 = \sqrt{\frac{(h/a)^2 + (k/b)^2 + (l/c)^2}{(h/a(T))^2 + (k/b(T))^2 + (l/c(T))^2}} - 1,$$

(B.2)

where $a, b, \text{ and } c$ refer to the values of those lattice parameters at 300 K. By replacing temperature-dependent values such as $a(T)$ with $a(T) = a(1 + \Delta a/a)$, we obtain the final result

$$\left( \frac{\Delta L}{L} \right)_{hkl} = \sqrt{\frac{(h/a)^2 + (k/b)^2 + (l/c)^2}{\left(\frac{h}{a(T)}\right)^2 + \left(\frac{k}{b(T)}\right)^2 + \left(\frac{l}{c(T)}\right)^2}} - 1.$$

(B.3)

The ratios $h/a, k/b, \text{ and } l/c$ are known, but we need to measure $\Delta a/a, \Delta b/b, \text{ and } \Delta c/c$ before we can use (B.3). In the case of the monoclinic structure, we must also determine $\beta(T)$. The procedure to indirectly measure $\beta(T)$ is described in the analysis in Chapter 5 leading to Equation (5.23).

The final calculated expressions are displayed in Equations (B.4) for cubic (a), tetragonal (b), hexagonal (c), orthorhombic (d), and monoclinic lattices (e). If we inspect the formulae, we see that the monoclinic calculation is equivalent to orthorhombic if $\beta = 90^\circ$, the orthorhombic calculation is equivalent to tetragonal if we set $b = a$ and $\Delta b/b = \Delta a/a$, and the tetragonal calculation is equivalent to cubic if we set $c = a$ and $\Delta c/c = \Delta a/a$. These observations are consistent with expectations. In the cubic case, we see that the linear thermal expansion along $[hkl]$ is independent of its direction (always $\Delta a/a$), which is consistent with the expectation that physical
properties be isotropic for cubic crystal structures.

\[
\left( \frac{\Delta L}{L} \right)_{\text{Cub}}^{\text{hkl}} = \frac{\Delta a}{a} \quad (B.4a)
\]

\[
\left( \frac{\Delta L}{L} \right)_{\text{Tet}}^{\text{hkl}} = \sqrt{\frac{(h^2+k^2)/a^2 + l^2/c^2}{(1+\Delta a/a)^2 + (1+\Delta c/c)^2}} - 1 \quad (B.4b)
\]

\[
\left( \frac{\Delta L}{L} \right)_{\text{Hex}}^{\text{hkl}} = \sqrt{\frac{(h^2+hk+k^2)/a^2 + 0.75(l^2/c^2)}{(1+\Delta a/a)^2 + (1+\Delta c/c)^2}} - 1 \quad (B.4c)
\]

\[
\left( \frac{\Delta L}{L} \right)_{\text{Ort}}^{\text{hkl}} = \sqrt{\left( \frac{h/a}{1+\Delta a/a} \right)^2 + \left( \frac{k/b}{1+\Delta b/b} \right)^2 + \left( \frac{l/c}{1+\Delta c/c} \right)^2} - 1 \quad (B.4d)
\]

\[
\left( \frac{\Delta L}{L} \right)_{\text{Mon}}^{\text{hkl}} = \frac{\sin \beta(T)}{\sin \beta} \sqrt{\left( \frac{h/a}{1+\Delta a/a} \right)^2 + \left( \frac{k\sin \beta(b)/b}{1+\Delta b/b} \right)^2 + \left( \frac{l/c}{1+\Delta c/c} \right)^2 - \frac{2hl\cos \beta(b)/(ac)}{(1+\Delta a/a)(1+\Delta c/c)}} - 1 \quad (B.4e)
\]
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