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THE THERMAL EXPANSION OF GADOLINIUM IN THE
VICINITY OF THE CURIE POINT

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Ph.D. Thesis Submitted to Iowa State University

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Date Transmitted: February 1977

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PREPARED FOR THE U.S. ENERGY RESEARCH AND DEVELOPMENT
ADMINISTRATION UNDER CONTRACT NO. W-7405-eng-82

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The thermal expansion of gadolinium in the
vicinity of the Curie point

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The c- and a-axis linear thermal expansivities of high purity single crystals of gadolinium have been measured in the temperature range 270 K to 320 K. Length changes were translated to capacitance changes with a modified normal geometry 3-terminal capacitance dilatometer. An ac 3-terminal capacitance bridge was employed to measure nominal 10 pF capacitances to a precision of 10^{-7} pF, which corresponds to a relative length change sensitivity of 10^{-10} . A 25 ohm platinum resistance thermometer was used to detect the dilatometer temperature to a precision of 10 μ K with an ac resistance bridge.

The c-axis expansivity was negative and had a large ($\approx 10^{-4}$ K $^{-1}$) peak at 293.435 K, while the a-axis expansivity was positive and had a smaller ($\approx 10^{-5}$ K $^{-1}$) peak at 293.363 K. The values of the Curie temperatures (T_c 's) and critical point exponents for the c- and a-axis crystals were obtained from fitting power law equations to the expansivities.

The c-axis expansivity exponents agree reasonably well with recently measured specific heat exponents and the $T > T_C$ expansivity exponent, α , also agrees with the value calculated by the 3-dimensional Heisenberg model. The a-axis expansivity exponents do not agree with the measured specific heat exponents or the 3-dimensional Heisenberg model calculation. This difference is explained in terms of anomalous behavior of the adiabatic elastic constants which indicate that, near T_C , the a-axis expansivity is not proportional to the specific heat while the c-axis expansivity (to good approximation) is proportional to the specific heat.

Comparing the magnetic contributions to the specific heat and the thermal expansivities yields estimates for the magnetic Grüneisen parameters at T_C as $\gamma_a^{(m)}(T_C) \approx -1.1$ and $\gamma_c^{(m)}(T_C) \approx -4.5$. Since both $\gamma_a^{(m)}$ and $\gamma_c^{(m)}$ are negative, the positive a-axis expansivity is the result of elastic crosscoupling. These Grüneisen parameters are consistent with the measured pressure dependence of the Curie temperature (dT_C/dP).

CHAPTER I. INTRODUCTION

Much research in the past fifteen years has been directed towards the study of phase transitions of order higher than one; i.e. phase transitions with no associated latent heat or discontinuous volume change. These phase transitions are designated as critical phenomena and the temperature, pressure magnetic field, etc. at which they occur is referred to as the critical point.

Phase transitions where critical phenomena may occur include those from liquid to gas, ferromagnet to paramagnet, order to disorder transitions in binary alloys, polarized to unpolarized ferroelectrics, superconductors to normal conductors, and superfluid to normal fluid. The equilibrium properties near the critical point in all these systems exhibit very similar behavior. In fact, near a critical point, the details of the system undergoing the phase transition seem irrelevant. This idea leads to the hypothesis of universality¹, which states that all phase transition problems may be divided into a small number of different classes depending only upon the dimensionality of the system and the symmetry of the ordered state. Within each class, all phase transitions have identical behavior and only the names of the variables are changed.

All critical phenomena are described in terms of a quantity known as an order parameter which is nonzero in the ordered phase and zero in the disordered phase. Examples of order parameters are the magnetization in a ferromagnet and the density difference between the liquid and gaseous phases for a liquid-gas system.

Magnetic systems have a variety of different symmetries in the ordered states and therefore provide a very fertile ground for studying the different universal classes of critical behavior. In the following sections, only ferromagnets will be considered, but it is important to reemphasize that by simply changing the names of the appropriate variables other systems may be described by the same formalism.

Thermodynamics Near the Critical Point

Basic considerations

Figure 1 shows projections of the equation of state surface for a ferromagnet,

$$f(H, M, T) = 0, \quad (1-1)$$

where H is the external magnetic field, M is the magnetization, and T is the temperature. As the temperature increases, M (for $H=0$) decreases to zero at the Curie temperature, T_C . The point $(T=T_C, H=0)$ is the critical point of this system and M is the order parameter. In order to discuss the behavior of various equilibrium properties of an isotropic ferromagnet, it is convenient to define the Gibbs potential, $G(T, H, P)$, through the differential relation

$$dG = - SdT - MdH + VdP \quad (1-2)$$

where S is the entropy, P is the pressure, and V is the volume. Near the

Figure 1. Projections of the equation of state surface, $f(H, M, T) = 0$, onto the M-T and H-M planes.

critical point, the first derivatives of $G(T,H,P)$, e.g.

$$S = - \left(\frac{\partial G}{\partial T} \right)_{H,P}, \quad M = - \left(\frac{\partial G}{\partial H} \right)_{T,P}, \quad \text{and} \quad V = \left(\frac{\partial G}{\partial P} \right)_{T,H} \quad (1-3)$$

are continuous (i.e. no latent heat or discontinuities in the magnetization or volume), while the second-order derivatives, e.g. the isothermal susceptibility

$$\chi_T = \left(\frac{\partial M}{\partial H} \right)_{T,P} = - \left(\frac{\partial^2 G}{\partial H^2} \right)_{T,P} \quad (1-4a)$$

the specific heat

$$C_{H,P} = T \left(\frac{\partial S}{\partial T} \right)_{H,P} = - T \left(\frac{\partial^2 G}{\partial T^2} \right)_{H,P} \quad (1-4b)$$

and the volume thermal expansivity

$$\beta_{H,P} = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_{H,P} = - \frac{1}{V} \left(\frac{\partial S}{\partial P} \right)_{T,H} = \frac{1}{V} \left\{ \frac{\partial}{\partial T} \left[\frac{\partial G}{\partial P} \right]_{T,H} \right\}_{H,P} \quad (1-4c)$$

tend to become large and may even become infinite at $(T=T_C, H=0)$. This is illustrated by the H versus M plot in Figure 1, since the isothermal susceptibility, which is the inverse of the slope, becomes large for $(T=T_C, H=0)$. Similarly, a plot of the entropy, S , versus temperature would show a large $(dS/dT)_P$ at $(T=T_C, H=0)$, and hence a large value of the specific heat.

The physical origin of the singularities in the second-order derivatives is tied to the spatial extent of coherent fluctuations in the local magnetization density.² In order to see this, a pair correlation function which defines this spatial extent is written as

$$\Gamma(\vec{r}, \vec{r}') = \langle (m_z(\vec{r}) - \langle m_z(\vec{r}) \rangle) (m_z(\vec{r}') - \langle m_z(\vec{r}') \rangle) \rangle \quad (1-5)$$

where $m_z(\vec{r})$ is the z-component of the magnetization density at position $\vec{r}$. The brackets $\langle \rangle$ designate the canonical thermodynamic average which is defined by

$$\langle m_z(\vec{r}) \rangle = \frac{\text{Tr}[m_z(\vec{r}) \exp(-\mathcal{H}/kT)]}{\text{Tr}[\exp(-\mathcal{H}/kT)]} \quad (1-6)$$

where $\mathcal{H}$ is the system Hamiltonian and Tr denotes a sum over all allowed states. Classically,

$$\Gamma(\vec{r}, \vec{r}') \propto kT \frac{\exp[-|\vec{r}-\vec{r}'|/\xi(T)]}{|\vec{r}-\vec{r}'|} \quad (1-7)$$

where $\xi(T)$ (the correlation length) goes to infinity as T approaches T_C ($T \rightarrow T_C$). Thus, in this limit, the range of $\Gamma(\vec{r}, \vec{r}')$ becomes infinite (for a perfect crystal of infinite extent). In a uniform applied field (in the z-direction), the isothermal susceptibility divided by the volume is

$$\frac{\chi_T}{V} = \frac{1}{kT} \int d^3r \Gamma(\vec{r}, 0), \quad (1-8)$$

so the large range in Γ as $T \rightarrow T_C$ due to correlated fluctuations gives rise to a large χ_T . Similarly, a measure of correlated fluctuations in the energy density

$$E(\vec{r}) = E_0(\vec{r}) - m_z(\vec{r}) H_z \quad (1-9)$$

is given by

$$\Gamma_{EE}(\vec{r}, \vec{r}') = \langle (E(\vec{r}) - \langle E(\vec{r}) \rangle) (E(\vec{r}') - \langle E(\vec{r}') \rangle) \rangle. \quad (1-10)$$

Since the specific heat C_H can be written as

$$C_H = \frac{1}{kT^2} \int d^3r \Gamma_{EE}(\vec{r}, 0), \quad (1-11)$$

a large range in Γ_{EE} as $T \rightarrow T_C$ gives rise to a large C_H .

Relationship between the specific heat and thermal expansivities

Both the specific heat and the volume thermal expansivity are derivatives of the entropy (Eqns. (1-4b) and (1-4c)), so their behavior must be related. Buckingham and Fairbank³ developed a thermodynamic relationship between the specific heat and the volume thermal expansivity for liquid helium near the superfluid-normal fluid (Lambda) transition. An extension of this relationship to cubic magnetic materials near the Curie temperature gives

$$\beta_{P,H=0} = \frac{1}{T_C} \frac{dT_C}{dP} C_{P,H=0} - \frac{dT_C}{dP} \left(\frac{\partial s}{\partial T} \right)_{\epsilon,H=0} \quad (1-12)$$

where s is the entropy per unit volume, and $\epsilon = (T/T_C) - 1$. The only assumption made in Eqn. (1-12) is that ϵ is a thermodynamic function of state of two independent variables, i.e. $\epsilon = \epsilon(T, P) = (T/T_C(P)) - 1$. Presumably, the second term in Eqn. (1-12) varies only slowly with temperature since it is a derivative taken at constant relative distance from the Curie temperature and hence, sufficiently near T_C , $C_{P, H=0}$ and $\tilde{\beta}_{P, H=0}$ are proportional to each other.

Equation (1-12) is written for magnets with isotropic (cubic) crystal lattices. Barron⁴ and Munn⁵ have discussed the relationship between the specific heat and linear thermal expansivities for anisotropic crystals in terms of a Grüneisen type model. In the following discussion, only axial crystals⁵ (e.g. hexagonal, tetragonal, etc.) will be discussed.

For axial crystals, there are two independent linear thermal expansion coefficients, defined by

$$\tilde{\alpha}_P^c = \left(\frac{\partial \ln c}{\partial T} \right)_P \quad \text{and} \quad \tilde{\alpha}_P^a = \left(\frac{\partial \ln a}{\partial T} \right)_P \quad (1-13)$$

where c and a are the dimensions of the crystallographic unit cell.

Considering separate lattice (ℓ), electronic (e), and magnetic (m) contributions these expansivities can be written as

$$\tilde{\alpha}_P^c = \sum_K \tilde{\alpha}_P^{c(K)} = \tilde{\alpha}_P^{c(\ell)} + \tilde{\alpha}_P^{c(e)} + \tilde{\alpha}_P^{c(m)} \quad (1-14a)$$

and

$$\tilde{\alpha}_P^a = \sum_K \tilde{\alpha}_P^{a(K)} = \tilde{\alpha}_P^{a(\ell)} + \tilde{\alpha}_P^{a(e)} + \tilde{\alpha}_P^{a(m)} \quad (1-14b)$$

Two Grüneisen parameters can be defined for each contribution as

$$\gamma_a^{(K)} = \frac{1}{2c_v^{(K)}} \left(\frac{\partial s^{(K)}}{\partial \ln a} \right)_{c,T} \quad (1-15a)$$

and

$$\gamma_c^{(K)} = \frac{1}{c_v^{(K)}} \left(\frac{\partial s^{(K)}}{\partial \ln c} \right)_{a,T} \quad (1-15b)$$

When the entropy density for component (K), $s^{(K)}$, depends on c and a only through a characteristic temperature $\theta^{(K)}$,

$$s^{(K)} = s^{(K)} \left(\frac{\theta^{(K)}(a,c)}{T} \right), \quad (1-16)$$

then Eqns. (1-15a) and (1-15b) imply that $\gamma_a^{(K)}$ and $\gamma_c^{(K)}$ are functions of c and a only:

$$\gamma_a^{(K)} = - \left(\frac{\partial \ln \theta^{(K)}}{\partial \ln a} \right)_c \quad (1-17a)$$

and

$$\gamma_c^{(K)} = - \left(\frac{\partial \ln \theta^{(K)}}{\partial \ln c} \right)_a \quad (1-17b)$$

Equations (1-15a) and (1-15b) can be written in terms of the linear thermal expansivities for $P=0$ ⁵ as

$$\gamma_a^{(K)} = \frac{1}{c_{P=0}^{(K)}} [(c_{11}^s + c_{12}^s) \tilde{\alpha}_{P=0}^{a(K)} + c_{13}^s \tilde{\alpha}_{P=0}^{c(K)}] \quad (1-18a)$$

and

$$\gamma_c^{(K)} = \frac{1}{c_{P=0}^{(K)}} [2c_{13}^s \tilde{\alpha}_{P=0}^{a(K)} + c_{33}^s \alpha_{P=0}^{c(K)}] \quad (1-18b)$$

The adiabatic elastic constants c_{ij}^s are defined through the relationship

$$c_{ij}^s = \left(\frac{\partial \sigma_i}{\partial \eta_j} \right)_{\eta', s} \quad (1-19)$$

where the σ_j 's and the η_j 's are the stress and strain components and η' denotes that all other components of η are held constant while performing the differentiation.

Equations (1-18a) and (1-18b) can be solved for $\tilde{\alpha}_{P=0}^a(K)$ and $\tilde{\alpha}_{P=0}^c(K)$ to yield

$$\tilde{\alpha}_{P=0}^a(K) = c_{P=0}^s \left[\frac{c_{33}^s \gamma_a^{(K)} - c_{13}^s \gamma_c^{(K)}}{c_{33}^s (c_{11}^s + c_{12}^s) - 2(c_{13}^s)^2} \right] \quad (1-20a)$$

and

$$\tilde{\alpha}_{P=0}^c(K) = c_{P=0}^s \left[\frac{(c_{11}^s + c_{12}^s) \gamma_c^{(K)} - 2c_{13}^s \gamma_a^{(K)}}{c_{33}^s (c_{11}^s + c_{12}^s) - 2(c_{13}^s)^2} \right] \quad (1-20b)$$

The relationship between the total linear thermal expansivities $\tilde{\alpha}_{P=0}^a$ and $\tilde{\alpha}_{P=0}^c$ and the total specific heat $c_{P=0}$ is obtained by summing up all the contributions in Eqns. (1-20a) and (1-20b) and defining total Grüneisen γ 's through

$$\gamma_a = (\sum_K c_{P=0}^{(K)} \gamma_a^{(K)}) / c_{P=0} \quad (1-21a)$$

and

$$\gamma_c = (\sum_K c_{P=0}^{(K)} \gamma_c^{(K)}) / c_{P=0} \quad (1-21b)$$

to obtain

$$\tilde{\alpha}_{P=0}^a = c_{P=0} \left[\frac{c_{33}^s \gamma_a - c_{13}^s \gamma_c}{c_{33}^s (c_{11}^s + c_{12}^s) - 2(c_{13}^s)^2} \right] \quad (1-22a)$$

$$\tilde{\alpha}_{P=0}^c = c_{P=0} \left[\frac{(c_{11}^s + c_{12}^s) \gamma_c - 2c_{13}^s \gamma_a}{c_{33}^s (c_{11}^s + c_{12}^s) - 2(c_{13}^s)^2} \right] \quad (1-22b)$$

Equations (1-22a) and (1-22b) imply that the specific heat and linear thermal expansivities will be proportional near T_c if the c_{ij}^s 's and the γ 's are slowly varying functions of temperature.

Power law behavior

Having established that various equilibrium properties in ferromagnets behave anomalously near the critical point, the next step is to describe the behavior of these quantities in some quantitative fashion.

Experimentally, it has been found that, near T_c , the behavior of thermodynamic quantities often follows a simple power law in terms of the temperature. If $g(\epsilon)$ is such a quantity, with $\epsilon = (T/T_c) - 1$, then the power law behavior is written as

$$g(\epsilon) \sim |\epsilon|^\lambda \quad (1-23)$$

where λ is called the critical point exponent. The definitions of the critical exponents⁶ for various thermodynamic quantities are given in Table 1.

Table 1. Definitions of critical-point exponents for magnetic systems.

Exponent	Definition	Conditions ϵ^a H M	Quantity
α'	$C_H \sim \epsilon ^{-\alpha'}$	<0 $0 \neq 0$	specific heat at constant magnetic field
α	$C_H \sim \epsilon ^{-\alpha}$	>0 0 0	
β	$M \sim \epsilon ^\beta$	<0 $0 \neq 0$	magnetization
γ'	$\chi_T \sim \epsilon ^{-\gamma'}$	<0 $0 \neq 0$	zero field isothermal susceptibility
γ	$\chi_T \sim \epsilon ^{-\gamma}$	>0 0 0	
δ	$H \sim M M ^{\delta-1}$	$0 \neq 0 \neq 0$	critical isotherm
ν'	$\xi \sim \epsilon ^{-\nu'}$	<0 $0 \neq 0$	correlation length
ν	$\xi \sim \epsilon ^{-\nu}$	>0 0 0	
η	$\Gamma(\vec{r}, \vec{r}') \sim \vec{r} - \vec{r}' ^{-(1+\eta)}$	0 0 0	pair correlation function for 3-dim.

^a $\epsilon = T/T_C - 1$, where T_C is the Curie temperature.

Generally the power law behavior is only the leading term describing the quantity near T_C , so that Eqn. (1-23) must be replaced with

$$g(\epsilon) = X_1 |\epsilon|^\lambda (1 + X_2 |\epsilon|^\gamma + \dots) \quad (1-24)$$

$$+ Z_0 + Z_1 \epsilon + Z_2 \epsilon^2 + \dots$$

where the terms

$$X_2 |\epsilon|^\gamma + \dots, \gamma > 0$$

represent corrections to the primary power law behavior and the power series

$$Z_0 + Z_1 \epsilon + Z_2 \epsilon^2 + \dots$$

is intended to represent all regular magnetic behavior and other contributions. If $\lambda < 0$, $g(\epsilon) \rightarrow \infty$ as $T \rightarrow T_C$, but if $0 < \lambda < 1$, $g(\epsilon) \rightarrow Z_0$ as $T \rightarrow T_C$, giving a finite cusp. The case $\lambda=0$ is defined here to represent a logarithmic divergence (i.e. replace $X_1 |\epsilon|^\lambda$ by $X_1 \ln |\epsilon|$ for $\lambda=0$).

For restricted values of ϵ (e.g. $|\epsilon| < 0.1$), a simplified form⁷ of Eqn. (1-24),

$$g(\epsilon) = X_1 |\epsilon|^\lambda + Z_0 + Z_1 \epsilon \quad (1-25)$$

is usually employed to represent the power law behavior. The parameters are in general different for $\epsilon < 0$ and $\epsilon > 0$, so that in order to fit

Eqn. (1-25) to experimental data, a nonlinear fitting procedure must be used which will fit many parameters simultaneously.

Scaling hypothesis

It must be pointed out that the exponents defined in Table 1 are not all independent. Indeed, using basic thermodynamic relations, certain combinations of exponents can be shown to satisfy inequalities such as

$$\alpha' + 2\beta + \gamma' \geq 2 \quad (1-26)$$

Exact relationships between the exponents can be found by making the hypothesis, due to Widom⁸ and Domb and Hunter,⁹ that the singular part of the Gibbs potential, $G^*(\epsilon, H)$, is a generalized homogeneous function of ϵ and H . Using the notation due to Stanley,¹⁰ this hypothesis (known as the static scaling hypothesis), is written mathematically as

$$G^*(\lambda^{a_1} \epsilon, \lambda^{a_2} H) = \lambda G^*(\epsilon, H) \quad (1-27)$$

for any value of the number λ . By differentiating this equation to obtain various thermodynamic quantities, it is apparent that the critical exponents associated with these quantities are all combinations of a_1 and a_2 and hence may be related to one another. Some examples of these relationships are

$$\alpha' + \beta(\delta + 1) = 2, \quad (1-28a)$$

$$\alpha' + 2\beta + \gamma' = 2, \quad (1-28b)$$

$$\alpha = \alpha' , \quad (1-28c)$$

and

$$\gamma = \gamma' , \quad (1-28d)$$

with others listed by Stanley.¹¹ Equation (1-27) also predicts a specific form for the magnetic equation of state as

$$M(\epsilon, H) = |\epsilon|^\beta f^\pm (H/|\epsilon|^{\beta\delta}) \quad (1-29)$$

where "+" and "-" refer to $\epsilon > 0$ and $\epsilon < 0$. Equation (1-29) implies that if the magnetization is scaled by $|\epsilon|^\beta$ and is plotted versus the magnetic field as scaled by $|\epsilon|^{\beta\delta}$, all the magnetic equation of state data will lie on two curves. This is known as data collapsing.

Equation (1-27) does not specify a_1 and a_2 and therefore does not specify the values of any of the exponents. In order to actually calculate values of these exponents, a model Hamiltonian must be assumed and the thermodynamic properties near T_C calculated using the methods illustrated in the next section.

Critical Point Exponent Calculations

High temperature series expansions

Prior to the recent introduction of the renormalization group method of calculating critical point exponents, most calculations for models of real systems (e.g. 3-dimensional lattices) were performed using the high temperature power series expansion method. Basically, the method entails expanding the Gibbs potential

$$G(T, H) = -kT \ln \{ \text{Tr} [\exp(\frac{-H}{kT})] \} \quad (1-30)$$

in powers of H/kT , where H is the magnetic Hamiltonian for the system and Tr denotes a summation over all allowed states, to give

$$G(T, H) = -kT \ln \{ \text{Tr} [1 - \frac{H}{kT} + \frac{1}{2} (\frac{H}{kT})^2 + \dots] \} \quad (1-31)$$

Upon expanding the logarithm, Eqn. (1-31) customarily is written as

$$G(T, H) = -kT \sum_{\ell=0}^{\infty} \left(\frac{c_{\ell}}{\ell!} \right) \left(\frac{1}{kT} \right)^{\ell} \quad (1-32)$$

where the coefficients c_{ℓ} , called cumulants, are combinations of traces of various powers of the Hamiltonian. The appropriate derivatives of $G(T, H)$ give expansions for various thermodynamic functions (e.g. C_H , χ_T , etc.). If these thermodynamic functions have a power law type of behavior, the critical point exponents can be estimated by examining ratios of successive terms in the expansions.

As an example, consider a pure power law behavior for the isothermal susceptibility χ_T ($T > T_C$),

$$\chi_T = A \left(\frac{T}{T_C} - 1 \right)^{-\gamma} = A \left(\frac{T}{T_C} \right)^{-\gamma} \left(1 - \frac{T_C}{T} \right)^{-\gamma} \quad (1-33)$$

Expanding Eqn. (1-33) in powers of $1/T$ gives

$$\chi_T = A \left(\frac{T}{T_C} \right)^{-\gamma} \left\{ 1 + \gamma T_C \left(\frac{1}{T} \right) + \dots + \frac{\gamma(\gamma+1) \dots (\gamma+\ell-1)}{\ell!} T_C^{\ell} \left(\frac{1}{T} \right)^{\ell} + \dots \right\} \quad (1-34)$$

The ratio of the ℓ 'th term to the $\ell-1$ term, $R_{\ell/\ell-1}$, is

$$R_{\ell/\ell-1} = \frac{(\gamma+\ell-1)}{\ell} T_C = T_C \left(1 + \frac{\gamma-1}{\ell}\right). \quad (1-35)$$

Equation (1-35) implies that a plot of $R_{\ell/\ell-1}$ versus $1/\ell$ will yield a straight line with slope $T_C(\gamma-1)$ and ordinate intercept T_C . Often the terms of the expansion must be carried out to large ℓ before the ratios settle down to a straight line because of corrections to simple power law behavior (as in Eqn. (1-24)). Also, nonphysical singularities may affect the ratios so that they never settle down and other methods must be used to extract the critical exponents.

Ritchie and Fisher¹² have applied the high temperature series expansion method to Heisenberg models of general spin, $S=\frac{1}{2}$ to ∞ , on simple-cubic, body-centered-cubic, and face-centered cubic lattices. The Hamiltonian used was

$$\mathcal{H} = \frac{-J}{S^2} \sum_{(ij)} \vec{S}_i \cdot \vec{S}_j - \frac{mH}{S} \sum_{i=1}^N S_i^z$$

where $\vec{S}_i = (S_i^x, S_i^y, S_i^z)$ is the spin on lattice site i , m is the magnetic moment of the spin, J is the exchange parameter, H is the external magnetic field applied in the z direction, and (ij) denotes a sum over nearest neighbor sites. For all the lattices and spin magnitudes S , they calculated the same values for the isothermal susceptibility, correlation length, and correlation function exponents γ , ν , and η . Using the high temperature series expansion results for an $S=\infty$ Heisenberg model of

Stephenson and Wood,¹³ together with the scaling relationships, Ritchie and Fisher also estimated the values of the magnetization, specific heat, and the critical isotherm exponents β , α , and δ . The calculated values of α , β , δ , and γ will be listed later (see Table 2).

Renormalization group calculations

The most recent calculations of critical point exponents involve the technique of the renormalization group (R.G.) as developed by Wilson.¹⁴ Several review papers¹⁵⁻¹⁸ explain this technique in various levels of detail. Kadanoff¹⁹ employed the intuitive foundations of this technique to justify the scaling hypothesis, Eqn. (1-27). The basic idea is to reduce the number of spin variables of a ferromagnet by considering blocks of spins as if they were single effective spins with simple interactions and to renormalize the system to the length scale defined by the blocks.

As is outlined by Fisher,¹⁶ a transformation, τ , is constructed which when applied to the system Hamiltonian $\mathcal{H}$ gives a new Hamiltonian $\mathcal{H}'$ with the number of spin variables reduced such that the partition function, $Z = \text{Tr}[\exp(-\mathcal{H}/kT)]$, is preserved. The spatial lengths and spin magnitudes are rescaled to preserve the spin density and spin fluctuation magnitudes. The transformation is iterated and the initial Hamiltonian parameters varied to locate a so-called fixed point Hamiltonian $\mathcal{H}^*$ which does not change under the transformation and which defines the critical point properties. The manner in which the transformed Hamiltonian approaches $\mathcal{H}^*$ can be used to calculate the critical point exponents. The fact that

many different initial Hamiltonians will converge to the same fixed point Hamiltonian H^* is a mathematical method of confirming the hypothesis of Universality using the R.G. Furthermore, if the transformation τ is linearized for transformed Hamiltonians very near H^* , the static scaling hypothesis can be obtained for the Gibbs potential.

A system with an isotropic short range Hamiltonian,

$$H = -\frac{1}{2} \sum_{\vec{x}, \vec{x}'} J(\vec{x} - \vec{x}') \vec{S}_{\vec{x}} \cdot \vec{S}_{\vec{x}'}, \quad (1-37)$$

where $\vec{S}_{\vec{x}}$ is a n -dimensional spin ($n=1,2,3$ corresponding to the Ising, planar, and Heisenberg models) at lattice site x , can be solved exactly in 4 dimensions. In order to do calculations for real (3 dimensional) systems, the variable $4-d$ (d =lattice dimensionality) is defined and results are expanded in terms of it.²⁰ Wilson,²¹ Brezin, Wallace, and Wilson,²² and Brezin, LeGuillou et al.²³ have calculated several critical point exponents in terms of power series in $4-d$ for arbitrary n . Examples of such power series for isothermal susceptibility, magnetization, and specific heat exponents γ , β , and α are:¹⁶

$$\gamma = 1 + \frac{(n+2)}{2(n+8)} (4-d) + \dots \quad (1-38a)$$

$$\beta = \frac{1}{2} - \frac{3(4-d)}{2(n+8)} + \dots \quad (1-38b)$$

$$\alpha = \frac{(4-n)}{2(n+8)} (4-d) - \frac{(n+2)^2(n+28)}{4(n+8)^3} (4-d)^2 + \dots \quad (1-38c)$$

For $n=d=3$ (Heisenberg model in a 3-dimensional lattice), the values of the specific heat, magnetization, critical isotherm, and isothermal susceptibility exponents α , β , δ , and γ (to highest order in d presently available) will be listed later (see Table 2).

Experimental Results for Magnets

The discussion of experimental results will be restricted to systems with 3-dimensional spins interacting through some sort of isotropic short range exchange. Experimental results for systems with other forms of interactions and spin dimensionality (representing other universal classes) are discussed by Stanley²⁴ and Kadanoff *et al.*² Some general properties and critical point exponents of the cubic ferromagnets iron and nickel will be compared to results for the hexagonal ferromagnet gadolinium which was the subject of investigation in this experiment.

General properties

Iron and nickel have body-centered-cubic and face-centered-cubic crystal lattices respectively, while gadolinium has a hexagonal crystal lattice with a c/a ratio of 1.59²⁵ at room temperature which is less than the ideal close-packing ratio of 1.63.

The outer 3d and 4s electrons of the atoms are responsible for the magnetic and electrical properties in iron ($3d^6, 4s^2$) and nickel ($3d^8, 4s^2$). The 4s electrons are considered to form the conduction band and the 3d electrons have a relatively large exchange interaction. The ferromagnetic properties of iron and nickel are most likely described by a band model²⁶

in which the magnetic 3d electrons are not localized to a particular atom. In gadolinium ($4f^7, 5d, 6s^2$), the outer 5d and 6s electrons form the conduction band and the half-filled 4f shell is responsible for the magnetic properties. The magnetic 4f electrons are closely bound to the atoms in the metal and the exchange coupling between the spins of these electrons is considered to be of the indirect R.K.K.Y. type,²⁷ and is mediated by the conduction electrons.

The magnetic anisotropy, which gives rise to easy axes of magnetization, is relatively small for iron, nickel, and gadolinium. For iron and nickel, the easy axes are the cube edges and body diagonals, respectively.²⁸ For gadolinium, the easy axis is the c-axis for temperatures greater than 240 K.²⁹⁻³² Since the easy axis is the c-axis for gadolinium, the magnetic contribution to the c-axis linear expansivity will be negative while that for the a-axis will be positive due to magnetostriction effects.

Critical point exponent measurements

Table 2 gives a summary of some of the experimental critical point exponents for nickel, iron, and gadolinium along with the Curie temperature found for each measurement.

The different Curie temperatures which appear for the measurements for each magnet are probably due to differences in crystal purity. In general the higher T_c 's indicate better purity samples. The exact effect of impurities on the measured critical exponents are relatively unknown, but they (along with crystal inhomogeneities) could give rise to rounding

Table 2. Experimental and model calculation results for critical point exponents [α (specific heat, $T > T_C$), α' (specific heat, $T < T_C$), β (magnetization), δ (critical isotherm), and γ (isothermal susceptibility)].

MAGNET	T_C (K)	EXPONENTS	REF.
Nickel	631.415 ± 0.010	$\alpha = \alpha' = -0.091 \pm 0.002$	(7)
	627.4 ± 0.3	$\beta = 0.373 \pm 0.016$	(33)
		$\delta = 4.44 \pm 0.18$	
	627.4	$\gamma = 1.34 \pm 0.01$	(34)
Iron	1041.25 ± 0.03	$\alpha = \alpha' = -0.09 \pm 0.005$	(7)
	1042.01 ± 0.3	$\beta = 0.34 \pm 0.02$	(35)
	1044.0	$\gamma = 1.333 \pm 0.015$	(36)
Gd (past measurements)	291.20 ± 0.05	$\alpha = -0.09 \pm 0.05$	(37)
		$\alpha' = -0.32 \pm 0.05$	
	292.05 ± 0.15	$\beta = 0.370 \pm 0.10$	(33)
		$\delta = 4.39 \pm 0.10$	
	292.5 ± 0.5	$\gamma = 1.33$	(38)
	292.5 ± 0.02	$\alpha = \alpha' = 0$ (From c-Axis expansivity data)	(39)
Gd (This experiment)	293.3315 ± 0.0045	$\alpha = -0.1139 \pm 0.001$	c-Axis expansivity
		$\alpha' = -0.3858 \pm 0.0042$	
	293.3753 ± 0.0144	$\alpha = -0.04793 \pm 0.00207$	a-Axis expansivity
		$\alpha' = -0.2215 \pm 0.0078$	
THEORY	HIGH TEMPERATURE SERIES EXPANSION ^a	RENORMALIZATION GROUP ^a	
3-dim Heisenberg model	$\alpha = -0.09 \pm 0.04$	$\alpha = -0.10$	
	$\beta = 0.36 \pm 0.025$	$\beta = 0.389$	
	$\delta = 4.8 \pm 0.3$	$\delta = 4.46$	
	$\gamma = 1.375 \pm 0.02$	$\gamma = 1.325$	

^aSee the text.

of the data near T_C , thus obscuring the critical behavior. It should be apparent from Table 2 that the specific heat, magnetization, critical isotherm, and isothermal susceptibility exponents α , β , δ , and γ are in good agreement for iron, nickel, and gadolinium. The exponent α' has the same value as α for iron and nickel but not for gadolinium. Also the exponents α and α' , as measured by the c-axis linear thermal expansivity (Cadieu and Douglass³⁹), do not have the same values as obtained from the specific heat measurements (Lewis³⁷). However, the results of the c-axis linear thermal expansivity measurements for this experiment do seem to give the same exponents as obtained from the specific heat measurements, but the a-axis linear thermal expansivity measurements do not.

Comparison with theory

Table 2 also lists the calculated exponents for the three dimensional Heisenberg model as calculated by the two techniques discussed previously. It should be apparent that the measured values of α , β , γ , and δ for iron, nickel, and gadolinium are in good agreement with this model calculation. This is a rather striking verification of universality since the exchange mechanism in iron and nickel is basically different from that in gadolinium.

The scaling theory prediction that $\alpha=\alpha'$ appears to be verified for iron and nickel but not for gadolinium. Since rounding in the gadolinium specific heat data³⁷ occurred at $|T-T_C| \sim 0.5$ K on the $T < T_C$ side of the transition, the region where $\alpha=\alpha'$ may be valid may have been inaccessible.

Indeed, the c-axis linear thermal expansion coefficient obtained in this experiment does seem to have $\alpha=\alpha'$, but only for data with $|T-T_C| < 0.3$ K on the $T < T_C$ side of the transition (see Chapter IV).

The predicted proportionality between the specific heat and the c-axis linear thermal expansivity data due to Cadieu and Douglass³⁹ does not appear to exist. However, since no apparent attempt was made by them to fit an equation, other than a logarithmic one, to the expansion data, this discrepancy may not be real.

This experiment

Much higher purity crystals of gadolinium now are available due to the recent application to gadolinium of the electrotransport method of purification.⁴⁰ There was the hope that these higher purity crystals would show less rounding and would allow investigations closer to T_C than previously was possible.

Thermal expansivity measurements are technically easier to perform near a phase transition than specific heat measurements and in addition critical point expansivity measurements could be made on both c and a-axis crystals. From the presumed proportionality between the specific heat and the linear thermal expansivity, it was hoped that this experiment would give further information regarding the exponents α and α' .

Experimental Method

Kroeger⁴¹ has summarized the various techniques presently employed for the measurement of the linear thermal expansion coefficient. Past

x-ray measurements^{25,42} of the lattice parameters of gadolinium indicate the relative length changes involved in the temperature range 270 K to 320 K are approximately -0.1% and +0.05% for c and a-axis crystals. Near the Curie temperature (~293 K), the magnitude of the linear expansion coefficient for a c-axis crystal is approximately 10^{-4} K^{-1} .^{39,42} In order to obtain reliable data within 30 mK ($|\epsilon| \sim 10^{-4}$) of T_C , temperature intervals of 10 mK or less must be employed, with relative length changes of roughly 10^{-6} . For 0.1% accuracy, this requires a relative length change sensitivity of 10^{-9} (0.1 Å for a 1 cm sample).

The required sensitivity can be achieved with a 3-terminal capacitance dilatometer of the type developed by White.^{43,44} Basically, the dilatometer is a shielded parallel plate capacitor with one plate fixed and the other attached to the sample. The capacitance, C, for parallel plates of area, A, and separation, g, is

$$C = \frac{\epsilon_0 A}{g}, \quad (1-39)$$

where ϵ_0 is the permittivity of free space, with a sensitivity to gap changes given by

$$\frac{\Delta C}{\Delta g} = - \frac{\epsilon_0 A}{g^2} = - \frac{C}{g}. \quad (1-40)$$

Three common geometries for capacitance dilatometers are in Figure 2. Each geometry is a 3-terminal configuration since the capacitors are completely shielded with the effective area of the plates determined by a

Figure 2. Common three-terminal capacitance dilatometer geometries.

grounded guard ring (which includes the dilatometer body) as the third terminal. An ac 3-terminal capacitance bridge which employs ratio transformers (see Chapter 11) is capable of measuring 10 pF capacitances with a precision of 10^{-7} pF. For a 10^{-2} cm gap, g , Eqn. (1-40) implies that this bridge can sense gap changes of $g \sim 0.01 \text{ \AA}$. In both the normal and inverted geometries (Fig. 2), the thermal expansivity of the sample is measured relative to the dilatometer body (usually copper) since the entire dilatometer-sample system changes temperature together. For sample expansivities with the same magnitude as that of copper, or for limited temperature intervals, the normal geometry is most useful. When the sample expansivities are much greater than that of copper and measurements are desired at low temperatures, the inverted geometry is most useful. In the absolute geometry, only the sample changes temperature and hence the thermal expansion coefficient is determined absolutely.

Since the Curie temperature of gadolinium is about 293 K and since an absolute thermal expansion measurement holds no real advantage over a relative measurement to determine critical point exponents, a modified normal geometry was used in this experiment (see Chapter 11).

It is difficult to obtain the perfectly parallel plates experimentally so that Eqns. (1-39) and (1-40) can be used precisely, and in general, a tip angle always exists between the plates. Tilford⁴⁵ has calculated the capacitance, C , of nonparallel plates of area, A , average separation, g , and tip angle, θ , as

$$C = \frac{2\pi\epsilon_0 g}{\sin^2 \theta} \left\{ 1 - \left[1 - \frac{A \sin^2 \theta}{\pi g^2} \right]^{\frac{1}{2}} \right\}, \quad (1-41)$$

or to first order in $\sin^2 \theta$,

$$C \approx \frac{\epsilon_o A}{g} \left\{ 1 + \frac{A \sin^2 \theta}{4\pi g^2} \right\} \quad (1-42)$$

It may be noted from this equation that for small θ , changes in capacitance can be related to gap changes by the parallel plate Eqn. (1-39) to good precision as long as θ does not change significantly with temperature. However, if such changes are significant, Eqn. (1-41) should be used.

CHAPTER 11. APPARATUS

This chapter describes the hardware and electrical equipment used in this experiment. A general description of the dilatometer and vacuum system will be followed by more detailed descriptions.

The actual capacitance dilatometer is similar to the normal geometry dilatometer sketched in Figure 2. Since it must be isothermal to 10^{-6} K close to T_C , it is surrounded by three isothermal shields (Figure 3), labeled No. 1, No. 2, and No. 3, respectively, with the degree of temperature control becoming more sophisticated the closer the shield is to the dilatometer. The outer dewar is used primarily as a support for the dilatometer system and provides no other function. It as well as the space between it and shield No. 1 are left at atmospheric pressure.

Shield No. 1 (S#1) is roughly at room temperature and shield No. 2 (S#2) is cooled to -10^0 C with the thermoelectric coolers. A water cooling line removes the exhaust heat from these coolers. The temperature of S#2 is controlled to ± 5 mK. Shield No. 3 (S#3) is controlled at a temperature which is within a few millikelvin of the dilatometer using a differential temperature controller, while the primary temperature control for the system is on the dilatometer itself.

Vibration isolation is achieved by mounting the dewar on inner tubes, and by using flexible stainless steel tubing on the pumping lines. The Helmholtz coils were used to reduce the earth's magnetic field to less than 8×10^{-7} weber/m² (8×10^{-3} gauss) at the sample location.

Figure 3. Basic vacuum and dilatometer system. The vacuum spaces are labeled 1, 2, and 3.

Vacuum and Refrigeration System

Shield No. 1 (S#1)

This shield was constructed using 6.5 in. outer diameter, 0.063 in. thick brass pipe. The flanges are made from brass, while the bottom plate is made from copper. The total length of S#1 is 25 in.

As can be seen in Figure 3, S#1 has a brass ring soldered into the top flange which enables it to be placed in the outer dewar. The cooling water lines and electrical leads for the coolers pass through holes in this ring.

The bottom flange is demountable to give access to the coolers. A detail of the bottom flange and cooler configuration is shown in Figure 4. Two flexible copper cooling coils may be stretched to remove the clamping screws for the coolers. The cooling coil solders into a right-angle feedthrough which mates with a length of copper tubing outside of S#1.

Vacuum space 1 (Figures 3 and 4) is evacuated by a 0.33 h.p. mechanical vacuum pump (Welch Scientific Co. R-1405). The pressure in this space (roughly one micron) is monitored by a thermocouple gauge (Varian type 501) located on the pumping line.

Refrigeration

The mounting configuration of the thermoelectric coolers is shown in Figure 4. The coolers (Borg and Warner model 930-71) are capable of establishing a temperature difference of 68°C at no load or can transfer 19 watts with zero temperature difference. In practice, S#2 can be cooled to -16°C with a water flow of 0.5 gallons/min maintained in the cooling coil.

Figure 4. Detail of the bottom flange of Shield No. 1 and the mounting configuration for the thermoelectric coolers on the bottom of Shield No. 2. Only one feedthrough is shown.

The coolers are clamped between a 0.25 in. thick copper plate and the bottom of S#2 with stainless steel screws and Nylon washers. An 8 in. section of the cooling coil is soldered to the lower or clamping plate.

Figure 4 shows one of the two electrical feedthroughs used for the thermoelectric coolers. Each feedthrough has two 16 gauge copper wires potted in a Stycast (Emerson and Cummings, 2850 GT) cylinder which is located on the end of a 0.25 in. stainless steel tube.

Shield No. 2 (S#2)

Figure 5 is a sketch of S#2 and the interior of the apparatus. This shield was constructed from a 5 in. diameter 0.125 in. thick copper pipe. The flange is made from brass, while the bottom plate is copper. S#2 is suspended 8.6 in. below the top flange of S#1 and has an assembled length of 13.5 in.

An 89.4 ohm heater is wound noninductively in a spiral band over the length of the wall. Thirty feet of Manganin wire was wound on a nylon mesh base and glued down with Stycast. A copper clamp for the temperature control sensor is epoxied with stycast between heater bands at the middle of the shield. Electrical tie points, located as indicated in Figure 5, are copper strips which are separated from S#2 by a nylon mesh and glued down with Stycast.

All of the wiring for the temperature control sensor and heater for S#2 pass through a 7 pin glass-to-metal seal (Electrical Industries #73SFR/40W-RP-P7A) which is located on a stand-off on the top flange of S#1 (Figure 3).

Figure 5. Detail of Shield No. 2 (S#2) and the interior of the apparatus. Shield No. 3 (S#3) and the dilatometer are shown.

Vacuum Space 2 (Figures 3 and 4) is evacuated by an air cooled oil-diffusion pump (Consolidated Vacuum Corp. MCF 60-05) which is backed by a 1 h.p. mechanical pump (Welch model 1376). The pressure in space 2 (less than 0.1 micron) is monitored by a thermocouple gauge and an ionization gauge (National Research Corp. type 507) located on the pumping line to space 2.

Shield No. 3 (S#3)

This inner-most shield is constructed from 4.13 in. diameter, 0.125 in. thick copper pipe. With the copper bottom plate and brass flange, S#3 has a total length of 9.5 in. and is suspended 2.5 in. below S#2 by four stainless steel tubes, of which two are 0.5 in. diameter and two are 0.25 in. diameter.

A 124.8 ohm, Manganin heater is wound noninductively on S#3 in the same manner as for S#2. A temperature control sensor clamp and electrical-tie points are located as indicated in Figure 5. The wiring for the temperature control sensor and heater pass through a 7 pin glass-to-metal seal which is located on the pumping line to space 2 (Figure 3).

Vacuum Space 3 is evacuated with the same mechanical-diffusion pump system used for space 2. The pressure is monitored by a thermocouple gauge on the pumping line to space 3.

Capacitance Dilatometer

The dilatometer design shown in Figures 6 (side view) and 7 (top view) is a modification of the normal geometry (Figure 2) in which the differential expansion between the sample and dilatometer body (cell)

Figure 6. A side-view cross section of the dilatometer and sample.

Figure 7. A top-view cross section of the dilatometer.

is measured by a guarded 3-terminal parallel plate capacitor. The low side of the capacitor is balanced on the sample by six 0.012 in. stainless steel wires of which only two are shown in Figure 6 and which have locations as indicated in Figure 7. Four of the wires act as a rigid hinge, so that the motion of the low side is on the arc of a circle rather than purely vertical. Four guarded high side capacitor plates, only two of which are shown in Figure 6, while all four are indicated by the solid circles in Figure 7, measure the average gap and can be used to calculate the angle of tip between the high and low sides. The effect of changing tip angle on the calculation of the thermal expansion will be discussed in the data analysis section (Chapter III).

The capacitance dilatometer is constructed from electrolytic tough pitch copper (except for the brass top flange and adjustment sleeve) which was vacuum-annealed at 300° F for four hours after the pieces were machined. The copper pieces all were gold-plated to avoid unstable oxide formation and to promote thermal contact in the dilatometer joints. The following subsections describe some parts of the dilatometer in detail.

Dilatometer body or cell

The capacitance cell consists of a copper cylinder to which a top plate containing the high sides and a base plate is bolted (Figure 6). The cylinder is 2 in. diameter, 0.25 in. thick, 1.25 in. tall and has two windows (Figure 7) of height 0.75 in. and width 1 in. for access when installing a sample. These windows are covered with a 0.010 in. thick copper shield which bolts to the top flange of the dilatometer. The cell

base has an A-701 epoxy-filled gap of width 0.004 in. which electrically isolates the central part of the base from the rest of the cell. This central part of the base makes electrical connection with the suspended capacitor low side plate through the center post and sample.

Capacitor high-sides

As shown in Figure 7, three side plates (labeled side A, side B, and side C) are spaced at 120° intervals on a radius of 0.4375 in. around a central plate. The high sides are electrically isolated from the cell by an epoxy-filled (Armstrong A-701) gap of width 0.004 in. The effective areas of these plates (including half the gap to correct for field perturbations⁴⁶) were measured with a traveling microscope. For each of four different diameters, ten measurements were taken for the central plate and five measurements for each side plate. Each area was calculated as the area of a perfect circle with a diameter equal to the average of all the diameter measurements. The results are shown in Table 3.

The electrical connections to the high sides (Figure 6) are screwed to the top side of the plates. Gold-plated female pins soldered into the screws mate to male pins soldered to the center conductor of coaxial cables. A cylinder of Stycast is potted around the male pin and the end of the cable shield. The coaxial cable (Uniform Tubes UT-34SS) has a stainless steel outer conductor (0.034 in. diameter) and an inner conductor of 0.008 in. diameter, silver-plated, copper-clad, steel wire; the dielectric is T.F.E. teflon. These cables pass through a solder seal on the top of S#2 and then through a Stycast feedthrough on the top of S#1 (Figure 3).

Table 3. Results of traveling microscope measurements of the effective radii and areas of the capacitor high-side plates.

PLATE	Average RADIUS (cm.)	R.M.S.D. ^a (PERCENT)	Average AREA (cm. ²)	R.M.S.D. ^a (PERCENT)	Average GAP (cm.)
Central	0.6298	0.045	0.2459	0.09	0.0095
Side A	0.1589	0.12	0.07935	0.24	0.0107
Side B	0.1591	0.13	0.07950	0.26	0.0113
Side C	0.1593	0.15	0.07972	0.30	0.0108

^aR.M.S.D. = Root Mean Square Deviation.

Capacitor low side assembly

The capacitor low side assembly was machined from a single piece of copper in the shape of a circular table with three legs. This geometry is necessary so that a sample can be mounted in the cell. The table top is 0.125 in. thick and 1.25 in. in diameter. The 0.625 in. long legs, of which one is shown in Figure 6, have locations as indicated in Figure 7 and are spaced 120° apart on a radius of 0.313 in. The suspension wires are potted in stycast insulators which are inserted in the legs of the low side.

The low side coaxial cable connects to the central post of the cell base (and hence to the capacitor low side) in a similar manner to the high side cables and passes through a solder seal on S#2 and stycast seal on S#1 (Figure 3).

Center post and adjustment sleeve

A sliding copper post (Figure 6) forms a pedestal for the sample which can be adjusted to hold samples up to 1.125 in. long. This post is 0.325 in. diameter and 1.625 in. long. A 0.065 in. square groove milled in the side of the post serves as a guide to prevent rotation. The post is clamped with a plastic-tipped screw on the opposite side of the groove.

The brass adjustment sleeve bolts to the central part of the cell base. The micrometer in the base of the sleeve can be used to raise or lower the central post to obtain an appropriate capacitor gap (usually 0.004 in.). Once the gap is set, the adjustment sleeve is removed.

Thermometry and heater block

A 0.375 in. curved copper block bolts to the side of the cell. Two holes (Figure 7) are drilled vertically through the block, one to contain a primary temperature sensor and the other to contain two temperature control sensors. Two 50 ohm wire-wound resistors in copper clips are epoxied with Stycast to the edges of the block. A piece of 25 conductor ribbon cable was epoxied with Stycast to the block to provide electrical tie points for the sensors and heater wiring. The dilatometer wiring passes through glass-to-metal seals located on the pumping line for space 3 (Figure 3).

Capacitance Measurements

Two 3-terminal bridges were employed for the measurement of capacitances. One is a type 1615A General Radio capacitance bridge (GR Bridge). The other is a more sensitive bridge, suggested by Campbell⁴⁷ and developed by Thompson.⁴⁸ This bridge is of local construction and will be referred to as the Thompson bridge. Both bridges have the same basic design and employ identical oscillators (operated at 1078 hz) and null detectors.

A schematic diagram of the basic 3-terminal bridge is shown in Figure 8. The 3-terminals referred to in the bridge name are the capacitor high side (attached to the transformer), low side (attached to the detector), and guard shield (grounded to the transformer center top). The guard

AT BALANCE $V_x j\omega C_x = V_s j\omega C_s \Rightarrow C_x = C_s \frac{V_s}{V_x}$

----- SHIELD

Figure 8. The basic three-terminal capacitance bridge.
The dotted lines indicate electrostatic shielding.

shield-to-low side capacitance shunts the detector and the guard shield-to-high side capacitance shunts the transformer. Therefore, these capacitances have no effect on the bridge balance.

In order to measure the main and side plate capacitances (Figures 6 and 7) with respect to a common low side, a switching arrangement was employed to select the appropriate high side while grounding the high sides not being measured. These grounded plates then become part of the low side-to-guard shield capacitance. The ratio transformer adjusts the voltage across the standard capacitor C_s and balance is achieved when the currents through C_s and the unknown capacitor C_x are equal. This gives the balance condition indicated in Figure 8.

The theoretical relationship between the bridge voltage sensitivity, δV , and the capacitance sensitivity, δC , is

$$\frac{\delta V}{V} \approx \frac{\delta C}{C_c} \quad (11-1)$$

where V is the oscillator voltage and C_c is the shield-to-low-side shunt capacitance (usually several thousand pF). The GR bridge capacitance sensitivity is limited by voltage noise in the bridge (see next section) while the Thompson bridge capacitance sensitivity is limited by the voltage sensitivity of the detector. The null detectors used for both the GR bridge and Thompson bridge are dual-phase lock detectors identical to the one described by Kroeger,⁴¹ and have ultimate voltage sensitivity of

$\delta V \sim 2 \text{ nV}$. For the Thompson bridge $C_C \sim 2000 \text{ pF}$ and $V \sim 50 \text{ volts r.m.s.}$ so that Eqn. (11-1) implies $\delta C \sim 10^{-7} \text{ pF}$. For a nominal 10 pF capacitor this represents a relative sensitivity of 10^{-8} .

GR bridge

This bridge uses ten taps on the main transformer to provide ten voltage steps across six reference capacitors (10^{-4} pF , 10^{-3} pF , ..., 10 pF) to give six decades of bridge balancing. The off-balance from the detector is fed to a chart recorder (Moseley, type 7100B) and one further digit can be estimated.

The conductive component of the signal (quadrature) was balanced by an external conductance "T" since the losses of the unknown capacitances were too small (conductances $< 2 \text{ pmhos}$) to be balanced by the existing GR bridge quadrature balancing network.

A thermostated (to $\pm 1 \text{ mK}$) reference capacitor (General Radio type 1403-G, 10 pF) was monitored to document time-dependent drifts. These were found to be as large as $5 \times 10^{-5} \text{ pF}$ in a period of 24 hours, and presumably were due to room temperature changes, since the internal bridge standards are not temperature controlled. The temperature coefficient of the 10 pF bridge standard is $5 \text{ ppm/}^\circ\text{C}$ so a 1°C change in room temperature could give rise to the observed effects. In an attempt to remove these effects, the thermostated reference (C_R) was measured for each set of sample capacitances (C_M , C_A , C_B , C_C) which were then divided by the reference measurement and multiplied by the calibrated value of C_R (10 pF).

The circuit noise was about $0.1 \mu\text{V}$ peak to peak for this bridge. Since $C_c \sim 1000 \text{ pF}$ and $V \sim 30 \text{ V r.m.s.}$ (Eq. 11-1), this corresponds to a limit on the capacitance sensitivity for this bridge of 10^{-6} pF . The accuracy of the capacitance readings as indicated by measurements on the thermostated reference was approximately 0.02%.

Thompson bridge

The GR bridge did not have sufficient sensitivity and stability to be able to use 10 mK temperature intervals near the Curie point in gadolinium, since the capacitance changes had to be measured to 10^{-7} pF . A Thompson bridge, capable of this sensitivity, was located in an adjoining room to where this experiment was performed. Due to the immovable nature of the bridge standards for this instrument, coaxial cables 50 feet long were used to connect the dilatometer and the bridge.

The Thompson bridge is shown in Figure 9 and is discussed in detail by Kroeger.⁴¹ This bridge employs two ratio transformers and 100 pF and 0.1 pF standard capacitances to give nine decades of capacitive balancing. Another ratio transformer, with a 90° phase-shifted output, is employed for the quadrature balancing.

This bridge has two basic advantages over the GR bridge:

- (1) The standards are temperature-controlled to give capacitance stability at the 10^{-8} pF level.^{45,49}
- (2) The bridge linearity depends on ratio-transformers rather than the matching of many different capacitors.

SHIELDS ARE NOT SHOWN

Figure 9. Detailed circuit schematic of the Thompson bridge for three terminal capacitance measurements.

Thermometry and Temperature Control

Temperature measurement and control sensors all are platinum resistance thermometers (PRT's). The primary measurement sensor (located on the cell in Figures 6 and 7) is a Leeds and Northrup 25 ohm element (NBS type, model No. 8164, serial No. 1676930) calibrated by the National Bureau of Standards on the International Practical Temperature Scale of 1968. All control sensors (Figures 5 and 7) are 100 ohm (De Gussa model No. W63-01) elements.

Temperature measurement

A double ac potentiometer or Anderson bridge⁵⁰ was built to measure the resistance of the 25 ohm PRT. A schematic diagram of this bridge is shown in Figure 10. A constant amplitude voltage, V_1 , across the resistance R_S is provided by the operational amplifier (Analog Devices 118 K). This results in a constant amplitude current in the 25 ohm PRT (R_T),

$$I = V_1 / R_S. \quad (11-2)$$

The ratio transformer provides a fraction x of V_2 which can be made equal to the voltage across R_T , giving the balance condition:

$$x V_2 = V_1 (R_T / R_S) \quad (11-3)$$

The transformer T_1 has a 100 turn primary and two 100 turn secondaries which are wound on a supermalloy tape-wound toroid core (Arnold Engineering 6T6100-S2-AA). The secondaries are electrostatically shielded

Figure 10. Schematic diagram of the four terminal ac resistance bridge.

from the primary by a grounded layer of copper tape. The primary inductance is approximately 0.5 Henries and the voltage outputs of the two secondaries have amplitudes equal to 2×10^{-5} with a phase difference of six microradians. Taps on the secondaries allow multiples of the ratio V_2/V_1 from 0.1 to 10. Usually the full secondaries are employed to give $V_1 = V_2$.

Commercially available ratio transformers have a maximum of seven digits available. In order to obtain ten digits, two seven dial ratio transformers (Gertsch AC Ratio Standard, model 1011, serial Nos. 120 and 272, ± 0.2 ppm ratio accuracy) are connected in parallel and the output of one is stepped down with a 1000-1 transformer.⁵¹

Transformer T_2 (Triad G-10) is the input transformer for the detector. It has a primary inductance of eight Henries and a turns ratio of 1 to 37.7. The null detector is a narrow-band amplifier and dual phase lock-in detector of the same type used in the capacitance bridges.

The oscillator (Optimation model AC-15, modified for constant current output, 0.01% amplitude and frequency stability) is set to drive 1 mA r.m.s. into the primary of T_1 (producing 1 volt r.m.s. in both secondaries) at 270 hz.

The standard resistance R_S is a four terminal resistor (Electro-science Industry Inc., model No. RF4-R) with a calibrated resistance of 999.995 ± 0.005 ohms. A second standard resistance R_S^I (not shown in Figure 10) of the same type has a value of 99.9977 ± 0.0005 ohms and is in series with R_T . Both R_S and R_S^I are temperature controlled to ± 1 mK.

Bridge stability

In general, the bridge was operated with $V_1 = V_2 = 1$ volt r.m.s. to give a current of 1 mA r.m.s. in R_S , R_S^1 , and R_T . The ratio R_S^1/R_S appears to drift 0.02 ppm in a 24 hour period. Since R_S and R_S^1 both are temperature controlled and presumably have similar temperature coefficients, this drift was attributed to thermal effects in the ratio transformers. By calculating the resistance R_T in terms of R_S^1 ,

$$R_T = \frac{(R_T/R_S)}{(R_S^1/R_S)} R_S^1 \quad (11-4)$$

the effect of bridge drift hopefully is removed.

Bridge sensitivity

Circuit noise is about 3 nV peak to peak at the detector, giving an ultimate voltage sensitivity of 1 nV. This corresponds to a temperature sensitivity of 10 microkelvin as measured by R_T .

Bridge accuracy

Although R_T has a calibration accurate to 0.1 mK, the actual temperature accuracy is limited by the calibration of R_S^1 if R_T is calculated from Eqn. (11-4). Since R_S^1 is calibrated to ± 5 ppm, the temperature can only be accurate to

$$\Delta T \approx \frac{1}{0.004} \frac{\Delta R}{R} \approx \pm 1 \text{ mK} . \quad (11-5)$$

Figure 11. dc Wheatstone resistance bridge.

S#2 temperature control

The dc Wheatstone bridge in Figure 11 was used to sense the temperature. The two Manganin potential leads of the PRT are matched to have the same resistance R_L and are kept in the same thermal environment. A third lead supplies current to the PRT. In this configuration, the balance condition for the bridge is

$$(R_T + R_L)100 \, \Omega = (R_S + R_L)100 \, \Omega \quad (11-6)$$

and the PRT lead resistances cancel. The null detector is a dc amplifier circuit which consists of two operational amplifiers (Fairchild UA-741) and has a maximum sensitivity of ± 1 microvolt (corresponding to ± 2.5 mK in temperature) with a power supply voltage of 0.5 V.

The detector output is fed to the integral-proportional controller circuit shown in Figure 12. A proportional amplifier gives quick response V_A while an integrator gives slow response V_B to changes in V_{IN} . The integrator also produces a constant V_B for $V_{IN} = 0$. An adder sums V_A and V_B and a diode on the output provides a shutoff for negative voltages, V_C , at the adder output. The output V_{OUT} of the controller is used to slave a programmable power supply (Lambda LP-521-FM) which operates the thermoelectric coolers (Figures 3 and 4). Control is usually maintained to ± 5 mK.

$$V_A \approx (1 + R_2/R_1) V_{IN}$$

$$V_B \approx \int V_{IN} dt / R_3 C$$

$$V_C \approx -(V_A + V_B)$$

$$V_{out} \approx \begin{cases} V_C, & V_C > 0 \\ 0, & V_C < 0 \end{cases}$$

Figure 12. Circuit schematic of the integral-proportional temperature controller.

Figure 13. A simple four-terminal ac resistance bridge as used to monitor either the dilatometer, or the dilatometer-S#3 temperature difference via R_T .

Dilatometer temperature control

The ac bridge shown in Figure 13, which monitors the dilatometer, uses a temperature controlled (to ± 1 mK) decade box and an effective 1 ohm ten turn potentiometer as the reference R_S . The signal across the dilatometer PRT, R_T , is inverted by the transformer T_A (Singer model No. ST-248B) and is compared with the signal across R_S .

The oscillator (Hewlett Packard 204C), operated at 445 hz with a signal level of 0.25 V r.m.s., is synchronized to the reference signal of the lock-in amplifier (Princeton Applied Research model 120). The detector input transformer T_B (Triad G-10) has a turns ratio of 1 to 18.8. The detector output is fed to an integral-proportional controller (Figure 12), with a current-amplified output (Figure 14), which powers the dilatometer heater resistors (Figures 5 and 7). The cell temperature is controlled to ± 5 microkelvin.

S#3 temperature control

A second ac bridge, identical with that shown in Figure 13, was used with a PRT (R_T) on S#3 and a second PRT (R_T^1) on the dilatometer as the reference resistance. This configuration senses the temperature difference between S#3 and the dilatometer. A seven dial ratio transformer (Gertsch model 1011) across R_T^1 is used to achieve the bridge balance. The oscillator (Hewlett Packard 3311-A) is operated at 380 hz with a signal level of 0.28 V r.m.s. The detector (Princeton Applied Research model 186) has adequate sensitivity so that an input transformer T_B is not necessary. An integral proportional controller (Figure 12) with a current amplified output (Figure 14) is used to power the heater on S#3 (Figure 5).

Figure 14. Schematic circuit of the current amplifier used in conjunction with the integral-proportional controller (Figure 12) to power the heaters on S#3 and the dilatometer.

Since R_T and R_T^I are not identical PRT's, the isothermal ratio R_T/R_T^I was determined in-situ as a function of the dilatometer temperature by adjusting the ratio transformer setting until the dilatometer controller power dropped to zero. The ratio R_T/R_T^I varied from 1.001 to 1.003 in the temperature range 270 K to 320 K. During the gadolinium measurements, the ratio R_T/R_T^I was set so that $T_{\text{dilatometer}} - T_{S\#3} \approx 5 \text{ mK}$. This temperature difference was controlled to better than $\pm 0.1 \text{ mK}$.

Gadolinium Crystals

Both the c and the a-axis gadolinium crystals were grown by B. J. Beaudry at this laboratory using the recrystallization or grain growth method developed by Nigh.⁵² Ninety gram arc-melt buttons are heated to 1175°C for 40 hours to achieve grain growth.

c-Axis crystal

One large grain from an arc-melt button was aligned parallel to the c-axis, cut, and ground to a cylinder of length 1.3 cm and diameter 0.6 cm. The purity analysis of this crystal is shown in Table 4.

This crystal then was electrotransported⁴⁰ by F.A. Schmidt to remove carbon, nitrogen, and oxygen impurities. In this process, polycrystalline rods of gadolinium of the same purity are butt-welded to the crystal and a current density of approximately 524 amp/cm^2 is passed through the rod for 913 hours in a 135 Torr helium atmosphere, with the crystal temperature roughly 1200°C . After the process is complete, the crystal-polycrystal

Table 4. Impurity analysis of c-Axis gadolinium (Spark source mass spectrographic analysis except as noted.).

ELEMENT	ATOMIC PPM	ELEMENT	ATOMIC PPM	ELEMENT	ATOMIC PPM
H	9.	Zn	0.1	Pr	0.21
Li	< 0	Ga	< 0.1	Nd	2.
Be	< 0.01	Ge	< 0.2	Sm	≤ 0.4
B	0.01	As	< 0.1	Eu	≤ 0.08
C	28. ^a	Se	< 0.5	Tb	6.
N	23. ^b	Br	< 0.1	Dy	≤ 0.6
O	59. ^b	Rb	< 0.05	Ho	≤ 0.2
F	3. ^c	Sr	< 0.1	Er	≤ 0.4
Na	0.2	Y	2.2	Tm	< 0.3
Mg	< 1.	Zr	0.2	Yb	≤ 2.
Al	0.4	Nb	≤ 3.	Lu	4.
Si	≤ 0.2	Mo	< 2.	Hf	≤ 0.5
P	≤ 0.05	Ru	< 0.8	Ta	6.
S	≤ 0.5	Rh	< 0.2	W	4.
Cl	4.	Pd	< 0.4	Re	< 0.8
K	-----	Ag	< 0.1	Os	< 2.
Ca	≤ 0.2	Cd	< 0.1	Ir	< 3.
Sc	0.1	In	0.05	Pt	0.4
Ti	≤ 0.3	Sn	< 0.04	Au	0.04
V	≤ 0.5	Sb	< 0.08	Hg	< 0.2
Cr	1.	Te	< 0.1	Tl	< 0.4
Mn	0.04	I	< 0.06	Pb	0.08
Fe	40.	Cs	< 0.04	Bi	< 0.08
Co	0.04	Ba	< 0.08	Th	≤ 2.
Ni	1.	La	0.73	U	< 0.2
Cu	4.	Ce	1.2		

^aCombustion analysis.^bVacuum Fusion analysis.^cAbsorption analysis.

welds are cut and the crystal electropolished. A crystal of similar initial purity and processed in the same manner had a resistivity ratio of

$$\frac{R(273 \text{ K})}{R(4.2 \text{ K})} \approx 300 .$$

The final crystal was found to have slightly rounded ends and a length of 0.4584 ± 0.0002 in. at 24° C .

a-Axis crystal

Another arc-melt button with the purity analysis given in Table 5 had a large a-axis grain which was cut into a cylinder 1.6 cm long and 0.6 cm in diameter. This crystal was annealed at 800° C for two hours and electropolished to obtain sharp x-ray patterns. The crystal was found to have irregular ends so these were gently polished flat and perpendicular to the length. The crystal then was electropolished twice. The final length of the crystal was found to be 0.6005 ± 0.0001 in. at 24° C . This crystal was not electrotransported due to time limitations.

Table 5. Impurity analysis of a-Axis gadolinium (Spark source mass spectrographic analysis, except as noted.).

ELEMENT	ATOMIC PPM	ELEMENT	ATOMIC PPM	ELEMENT	ATOMIC PPM
H	5. ^a	Zn	0.04	Pr	4.5
Lq	< 0.05	Ga	< 0.03	Nd	< 0.7
Be	< 0.000	Ge	< 0.07	Sm	< 0.05
B	< 0.1	As	< 0.02	Eu	< 0.2
C	9. ^b	Se	< 0.2	Tb	2.0
N	3. ^a	Br	< 0.08	Dy	< 0.6
O	35. ^a	Rb	0.001	Ho	0.3
F	20. ^c	Sr	0.02	Er	0.7
Na	40.	Y	20.	Tm	0.1
Mg	0.07	Zr	< 0.2	Yb	0.6
Al	< 2.	Nb	< 6.	Lu	< 0.3
Si	2.7	Mo	< 0.5	Hf	< 0.7
P	0.09	Ru	< 0.2	Ta	0.3
S	< 0.07	Rh	< 0.05	W	7.
Cl	0.4	Pb	< 0.1	Re	< 0.3
K	< 0.07	Ag	0.05	Os	< 0.5
Ca	< 1.	Cd	< 0.05	Ir	< 0.3
Sc	0.39	In	< 0.03	Pt	< 0.4
Ti	9.7	Sn	< 0.08	Au	< 0.04
V	0.2	Sb	< 0.03	Hg	< 0.07
Cr	5.8	Tc	< 0.05	Tl	< 0.03
Mn	0.02	I	< 0.03	Pb	< 0.1
Fe	40.	Cs	< 0.003	Bi	< 0.02
Co	< 0.02	Ba	0.2	Th	< 0.5
Ni	0.6	La	1.2	U	< 0.2
Cu	3.4	Ce	1.4		

^aVacuum Fusion analysis.^bCombustion analysis.^cAbsorption analysis.

CHAPTER III. PROCEDURE AND DATA ANALYSIS

Experimental Procedure

Crystal mounting and low side adjustment

Since the motion of the capacitor low side is on the arc of a circle, the sample must be free standing and able to rotate slightly about a horizontal axis. The c-axis crystal had slightly rounded ends and could be installed as is, but the a-axis crystal had flat ends so rounded copper caps, held in place with stainless steel split rings, were mounted on the sample and centerpost.

The sample was held in place with forceps while adjusting the centerpost until contact was made with the capacitor low side. The micrometer then was adjusted until the central plate capacitance C_m was approximately 10 pF, which corresponded to a gap of approximately 0.004 in., after which the centerpost was clamped in place and the adjustment sleeve removed.

The low side suspension wires were adjusted until the angle of tip between the low side and the high sides was less than 0.05 milliradians, as determined by the side plate capacitances C_A , C_B , and C_C .

Initial cooldown

After the apparatus was assembled, vacuum spaces 1 to 3 (Figure 3) all were evacuated. Spaces 2 and 3 then were backfilled with approximately 100 microns of helium gas and the thermoelectric coolers switched on. A period of 24 hours was required for S#2, S#3, and the dilatometer to be

cooled to approximately -10°C . After this was accomplished, space 2 was evacuated to about 0.1 micron and temperature control was initiated on S#2.

Data acquisition

Each set of data consisted of the resistance R_T of the primary PRT on the dilatometer (and hence the temperature) and measurements of the main and side plate capacitances C_M , C_A , C_B , and C_C . The procedure used for taking a data set is as follows. After one set of data is taken, the dilatometer temperature controller is reset to the next temperature and S#3 is brought to within 5 mK of the dilatometer and controlled to ± 0.1 mK after dilatometer control has been established to ± 5 microkelvin. This process takes anywhere from 15 minutes to an hour, corresponding to temperature changes of 0.01 K to 2.5 K. A period of 0.5 to 2 hours then is required for the sample, dilatometer, and S#3 to come to thermal equilibrium. This is indicated by minimal drifts in C_M with time.

Two consecutive data sets (R_{T1} , C_{M1} , C_{A1} , C_{B1} , C_{C1}) and (R_{T2} , C_{M2} , C_{B2} , C_{C2}) are combined (see data analysis section) to calculate the thermal expansion at temperature

$$T = (T_1 + T_2)/2 \quad (III-1)$$

The temperature interval

$$\Delta T = T_2 - T_1 \quad (III-2)$$

between the two data sets is chosen to minimize finite interval corrections (see the data analysis section).

For the c-axis crystal, the GR bridge and Thompson bridge were used to measure capacitance for ΔT 's > 25 mK and ΔT 's < 25 mK respectively. For the a-axis crystal, the Thompson bridge was used for the majority of the capacitance measurements since the a-axis expansions generally are an order of magnitude less than the c-axis expansions.

Data Analysis

Calculation of the thermal expansivities

A simplified drawing of the capacitance dilatometer is shown in Fig. 15. The length S may be regarded as positive or negative corresponding to the centerpost extending into the cell (as pictured) or, for samples greater than 1 in. in length, into the central part of the cell base. Figure 15 can be used to relate observed changes in gap, Δg , with temperature changes, ΔT , to the difference between the expansivity, $\tilde{\alpha}$, of the sample and of copper, $\tilde{\alpha}_{Cu}$, with an additional term $(\Delta L_{cell}/\Delta T)$ which is caused by the cell construction, as

$$\frac{\Delta g}{\Delta T} = -\tilde{\alpha}l + \tilde{\alpha}_{Cu}(l + g) + \frac{\Delta L_{cell}}{\Delta T} \quad (III-3)$$

For nonparallel plates of area A , mean separation g , and tip angle θ , Eqn. (I-41), can be solved for g to give,

$$g = \frac{\epsilon_0 A}{C} + \frac{C \sin^2 \theta}{4\pi\epsilon_0} \quad (III-4)$$

The temperature dependence of g is obtained for small θ as

Figure 15. Simplified drawing of the dilatometer showing the relevant lengths involved in the thermal expansivity calculation.

$$\frac{\Delta q}{\Delta T} \approx \left(-\frac{\epsilon_o A}{C} \right) \frac{1}{C} \frac{\Delta C}{\Delta T} + \left(\frac{2\epsilon_o A}{C} \right) \tilde{\alpha}_{Cu} + \left(\frac{C\theta}{2\pi\epsilon_o} \right) \frac{\Delta \theta}{\Delta T} \quad (III-5)$$

Substituting Eqns. (III-5) and (III-4) into Eqn. (III-3) and solving for $\tilde{\alpha}$, gives for this case,

$$\tilde{\alpha} \approx \tilde{\alpha}_{Cu} + \frac{\epsilon_o A}{C\ell} \left[\frac{1}{C} \frac{\Delta C}{\Delta T} - \tilde{\alpha}_{Cu} \right] - \frac{C\theta}{2\pi\epsilon_o \ell} \frac{\Delta \theta}{\Delta T} + \frac{1}{\ell} \frac{\Delta L_{cell}}{\Delta T} \quad (III-6)$$

For the temperature range from 270 K to 320 K, the lengths of the c- and a-axis gadolinium crystals change by 0.15% and 0.03% respectively and the areas of the high side plates by 0.2%. Therefore, the length ℓ and central plate area A used in Eqn. (III-6) may, to good approximation, be assumed to have values equal to the measured room temperature values.

For a temperature interval $\Delta T = T_2 - T_1$, the C and ΔC to be used in Eqn. (III-6) are calculated from the central plate capacitances as

$$\Delta C = C_{m2} - C_{m1} \quad (III-7a)$$

and

$$C = \sqrt{C_{m1} C_{m2}} \approx (C_{m1} + C_{m2})/2, \quad (III-7b)$$

where the approximation for C is legitimate if $\Delta C/C$ is small.

The term involving the changes in tip angle $\Delta \theta$ is calculated from changes in the side plate capacitances C_A , C_B , and C_C . Figure 16 is a

Figure 16. Top view of the capacitor low side, which is tipped out of the page. Side plates A, B, and C are located at distances g_A , g_B , and g_C above the areas indicated by the shaded circles.

top view of the low side plate, which is assumed to be tipped at an angle θ' out of the plane of the page about the axis indicated. If the gaps between high side plates A, B, and C and the low side are g_A , g_B , and g_C respectively, this geometry gives

$$r \sin \phi \sin \theta' = g_A - \bar{g} , \quad (III-8a)$$

$$r \sin (60-\phi) \sin \theta' = g_B - \bar{g} , \quad (III-8b)$$

and

$$r \sin (60+\phi) \sin \theta' = g_C - \bar{g} , \quad (III-8c)$$

where

$$\bar{g} = (g_A + g_B + g_C)/3 \quad (III-9)$$

is the average plate separation.

Equations (III-8a) and (III-8b) can be combined, assuming the angle θ' is small and using the parallel plate relation (I-39), to give

$$\theta' \approx \frac{\epsilon_0}{3r} \left[3 \left(\frac{A_B}{C_B} - \frac{A_C}{C_C} \right)^2 + \left(2 \frac{A_A}{C_A} - \frac{A_B}{C_B} - \frac{A_C}{C_C} \right)^2 \right]^{\frac{1}{2}} , \quad (III-10)$$

where A_A , A_B , and A_C are the side plate areas which are assumed to be constant and having the values indicated in Table 3. For a temperature difference $\Delta T = T_2 - T_1$, the $\Delta \theta$ and θ to be used in Eqn. (III-6) are calculated as

$$\Delta \theta = \theta'(T_2) - \theta'(T_1) \quad (III-11a)$$

$$\theta = \frac{\theta'(T_2) + \theta'(T_1)}{2} \quad (III-11b)$$

Thermal expansivity of copper and the cell correction

In order to calculate the expansion of an arbitrary sample from Eqn. (III-6), $\tilde{\alpha}_{\text{Cu}}$ and $\frac{\Delta L_{\text{cell}}}{\Delta T}$ must both be known. Kroeger's data⁴¹ for the linear thermal expansion coefficient of copper can be represented to 0.04% between 270° C and 320° C as

$$\tilde{\alpha}_{\text{Cu}} (\text{K}^{-1}) = 1.64325 \times 10^{-5} + 1.03929 \times 10^{-8} (T - 270 \text{ K}) . \quad (\text{III-12})$$

The cell correction term $\frac{\Delta L_{\text{cell}}}{\Delta T}$ may be evaluated in an experiment with a copper sample in the dilatometer. For a copper sample ($\tilde{\alpha} = \tilde{\alpha}_{\text{Cu}}$), Eqn. (III-6) can be rewritten as

$$\frac{\Delta L_{\text{cell}}}{\Delta T} \approx - \frac{\epsilon_o A}{C} \left[\frac{1}{C} \frac{\Delta C}{\Delta T} - \tilde{\alpha}_{\text{Cu}} \right] + \frac{C \theta}{2\pi \epsilon_o} \left(\frac{\Delta \theta}{\Delta T} \right) . \quad (\text{III-13})$$

Expansion data were taken for a 1.125 in. long high purity copper sample and Eqn. (III-13) was used to calculate the cell correction giving the results indicated in Figure 17. A straight line was least squares fit to the data giving the equation

$$\frac{\Delta L_{\text{cell}}}{\Delta T} = 2.335644(T - 290) + 91.96121 \text{ Å/K}, \quad (\text{III-14})$$

which is the solid line in Figure 17. The relatively large data scatter (about 10%) is most likely due to thermal gradients in the dilatometer since S#3 was not temperature controlled during these measurements.

Figure 17. Graph of the cell correction term versus temperature. The solid line is the result of a linear least squares fit to the data (open circles).

Finite interval corrections

The thermal expansion coefficient is given by the actual slope (first derivative) of the $\ell(T)$ relation at a given temperature, while the data measure an average slope over a finite temperature interval. The difference between these two is calculated by Kroeger⁴¹ as

$$\delta\tilde{\alpha} \equiv \frac{1}{\ell} \frac{\Delta \ell}{\Delta T} - \tilde{\alpha}(T) = \frac{1}{24} \tilde{\alpha}^{II}(T) (\Delta T)^2 + \frac{1}{1920} \tilde{\alpha}^{IV}(T) (\Delta T)^4 + \dots, \quad (III-15)$$

where

$$\tilde{\alpha}(T) = \frac{1}{\ell} \left(\frac{\partial \ell}{\partial T} \right)_P \quad (III-16)$$

and $\tilde{\alpha}^{II}(T)$ and $\tilde{\alpha}^{IV}(T)$ are the second and fourth temperature derivatives of $\tilde{\alpha}$ (usually $\tilde{\alpha}^{II}(T)$ is sufficient to estimate the correction). The thermal expansivity data of Cadieu and Douglass³⁹ for a c-axis gadolinium crystal were used to estimate the ΔT 's necessary to minimize $\delta\tilde{\alpha}$. These values of ΔT were used for both the c and a-axis measurements.

After equations of the form of (I-25) were fit to the c and a-axis data, the second and fourth derivatives were obtained and the difference $\delta\tilde{\alpha}$ calculated. The $\delta\tilde{\alpha}$ for each data point is given in the Appendix along with the raw data. The difference $\delta\tilde{\alpha}$ usually entered at the 0.1% level and hence could be ignored.

CHAPTER IV. RESULTS

The results of the thermal expansion measurements for both the c- and a-axis gadolinium crystals are given in the Appendix and are plotted in Figures 18, 19, 20, and 21. Figures 18 and 19 are plots for the full temperature range of the experiment, 270 K to 320 K. The c-axis expansion is negative while the a-axis expansion is positive, with the magnitude of the c-axis peak approximately nine times larger than that for a-axis peak. The shaded 2 K intervals in Figure 18 and 19 are plotted on an expanded scale in Figures 20 and 21. The c-axis expansion has an extremum of $-87.3 \times 10^{-6} \text{ K}^{-1}$ at $T_{\text{peak}}^c = 293.435 \text{ K}$, while the a-axis expansion has a maximum of $10.4 \times 10^{-6} \text{ K}^{-1}$ at $T_{\text{peak}}^a = 293.363 \text{ K}$. The points in the vicinity of the peak were taken with 10 mK and 25 mK intervals for the c- and a-axis data, respectively. Therefore, the locations of the c- and a-axis peaks are only known to 5 mK and 15 mK respectively. For the c- and a-axis data, a change in curvature (inflection point) appears to occur at 0.3 K and 0.04 K, respectively, above the peak temperature. No such inflection point is apparent for the data below the peak temperature.

A power law equation of the form (I-25) must be fit by nonlinear least squares techniques to both the c- and a-axis data,

$$\tilde{\alpha} = \begin{cases} A|\epsilon|^{-\alpha} + B + E\epsilon, & T > T_c, \epsilon > 0 \\ A'|\epsilon'|^{-\alpha'} + B' + E\epsilon', & T < T_c, \epsilon' < 0. \end{cases} \quad (\text{IV-1})$$

Figure 18. A plot of the raw c-axis thermal expansivity data (solid circles) versus temperature. The shaded temperature interval is expanded, in Figure 20.

Figure 19. A plot of the raw a-axis thermal expansivity data (solid circles) versus temperature. The shaded temperature interval is expanded in Figure 21.

Figure 20. A plot of the raw c-axis thermal expansivity data (solid circles) within ± 1 K of the peak maximum, 293.4 K.

Figure 21. A plot of the raw a-axis thermal expansivity data (solid circles) within ± 1 K of the peak maximum, 293.4 K.

A library subroutine, ZXSSQ,⁵³ which uses a modified Marquardt algorithm,⁵⁴ was employed for fitting Eqn. (IV-1) to the data. Temperature intervals could be defined for $T > T_C$ and $T < T'_C$ so that data close to T_C (T'_C) or data away from T_C (T'_C) could be omitted from the fit. The subroutine minimized the quantity

$$\sum_{i=1}^m F_i^2 \equiv \sum_{i=1}^m \left(\frac{\tilde{\alpha}(T_i) - \tilde{\alpha}_{\text{CALC}}(T_i)}{\tilde{\alpha}(T_i)} \right)^2, \quad (\text{IV-2})$$

where $\tilde{\alpha}(T_i)$ and $\tilde{\alpha}_{\text{CALC}}(T_i)$ are the experimental and calculated (from Eqn. IV-1) expansivities at temperature T_i , and m is the number of data points. The root mean square deviation (RMSD) of the fit was defined as

$$\text{RMSD} \equiv \left[\frac{1}{m} \sum_{i=1}^m F_i^2 \right]^{\frac{1}{2}}. \quad (\text{IV-3})$$

The curvature matrix

$$\xi_{jk} = \sum_{i=1}^m \left[\frac{1}{F_i^2} \frac{\partial F_i}{\partial x_j} \frac{\partial F_i}{\partial x_k} \right], \quad (\text{IV-4})$$

where x_j , x_k are the fit parameters (e.g. A , A' , α , α' , etc.), can be inverted to obtain error matrix

$$\epsilon_{jk} = \xi_{jk}^{-1}, \quad (\text{IV-5})$$

with the error in the parameter x_j , Δx_j , given by⁵⁵

$$\Delta x_j = \sqrt{\epsilon_{jj}}. \quad (\text{IV-6})$$

c-Axis Crystal Fit Results

Table 6 contains the results of the fits of Eqn. (IV-1) to the data with various restrictions imposed on the parameters. Fits I through (fit VII will be discussed later) give RMSD's which are roughly the same, while the RMSD's for fits VIII and IX are three to four times larger. This implies that fits VIII and IX are poor representations of the data. Fit V, with the restrictions $T_C = T'_C$ and $B = B'$, gives results for B and T_C which are close to the values of the experiment peak height and location. For this reason, fit V is the most physically realistic representation of the data.

Figure 22 shows a log-log plot of $\tilde{\alpha} - B - E\epsilon$ versus $|\epsilon|$ which was calculated using the parameters of fit V. The solid and dashed curves are the calculated values of $A|\epsilon|^{-\alpha}$ and $A'|\epsilon|^{-\alpha'}$ for this fit. For $T > T_C$, the points deviate from the straight line at $|\epsilon| \sim 1.4 \times 10^{-3}$ which corresponds to the inflection point in Figure 20.

For $T < T_C$, the points for $|\epsilon| < 1.3 \times 10^{-3}$ appear to lie on a straight line parallel (same exponent) to the $T > T_C$ line for $|\epsilon| > 1.4 \times 10^{-3}$. In order to verify this postulate, Eqn. (IV-1) was fit to the data for $T < T_C$ and $|\epsilon| < 1.3 \times 10^{-3}$ and for $T > T_C$ and $|\epsilon| > 1.4 \times 10^{-3}$ with the further restriction $\alpha = \alpha'$. The result is the set of parameters in fit VII. The RMSD's of fit VII and V are approximately the same and the $T > T_C$ parameters are in fair agreement.

Since two separate equations appear to be required to describe the $T < T_C$ data for $|\epsilon| < 1.3 \times 10^{-3}$, and $|\epsilon| > 1.3 \times 10^{-3}$, all the $T < T_C$

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Table 6. c-Axis gadolinium fit results.

PARAMETER RESTRICTIONS	A $\pm \Delta A$ (10^{-4} K^{-1})	T_C $\pm \Delta T_C$ (K)	$-\alpha$ $\pm \Delta \alpha$	B $\pm \Delta B$ (10^{-4} K^{-1})	E $\pm \Delta E$ (10^{-4} K^{-1})
I. none	1.6669 ± 1.4828	293.2311 ± 0.1458	0.06697 ± 0.08344	-1.4606 ± 1.5661	0.2937 ± 0.2192
II. $T_C = T_C'$	3.1267 ± 2.6138	293.0047 ± 0.0160	0.03369 ± 0.03412	-2.9215 ± 2.6596	0.2276 ± 0.1554
III. $\alpha = 0$	0.0844 ± 0.0018	293.1086 ± 0.0324	-----	+0.1476 ± 0.0074	0.4456 ± 0.0410
IV. $B = B'$	1.6308 ± 0.1252	293.2320 ± 0.0296	0.06926 ± 0.00730	-1.4214 ± 0.1306	0.2838 ± 0.0477
V. $T_C = T_C', B = B'$	1.1901 ± 0.0080	293.3252 ± 0.0184	0.1139 ± 0.0027	-0.9365 ± 0.0055	0.1840 ± 0.0507
VI. $T_C = T_C', \alpha = 0$	0.08329 ± 0.00185	293.1341 ± 0.0336	-----	+0.1431 ± 0.0075	0.4691 ± 0.0405
VII. $T_C = T_C', B = B',$ $\alpha = \alpha'$	1.2394 ± 0.0163	293.3330 ± 0.0156	0.1030 ± 0.0059	-1.004 ± 0.030	0.2387 ± 0.0573
VIII. $T_C = T_C', B = B',$ $\alpha = \alpha'$	3.7809 ± 1.1965	292.8971 ± 0.0275	0.03109 ± 0.01210	-3.5224 ± 1.2198	-0.1117 ± 0.1233
IX. $T_C = T_C'$ $\alpha = \alpha' = 0$	0.07008 ± 0.00065	293.4371 ± 0.0174	-----	0.09273 ± 0.00268	0.7186 ± 0.0176

A' $\pm \Delta A'$ (10^{-4} K^{-1})	T_c' $\pm \Delta T_c'$ (K)	$-\alpha'$ $\pm \Delta \alpha'$	B' $\pm \Delta B'$ (10^{-4} K^{-1})	RMSD (%)	m	FIT RANGES (K)
1.6544 ± 0.0472	294.0194 ± 0.0478	0.2665 ± 0.0249	-1.1792 ± 0.0475	0.74	40	293.8 < T < 313.0 278.3 < T < 293.3
1.9570 ± 0.0912	-----	0.5105 ± 0.0139	-0.8454 ± 0.0044	0.95	37	293.8 < T < 313.0 278.3 < T < 293.1
1.6969 ± 0.0128	294.0295 ± 0.0741	0.2777 ± 0.0179	-1.1657 ± 0.0432	0.74	37	293.8 < T < 313.0 278.3 < T < 293.1
1.7796 ± 0.0887	294.3121 ± 0.1197	0.1984 ± 0.0275	-----	0.74	40	
1.6428 ± 0.0231	-----	0.3931 ± 0.0061	-----	0.83	35	293.8 < T < 313.0 278.3 < T < 292.8
1.8473 ± 0.0373	-----	0.4556 ± 0.0115	-0.8852 ± 0.0083	0.80	35	293.8 < T < 313.0 278.3 < T < 292.8
0.3821 ± 0.0448	-----	-----	-----	0.91	25	293.8 < T < 313.0 292.8 < T < 293.3
3.3452 ± 0.2230	-----	-----	-----	3.02	33	293.8 < T < 313.0 278.3 < T < 292.7
0.1287 ± 0.0024	-----	-----	-0.04535 ± 0.01050	2.61	35	293.8 < T < 313.0 278.3 < T < 292.8

Figure 22.. A log-log plot of the power-law term versus ϵ , for the c-axis data.

data together with the $T > T_C$ data for $|\epsilon| > 1.4 \times 10^{-3}$ were refit (fit X) to the relations

$$\tilde{\alpha} = \begin{cases} A|\epsilon|^{-\alpha} + B + E\epsilon, & T > T_C, |\epsilon| > 1.4 \times 10^{-3} \\ A'|\epsilon|^{-\alpha'} + B + E\epsilon, & T < T_C, |\epsilon| > 1.3 \times 10^{-3} \\ A''|\epsilon|^{-\alpha} + B + E\epsilon, & T < T_C, |\epsilon| < 1.3 \times 10^{-3} \end{cases} \quad (\text{IV-7})$$

giving an RMSD of 0.79% for 41 data points and parameter values:

$$\begin{aligned} A \times 10^4 &= 1.1970 \pm 0.0039 \text{ K}^{-1} \\ A' \times 10^4 &= 1.6182 \pm 0.0123 \text{ K}^{-1} \\ A'' \times 10^4 &= 0.2689 \pm 0.0063 \text{ K}^{-1} \\ T_C &= 293.3315 \pm 0.0045 \text{ K} \\ \alpha &= 0.1139 \pm 0.0010 \\ \alpha' &= 0.3858 \pm 0.0042 \\ B \times 10^4 &= 0.9408 \pm 0.0035 \text{ K}^{-1} \\ E \times 10^4 &= 0.1718 \pm 0.0216 \text{ K}^{-1} \end{aligned}$$

This result is in fair agreement with the separate fits V and VII. The dash-dot line in Figure 22 represents the $A''|\epsilon|^{-\alpha}$ term of Eqn. (IV-7). A deviation plot of the data for fit X is shown in Figure 23. The insert shows the percent deviation for the $T > T_C$ points in the $|\epsilon| < 2 \times 10^{-3}$ range which are not included in the fit.

Figure 23. Deviation of the c-axis data from Eqn. (IV-7) using fit X parameters.

a-Axis Crystal Fit Results

The Eqn. (IV-1) was fit to the a-axis data in the same manner as the c-axis data. Table 7 contains the results of fits of Eqn. (IV-1) to the data under various parameter restrictions. Fits I through VI and VIII have RMSD's which are roughly the same. Fit VII has an RMSD which is factor of two greater and hence has restrictions which are probably incorrect. Fits V and VI give T_c 's equally close to the peak maximum and also give reasonable values for B and B'. There appears to be no reason for choosing fit V over fit VI to describe the data, but because the restrictions used in fit V best describe the c-axis data, fit V will be used to represent the a-axis data in the following discussion.

Figure 24 is a log-log plot of $\tilde{\alpha} - B - E\epsilon$ versus $|\epsilon|$ which was constructed from the parameters of fit V. The solid and dashed lines are the calculated value of $A|\epsilon|^{-\alpha}$ and $A'|\epsilon|^{-\alpha'}$. For $T > T_c$ the data deviate from the fit for $|\epsilon| \lesssim 2 \times 10^{-4}$, which corresponds to the inflection point in Figure 21. The $T < T_c$ data deviate from the fit for $|\epsilon| \lesssim 5 \times 10^{-4}$. It is uncertain whether a straight line can be drawn through the $T < T_c$ and $|\epsilon| < 3 \times 10^{-4}$ data parallel to the $T > T_c$ and $|\epsilon| > 3 \times 10^{-4}$ line since this is beyond the resolution of the data (a one percent change in $\tilde{\alpha}$ represents a change of 0.1 in $\tilde{\alpha} - B - E\epsilon$).

A deviation plot for fit V is shown in Figure 25. The insert shows the percentage deviation for points not included in the fit ($|\epsilon| < 4 \times 10^{-4}$).

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Table 7. Gadolinium a-axis fit results.

PARAMETER RESTRICTIONS	A $\pm \Delta A$ (10^{-6} K^{-1})	T_C $\pm \Delta T_C$ (K)	$-\alpha$ $\pm \Delta \alpha$	B $\pm \Delta B$ (10^{-6} K^{-1})	E $\pm \Delta E$ (10^{-6} K^{-1})
I. none	- 6.5903 ± 10.6212	293.3280 ± 0.0552	0.04440 ± 0.09208	11.947 ± 10.945	5.8127 ± 1.0439
II. $T_C = T_C'$	- 4.8187 ± 3.3331	293.3807 ± 0.0334	0.06115 ± 0.06108	10.213 ± 3.541	5.3775 ± 0.6714
III. $\alpha = 0$	- 0.24531 ± 0.00520	293.2762 ± 0.0105	-----	5.4466 ± 0.0264	5.7403 ± 0.2416
IV. $B = B'$	-13.646 ± 4.033	293.3062 ± 0.0151	0.01912 ± 0.00610	19.073 ± 4.042	5.6337 ± 0.2516
V. $T_C = T_C', B = B'$	- 5.7360 ± 0.1288	293.3753 ± 0.0144	0.04793 ± 0.00207	11.179 ± 0.132	5.2092 ± 0.1668
VI. $T_C = T_C', \alpha = 0$	- 0.21313 ± 0.00623	293.3566 ± 0.0168	-----	5.6027 ± 0.0296	4.6199 ± 0.1553
VII. $T_C = T_C', B = B',$ $\alpha = \alpha'$	- 9.6306 ± 0.8670	292.5154 ± 0.0463	0.07937 ± 0.01172	13.248 ± 0.960	15.463 ± 0.213
VIII. $T_C = T_C',$ $\alpha = \alpha' = 0$	- 0.14752 ± 0.01305	294.3208 ± 0.0624	-----	5.8368 ± 0.0623	4.0856 ± 0.4137

A' $\pm \Delta A'$ ($10^{-6} K^{-1}$)	T_C' $\pm \Delta T_C'$ (K)	$-\alpha'$ $\pm \Delta \alpha'$	B' $\pm \Delta B'$ ($10^{-6} K^{-1}$)	RMSD (%)	m	FIT RANGES (K)
-14.460 ± 4.998	293.8692 ± 0.1201	0.08769 ± 0.04605	17.821 ± 5.424	0.53	58	293.5 < T < 320.0 271.0 < T < 293.2
- 8.8017 ± 0.0893	-----	0.2170 ± 0.0209	11.245 ± 0.334	0.60	58	293.5 < T < 320.0 271.0 < T < 293.2
- 8.0570 ± 3.7834	292.2135 ± 1.4150	0.1864 ± 0.1737	11.174 ± 4.655	0.53	51	293.5 < T < 320.0 271.0 < T < 290.5
-15.703 ± 3.889	293.9181 ± 0.0984	0.07943 ± 0.02624	-----	0.52	58	293.5 < T < 320.0 271.0 < T < 293.2
- 8.8097 ± 0.0881	-----	0.2215 ± 0.0078	-----	0.60	58	293.5 < T < 320.0 271.0 < T < 293.2
- 8.8666 ± 0.0807	-----	0.2366 ± 0.0080	10.974 ± 0.122	0.60	58	293.5 < T < 320.0 271.0 < T < 293.2
- 7.7778 ± 0.9535	-----	-----	-----	0.93	54	293.5 < T < 320.0 271.0 < T < 292.2
- 1.0426 ± 0.0238	-----	-----	3.5126 ± 0.0884	0.55	50	294.6 < T < 320.0 271.0 < T < 293.2

Figure 24. A log-log plot of the power-law term versus ϵ , for the a-axis data.

Summary of Fit Results

Curie temperatures

The difference between the estimated peak temperature and the calculated Curie temperature T_C are $T_{\text{peak}}^c - T_C^c \sim 0.1$ K and $T_{\text{peak}}^a - T_C^a \sim 0.01$ K for the c- and a-axis crystals. The calculated Curie temperatures for the c- and a-axis crystals differ by $T_C^c - T_C^a \sim -44$ mK. This difference is about a factor of two greater than can be accounted for by the estimated errors in the T_C 's.

Exponents

The calculated exponents for the c-axis data are about a factor of two greater than the corresponding exponents for the a-axis data. The c-axis data for $T < T_C$ have a region close to T_C which is described with the same exponent which fits the $T > T_C$ data. It is inconclusive whether or not a similar region exists for the a-axis data.

Length and Volume Changes

The thermal expansion fit equations can be integrated to obtain the temperature dependences of the c- and a-axis lattice parameters, the c/a ratio, and the relative volume change. In the vicinity of the transition, the changes in the c- and a-axis parameter are calculated from the expressions

$$\frac{c(\epsilon)}{c(0)} = \exp \left[T_C \int_0^\epsilon \tilde{\alpha}^c d\epsilon \right]$$

and

$$\frac{a(\epsilon)}{a(0)} = \exp \left[T_C \int_0^\epsilon \tilde{\alpha}^a d\epsilon \right], \quad (\text{IV-8})$$

Figure 25. Deviation of the a-axis data from Eqn. (IV-1) using fit V parameters.

which follow from the definitions of the linear thermal expansion coefficients. The integrations in Eqn. (IV-8) were carried out assuming the parameters from fit V for the c-axis data and from fit V for the a-axis data hold for all $|\epsilon| \leq 0.1$. In order to plot the results versus temperature, a value of T_C must be used since,

$$T = T_C (\epsilon + 1) \quad (IV-9)$$

Since the c- and a-axis Curie temperatures differ by less than 0.02%, the choice of one Curie temperature over the other will have little effect on the integrated results. In carrying out the calculation in Eqns. (IV-8) and (IV-9), I have arbitrarily chosen $T_C = 293.375$ K, which is the a-axis value. The curves in Figure 26 show the percentage change in the c- and a-axis lattice parameters as a function of temperature.

Figure 26 is used together with the x-ray lattice parameters at T_C due to Darnell,²⁵ $c(T_C) = 5.783$ Å and $a(T_C) = 3.631$ Å, to calculate the c/a axis ratio. The c/a ratio is plotted in Figure 27.

The relative crystal volume change,

$$\frac{\Delta V}{V(T_C)} = \frac{c(T)}{c(T_C)} \frac{a^2(T)}{a^2(T_C)} - 1, \quad (IV-10)$$

is obtained by integrating the volume expansion coefficient

$$\tilde{\beta} = \tilde{\alpha}^c + 2\tilde{\alpha}^a. \quad (IV-11)$$

Figure 28 shows $\Delta V/V(T_C)$ versus temperature.

Figure 26. Percentage change in the c-axis (solid line) and a-axis (dashed line) lattice parameters as determined by integrating the linear thermal expansivities.

Figure 27. The c/a ratio as a function of temperature.

Figure 28. A plot of the percentage volume change versus temperature.

Errors

The absolute accuracy of the linear thermal expansion coefficient is rather unimportant in the calculation of the critical exponents. Uncertainties in such quantities in Eqn. (III-6) as $\tilde{\alpha}_{Cu}$, A , l , C , and the fitted curve $\Delta L_{cell}/\Delta T$ tend only to shift the data uniformly up or down and have little effect on the shape of the curves and hence the critical point exponents. For the c-axis data in the temperature range 270 K to 320 K, the absolute accuracy of the data is probably of the order of $\pm 1\%$ due to uncertainties in the central plate area A , and sample length l . For $T > 305$ K, the uncertainties in the cell correction fit equation begin to dominate and reach a maximum of $\pm 3\%$ at 313 K (highest temperature data point). For the a-axis data, the uncertainties in the assumed relation $\Delta L_{cell}/\Delta T$ dominate over the whole temperature interval 270 K to 320 K and limit the absolute accuracy to $\pm 3\%$.

The errors in the shape of the curves are determined mostly by the measured quantities ΔC and ΔT and any intrinsic instabilities of the dilatometer (as might be indicated by the data scatter from the fitted curve $\Delta L_{cell}/\Delta T$). These errors may be estimated from the RMSD's of the fits to the data. Fit X for the c-axis data has an RMSD of 0.8% and fit V for the a-axis data has an RMSD of 0.6%. The reading of ΔC and ΔT were always carried to four significant digits so that errors in these quantities only account for a few tenths of a percent. This implies that dilatometer instabilities may enter at the 0.5% level.

CHAPTER V. DISCUSSION

The c- and a-axis linear thermal expansion coefficients which have been measured in the temperature range from 270 K to 320 K have been expressed in terms of power law equations of the form Eqn. (1-22). All of the relevant physics associated with these measurements can be derived from these fits. Both the c- and a-axis measurements give information closer to the Curie temperature than was previously possible because sample-dependent rounding of the data did not seem to appear. In the past, a-axis thermal expansivity measurements^{25,42} have not had sufficient precision to demonstrate critical behavior, and therefore in this case the present measurements give obviously new information.

Fit X for the c-axis data and fit V (Table 5) for the a-axis data give Curie temperatures of $T_C^c = 293.3315 \pm 0.0045$ K and $T_C^a = 293.3753 \pm 0.0144$ K respectively. These T_C 's are higher than those for any of the past measurements in Table 2 (Chapter I) by approximately 1 K, indicating that both the c- and a-axis crystals are of much better quality than the crystals used in past measurements. The difference in the fit-derived Curie temperatures for the c- and a-axis crystals, $T_C^c - T_C^a = -43.8$ mK, is rather small, and indicates that these crystals have similar purities. The calculated a-axis Curie temperature is greater than the calculated c-axis Curie temperature in spite of the fact that the c-axis crystal was electrotransported and presumably has a higher purity than the a-axis crystal. The experimental locations of the expansivity peaks in the c- and a-axis data, however, do have $(T_{\text{peak}}^c - T_{\text{peak}}^a = 72 \text{ mK})$.

Apparently, the location of the experimental peaks in the expansivity gives a better indication of the relative crystal purity than the fitted Curie temperatures for crystals of similar purity. This is reasonable, because the Curie temperatures are calculated from data away from T_C ($|T - T_C| > 0.3$ K), and these probably are not affected appreciably by small differences in sample purity.

Cadieu and Douglass (C&D)³⁹ have plotted the peak temperature versus the resistance ratio

$$\Gamma = \frac{R(294 \text{ K})}{R(4.2 \text{ K})} \quad (\text{V-1})$$

for gadolinium crystals of different purity and obtained the relationship

$$T_{\text{peak}} = T_0 (1 - a/\Gamma) , \quad (\text{V-2})$$

where $T_0 = 293.3 \pm 0.1$ K and $a = 0.27 \pm 0.01$. This value for T_0 is probably a bit low since the c-axis crystal in this experiment gave $T_{\text{peak}}^c = 293.435$ K. If it is assumed that $\Gamma_c \approx 300$ for this c-axis crystal (see Chapter II) and this point is plotted along with the T_C vs Γ data used by C&D, then it appears that a straight line can still be drawn through the points if T_0 and a have values $T_0 = 293.7 \pm 0.1$ K and $a = 0.29 \pm 0.01$. The peak value $T_{\text{peak}}^a = 293.363$ K for the a-axis crystal then can be used with Eqn. (V-2) and the above values for T_0 and a to calculate $\Gamma_a \approx 250$. This indicates that the a-axis crystal purity is slightly less than the c-axis crystal purity.

The critical point exponents were calculated from fit X for the c-axis data as $\alpha = -0.1139 \pm 0.001$ and $\alpha' = -0.3858 \pm 0.0042$ using data in the range $|\epsilon| > 1.3 \times 10^{-3}$. Both α and α' are negative, indicating a finite cusp in the c-axis expansivity with height $B = -94.08 \times 10^{-6} \text{ K}^{-1}$. The values of α and α' agree fairly well with those from the specific heat measurements of Lewis³⁷ (i.e. $\alpha = -0.09 \pm 0.05$ and $\alpha' = -0.32 \pm 0.05$ from Table 2), indicating that the c-axis linear expansivity and the specific heat are proportional near T_C . The value of α is also in good agreement with the 3-dimensional Heisenberg model calculations in Table 2. The scaling prediction $\alpha = \alpha'$ seems to be satisfied only for $|\epsilon| < 1.3 \times 10^{-3}$ for the $T < T_C$ data and $|\epsilon| > 1.3 \times 10^{-3}$ for $T > T_C$. This could not be observed in the specific heat experiments³⁷ because data rounding occurred at $|\epsilon| \lesssim 2 \times 10^{-3}$.

The a-axis fit V gives $\alpha = -0.04793 \pm 0.0061$ and $\alpha' = -0.2215 \pm 0.0078$ from data in the range $|\epsilon| > 3 \times 10^{-4}$. Both exponents are negative corresponding to a finite cusp in the a-axis expansivity of height $B = 11.179 \times 10^{-6} \text{ K}^{-1}$. These exponents do not agree with either the specific heat exponents or the c-axis expansivity exponents.

The reason for this apparent discrepancy possibly can be traced to the temperature dependence of the adiabatic elastic constants (see Eqns. (I-22a) and (I-22b)). The adiabatic elastic constant data of Fisher and Dever (F&D),⁵⁶ Fisher, Manghnani, and Kikuta,⁵⁷ and Palmer, Lee, and Islam (PL&I)⁵⁸ indicate that small anomalies occur in $c_{33}^{(s)}$ and $c_{13}^{(s)}$ at T_C . To show the effect of these, Eqns. (I-22a) and (I-22b) can be rewritten as

$$\tilde{\alpha}_{P=0}^a = Q_a c_{P=0} \quad (V-3)$$

and

$$\tilde{\alpha}_{P=0}^c = Q_c c_{P=0} \quad (V-4)$$

where Q_a and Q_c are defined as

$$Q_a \equiv \frac{(c_{33}^s \gamma_a - c_{13}^s \gamma_c)}{c_{33}^s (c_{11}^s + c_{12}^s) - 2(c_{13}^s)^2} \quad (V-5)$$

and

$$Q_c \equiv \frac{(c_{11}^s + c_{12}^s) \gamma_c - 2c_{13}^s \gamma_a}{c_{33}^s (c_{11}^s + c_{12}^s) - 2(c_{13}^s)^2} \quad (V-6)$$

These equations suggest that anomalies in $c_{33}^{(s)}$ and $c_{13}^{(s)}$ can give rise to anomalies Q_a and Q_c , and hence a lack of proportionality between $\tilde{\alpha}_{P=0}$ and $c_{P=0}$.

In order to calculate the magnitudes of these anomalies, the Grüneisen parameters must be estimated. Using the data of PL&I, together with the value $c_{P=0}(T_C) = 0.08827$ cal/gm due to Griffel, Skochdopole, and Spedding,⁵⁹ and the fit values $\tilde{\alpha}_{P=0}^a(T_C) = 11.179 \times 10^{-6} \text{ K}^{-1}$ and $\tilde{\alpha}_{P=0}^c(T_C) = -94.08 \times 10^{-6} \text{ K}^{-1}$ in Eqns. (V-3), (V-4), (V-5), and (V-6), γ_c and γ_a are calculated as $\gamma_c(T_C) \approx -2.0$ and $\gamma_a(T_C) \approx -0.32$.

These γ 's are total Grüneisen parameters since they relate the total specific heat to the total linear thermal expansivities. Since both γ_c and γ_a are negative, and $|\gamma_c| > |\gamma_a|$, it is the elastic coupling term $c_{13}^{(s)}$ which gives rise to a small positive a-axis expansion along with the large negative c-axis expansion.

The magnetic Grüneisen parameters $\gamma_c^{(m)}$ and $\gamma_a^{(m)}$ can be obtained through Eqns. (I-20a) and (I-20b) which relate the magnetic contribution to the specific heat, $C_{P=0}^{(m)}$, and the magnetic contributions to the linear thermal expansivities $\tilde{\alpha}_{P=0}^{c(m)}$ and $\tilde{\alpha}_{P=0}^{a(m)}$. The c-axis expansivity appears to be dominated by magnetic contributions while the magnetic contributions to the specific heat and the a-axis expansivity appear to be roughly 50% of the total. Therefore, the various magnetic contributions at T_C can be estimated as $C_{P=0}^{(m)}(T_C) \approx 0.04414 \text{ cal/gm}$, $\tilde{\alpha}_{P=0}^{c(m)}(T_C) \approx -10^{-4} \text{ K}^{-1}$, and $\tilde{\alpha}_{P=0}^{a(m)}(T_C) \approx 5.6 \times 10^{-6} \text{ K}^{-1}$. Using these estimates in Eqns. (I-20a) and (I-20b) together with the elastic constant data of PL&I, the magnetic Grüneisen parameters are calculated at T_C as $\gamma_c^{(m)} \approx -4.5$ and $\gamma_a^{(m)} \approx -1.1$.

These γ 's can be related to the experimentally measured pressure dependence of the Curie temperature in the Grüneisen approximation $[s^{(m)}(T_C/T)]$ (Eqns. (I-17a) and (I-17b)) as follows. If T_C is a function of c and a only, $T_C = T_C(a, c)$, then dT_C/dP can be written

$$\begin{aligned} \frac{dT_C}{dP} &= T_C \left[2 \left(\frac{\partial \ln T_C}{\partial \ln a} \right)_c \frac{1}{a} \left(\frac{\partial a}{\partial P} \right)_c + \left(\frac{\partial \ln T_C}{\partial \ln c} \right)_a \frac{1}{c} \left(\frac{\partial c}{\partial P} \right)_a \right] \\ &= -T_C \left[2 \gamma_a^{(m)} \frac{1}{a} \left(\frac{\partial a}{\partial P} \right)_c + \gamma_c^{(m)} \frac{1}{c} \left(\frac{\partial c}{\partial P} \right)_a \right] \end{aligned} \quad (V-7)$$

Using F&D's values of

$$\frac{1}{a} \left(\frac{\partial a}{\partial P} \right)_c \approx -0.89 \times 10^{-6} \text{ bar}^{-1}$$

and

$$\frac{1}{c} \left(\frac{\partial c}{\partial P} \right)_a \approx -0.91 \times 10^{-6} \text{ bar}^{-1},$$

the calculated values for $\gamma_c^{(m)}(T_C)$ and $\gamma_a^{(m)}(T_C)$, and $T_C \approx 293.4$, Eqn. (V-7) yields

$$\frac{dT_C}{dP} \approx -1.7 \text{ mK/bar}$$

in good agreement with the measured pressure dependence of the Curie temperature due to Robinson et al.,⁶⁰

$$\frac{dT_C}{dP} \approx -1.6 \text{ mK/bar}$$

Since both the total and magnetic Grüneisen parameters have been estimated at T_C , the lattice Grüneisen parameters, $\gamma_c^{(\ell)}$ and $\gamma_a^{(\ell)}$, can be estimated from Eqns. (I-21a) and (I-21b) (assuming the electronic terms are negligible at these temperatures). Using the estimate that $c_{P=0}^{(\ell)} \approx c_{P=0}^{(m)} \approx \frac{1}{2} c_{P=0}$, Eqns. (I-21a) and (I-21b) become

$$\gamma_a = \frac{\gamma_a^{(m)}}{2} + \frac{\gamma_a^{(\ell)}}{2} \quad (\text{V-8a})$$

and

$$\gamma_c = \frac{\gamma_c^{(m)}}{2} + \frac{\gamma_c^{(\ell)}}{2} \quad (\text{V-8b})$$

With the above estimates for $\gamma_c^{(m)}$, $\gamma_a^{(m)}$, γ_c , and γ_m , the lattice Grüneisen parameters are obtained as $\gamma_a^{(l)} \approx \gamma_c^{(l)} \approx 0.5$, in reasonable agreement with the calculated values of $\gamma_a^{(l)} = 0.63$ and $\gamma_c^{(l)} = 0.55$ due to Rao and Menon.⁶¹

The data of PL&I now can be used to calculate the temperature dependence of Q_a and Q_c , assuming that the Grüneisen parameters are temperature-independent. Both Q_a and Q_c have peaks at T_c , but the variation of Q_a is about 35% for the temperature range 270 K to 320 K, while the variation in Q_c is only 7% over the same temperature range. According to Eqn. (V-3), $\tilde{\alpha}_{P=0}^a/Q_a$ is the specific heat and should have the same critical point exponents as $C_{P=0}$. Using the temperature dependence of Q_a as calculated above, together with the fit Eqn. (IV-1) and the parameters of fit V for the a-axis data, the ratio $\tilde{\alpha}_{P=0}^a/Q_a$ was calculated. Graphically, $\tilde{\alpha}_{P=0}^a/Q_a$ gave exponents $\alpha \approx -0.09$ and $\alpha' \approx -0.3$, in reasonable agreement with the c-axis results and the specific heat results of Lewis.³⁷ Although there is probably considerable uncertainty in this calculation, it does indicate that the temperature variation of Q_a is sufficiently large that $C_{P=0}$ and $\tilde{\alpha}_{P=0}^a$ are not proportional near T_c . The temperature variation of Q_c is sufficiently small that to a good approximation $\tilde{\alpha}_{P=0}^c$ and $C_{P=0}$ are proportional. To verify this, the quantity $\tilde{\alpha}_{P=0}^c/Q_c$ was calculated in the same manner as $\tilde{\alpha}_{P=0}^a/Q_a$. Graphically, the quantity $\tilde{\alpha}_{P=0}^c/Q_c$ gave exponents $\alpha \approx -0.14$ and $\alpha' \approx -0.4$ which are not greatly changed from the exponents calculated for the c-axis thermal expansivity.

Theoretical calculations of the critical point properties of thermodynamic quantities are usually made under the implicit assumption of

constant volume, whereas experimental data are always taken at constant pressure. The effect of volume changes on the theoretical Curie temperature may be estimated from the relationship,

$$\frac{d \ln T_C}{d \ln V} = \frac{1}{T_C} \left(\frac{dT_C}{dP} \right) \left(\frac{1}{V} \frac{dV}{dP} \right)^{-1}_T \quad (V-9)$$

Using, $dT_C/dP \approx -1.6$ mK/bar from Robinson et al.,⁶⁰ the volume compressibility,

$$\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T \approx -2.7 \times 10^{-6} \text{ bar}^{-1},$$

from F&D,⁵⁷ and $T_C \approx 293.4$ K, Eqn. (V-9) becomes

$$\frac{d \ln T_C}{d \ln V} \approx 2 \quad (V-10)$$

From Figure 28, the volume changes near T_C are less than 0.01% so the relative change in T_C would be 0.02% or $\Delta T_C \approx 0.06$ K. This implies that the assumption of constant volume in theoretical calculations should be adequate for describing thermodynamic quantities for gadolinium at constant pressure.

In summary, it appears that the c-axis expansivity of gadolinium can be expected to be proportional (to good approximation) to the specific heat near T_C but not the a-axis expansivity. The value of the exponent α obtained directly from the c-axis expansivity is in good agreement

with the Heisenberg model calculations (Table 2) for the $T > T_C$ specific heat exponent. The scaling relationship $\alpha = \alpha'$ appears to be satisfied only for the $T < T_C$ c-axis data with $|\epsilon| < 1.3 \times 10^{-3}$. Both the c- and a-axis expansivity data for $T > T_C$, appear to be in excess of the fit values for $|\epsilon| < 1.4 \times 10^{-3}$ and $|\epsilon| < 2 \times 10^{-4}$, respectively. Since data rounding implies a decrease in the expansivity, this effect probably has other physical origins. No similar effect occurs on the $T < T_C$ side of the transition. The use of thermal expansivity measurements to determine the specific heat critical point exponents apparently only has limited use for anisotropic crystals such as gadolinium. In choosing between the use of specific heat or thermal expansivity measurements to investigate critical phenomena, a thorough examination of the behavior of the elastic constants should first be pursued. If there is significant anomalous behavior, the specific heat should be chosen over the thermal expansivity. However, if the elastic constants are well behaved, then thermal expansivity measurements offer definite advantages in sensitivity and simplicity over specific heat measurements.

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ACKNOWLEDGMENTS

The author wishes to express his appreciation to several individuals who contributed to his graduate career and this thesis. Particular acknowledgments are due to:

Dr. Clayton A. Swenson for the suggestion of the thesis topic and many invaluable hints and suggestions in the design and operation of this experiment;

Dr. Gerhard L. Salinger for supervising the author during the sabbatical absence of Dr. Swenson and for many enlightening discussions;

The author's wife, Kathleen, for her patience and help with the preparation of this thesis;

And the author's parents and in-laws for providing support and many enjoyable weekends.

APPENDIX. EXPERIMENTAL DATA

The tables listed below, labeled A1 and A2, contain the linear thermal expansivity data for c- and a-axis gadolinium crystals in the temperature range 270 K to 320 K. Listed along with the raw data is the finite interval correction, $\delta\tilde{\alpha}$, calculated by Eqn. (III-15) using the parameters from fit X for the c-axis data and fit V for the a-axis data.

Each data point is identified by a five digit number in the first column. The first digit refers to the number of the laboratory notebook in which the data point is contained. The next three digits refer to the page number in the laboratory book and the last digit labels which point it is on that page.

Columns two and three give the average temperature, T, and interval, ΔT , used to calculate the linear thermal expansivity. T and ΔT are written to the nearest 0.01 mK which was the limit of the precision of the double ac potentiometer. The accuracy of T, however, is limited to a few mK (see Chapter 2).

Columns four, five, and six give the linear thermal expansivity, $\tilde{\alpha}$, (as calculated by Eqn. (III-6)) the finite interval correction, $\delta\tilde{\alpha}$, and the capacitance bridge employed to measure the gap changes (GR is the General Radio bridge and TH is the Thompson bridge). The precision of the c- and a-axis data was approximately $\pm 0.8\%$ and $\pm 0.6\%$ respectively, as indicated by the precision of the nonlinear least squares fits to the data. The absolute accuracy of a particular $\tilde{\alpha}$ is probably at worst $\pm 3\%$.

Table A1. Thermal Expansivity Data for c-axis gadolinium.

POINT NUMBER	T (K)	ΔT (K)	$\tilde{\alpha}$ (10^{-6} K^{-1})	$\delta \tilde{\alpha}$ (10^{-6} K^{-1})	BRIDGE EMPLOYED
61771	278.35496	2.55856	-43.676	-0.015	GR
61772	280.91539	2.56229	-47.202	-0.020	GR
61801	283.48896	2.58486	-50.872	-0.030	GR
61802	286.06723	2.57167	-55.321	-0.048	GR
61851	288.38257	2.05904	-60.868	-0.058	GR
61852	290.17482	1.52546	-65.705	-0.066	GR
70041	291.20594	0.53516	-70.644	-0.015	GR
61853	291.45917	1.04323	-71.585	-0.071	GR
70043	291.45955	1.04238	-71.884	-0.071	GR
70042	291.72713	0.50722	-73.197	-0.022	GR
61901	292.11341	0.26525	-74.913	-0.009	GR
70061	292.35175	0.51000	-76.183	-0.048	GR
61902	292.37360	0.25513	-76.040	-0.013	GR
70063	292.47862	0.76374	-76.970	-0.140	GR
60962	292.60672	0.29318	-78.176	-0.026	GR
70062	292.73362	0.25374	-78.922	-0.026	GR
61012	292.81218	0.10370	-80.161	-0.006	GR
61112	292.93751	0.10039	-80.934	-0.008	GR
61103	293.03945	0.10350	-81.899	-0.014	GR
61111	293.14184	0.10128	-82.695	-0.028	GR
61161	293.22998	0.07504	-84.007	-0.044	GR
70311	293.26319	0.06120	-84.267	-0.060	TH
61162	293.29337	0.05173	-84.776	-0.135	GR
70341	293.34457	0.02202	-85.464	-0.238	TH
70342	293.37108	0.01032	-85.747	-0.009	TH
70361	293.39176	0.01027	-86.229	-0.005	TH
70362	293.40787	0.02195	-86.800	-0.014	TH
70251	293.42139	0.05014	-86.801	-0.055	TH

Table A1. Continued.

POINT NUMBER	T (K)	ΔT (K)	$\tilde{\alpha}$ (10^{-6} K^{-1})	$\delta\tilde{\alpha}$ (10^{-6} K^{-1})	BRIDGE EMPLOYED
70223	293.42586	0.02048	-87.109	-0.008	TH
70383	293.43500	0.03232	-87.280	-0.018	TH
70252	293.44057	0.04990	-87.037	-0.039	TH
70253	293.45594	0.03968	-87.036	-0.019	TH
70381	293.47025	0.03818	-86.425	-0.015	TH
70254	293.47065	0.01026	-87.018	-0.001	TH
70273	293.48607	0.02058	-84.807	-0.003	TH
61421	293.50232	0.03536	-84.587	-0.009	GR
70382	293.50557	0.03245	-83.648	-0.007	TH
70271	293.52136	0.05000	-82.347	-0.014	TH
61422	293.54564	0.05127	-80.852	-0.012	GR
70272	293.57207	0.05141	-77.402	-0.010	TH
61423	293.59704	0.05154	-74.880	-0.008	GR
70293	293.62342	0.05129	-71.580	-0.007	TH
61481	293.65736	0.06884	-66.211	-0.010	GR
70291	293.67320	0.04827	-63.376	-0.004	TH
61482	293.73250	0.08144	-49.790	-0.009	GR
70292	293.73863	0.08260	-48.583	-0.009	TH
61483	293.79982	0.05320	-38.800	-0.003	GR
61491	293.85217	0.05150	-35.722	-0.002	GR
61551	293.90300	0.05012	-35.016	-0.002	GR
61552	293.97881	0.10149	-34.078	-0.006	GR
61553	294.13171	0.20431	-32.652	-0.017	GR
61561	294.38838	0.30903	-30.709	-0.022	GR
61591	294.82202	0.51113	-28.913	-0.032	GR
61621	295.45856	0.76194	-26.086	-0.037	GR
61651	296.38051	1.05236	-22.746	-0.036	GR
61693	297.42420	1.03501	-19.973	-0.020	GR

Table A1. Continued.

POINT NUMBER	T (K)	ΔT (K)	α (10^{-6} K^{-1})	$\delta \tilde{\alpha}$ (10^{-6} K^{-1})	BRIDGE EMPLOYED
61691	298.46834	1.05328	17.986	-0.013	GR
61692	299.76082	1.53167	16.172	-0.018	GR
61733	301.56203	2.07076	13.699	-0.021	GR
50121 ^a	303.72386	1.99887	11.715	-0.013	GR
61731	303.88925	2.58368	11.358	-0.020	GR
50122 ^a	304.72729	4.00574	10.845	-0.043	GR
50123 ^a	305.72673	2.00687	9.980	-0.009	GR
61732	306.47410	2.58602	9.356	-0.014	GR
50082 ^a	312.70287	4.00020	5.080	-0.016	GR

^aPoints taken without S#3 controlled.

Table A2. Thermal Expansivity Data for c-axis gadolinium.

POINT NUMBER	T (K)	ΔT (K)	$\tilde{\alpha}$ (10^{-6} K^{-1})	$\delta \tilde{\alpha}$ (10^{-6} K^{-1})	BRIDGE EMPLOYED
71141	271.22513	0.96596	5.8390	0.0001	GR
81051	271.72850	0.96909	5.9135	0.0001	TH
71142	272.19693	0.97763	5.8962	0.0001	GR
81052	272.70330	0.98051	5.9266	0.0001	TH
71201	273.16704	0.96260	5.9020	0.0001	GR
71202	274.13531	0.97393	6.0313	0.0001	GR
71203	275.11444	0.98433	6.1343	0.0001	GR
71204	276.59391	1.97462	6.2312	0.0005	GR
71205	278.56726	1.97207	6.3121	0.0006	GR
71231	280.54409	1.98159	6.4516	0.0008	GR
71232	282.52670	1.98364	6.6698	0.0010	GR
71281	284.49731	1.95758	6.8980	0.0014	GR
81111	285.48847	1.99033	7.0800	0.0018	TH
71282	286.46999	1.98778	7.2345	0.0023	GR
81112	287.21442	1.46157	7.3044	0.0015	TH
71283	287.95012	0.97247	7.3764	0.0008	GR
81113	288.44958	1.00875	7.5726	0.0011	TH
71284	288.93963	1.00655	7.6467	0.0013	GR
81114	289.44204	0.97617	7.7990	0.0015	TH
71341	289.93237	0.97894	7.9198	0.0019	GR
80311	290.40181	0.98237	7.9183	0.0025	TH
80312	291.16097	0.53596	8.1813	0.0013	TH
80341	291.68204	0.50618	8.3514	0.0018	TH
80342	292.18847	0.50668	8.5461	0.0034	TH
80381	292.54383	0.20504	8.8191	0.0011	TH
80382	292.74849	0.20428	8.9701	0.0017	TH
80451	292.95183	0.20239	9.0690	0.0034	TH
80452	293.10519	0.10433	9.2027	0.0020	TH

Table A2. Continued.

POINT NUMBER	T (K)	ΔT (K)	$\tilde{\alpha}$ (10^{-6} K^{-1})	$\delta \tilde{\alpha}$ (10^{-6} K^{-1})	BRIDGE EMPLOYED
80461	293.15609	0.20614	9.3764	0.0120	TH
80621	293.18136	0.04917	9.4873	0.0008	TH
80453	293.20826	0.10181	9.5544	0.0046	TH
80622	293.23196	0.05203	9.6947	0.0016	TH
80623	293.27055	0.02515	9.9784	0.0006	TH
80631	293.29650	0.02675	10.0127	0.0012	TH
80462	293.31061	0.10289	10.0651	0.0287	TH
80632	293.32322	0.02669	10.1779	0.0025	TH
80681	293.34915	0.02518	10.2960	0.0079	TH
81171	293.36221	0.02623	10.3801	0.0345	TH
81141	293.36295	0.02665	10.3839	0.0405	TH
80682	293.37443	0.02537	10.3078	-----	TH
81011	293.38694	0.02529	10.0058	0.0424	TH
80463	293.38726	0.05042	9.8922	0.2723	TH
80683	293.39900	0.02377	9.5199	0.0075	TH
81012	293.41279	0.02641	8.4456	0.0036	TH
80684	293.42420	0.02663	7.6913	0.0022	TH
80464	293.43765	0.05035	7.4646	0.0050	TH
80071	293.47738	0.10130	7.2476	0.0079	GR
80541	293.48890	0.05216	7.2242	0.0016	TH
80072	293.58083	0.10559	7.1097	0.0021	GR
80543	293.66820	0.10136	7.0870	0.0009	TH
80551	293.78490	0.13203	7.0199	0.0009	TH
80552	293.90139	0.10095	6.9448	0.0003	TH
80553	294.05347	0.20321	6.9240	0.0008	TH
80554	294.25559	0.20104	6.8732	0.0004	TH
80741	294.61137	0.51040	6.8233	0.0014	TH
80183	294.67542	0.20346	6.8100	0.0002	GR
80742	295.12282	0.51249	6.7651	0.0007	TH

Table A2. Continued.

POINT NUMBER	T (K)	ΔT (K)	$\tilde{\alpha}$ (10^{-6} K^{-1})	$\delta \tilde{\alpha}$ (10^{-6} K^{-1})	BRIDGE EMPLOYED
80242	295.54620	0.51044	6.6778	0.0005	GR
80743	295.63410	0.51008	6.6362	0.0004	TH
80801	296.68562	0.50540	6.6225	0.0002	TH
80271	296.84093	1.04044	6.5948	0.0008	GR
80244	296.84101	1.04060	6.5655	0.0008	GR
71402	297.86186	0.97793	6.5627	0.0004	GR
80803	298.48009	1.05801	6.5103	0.0004	TH
80811	299.51687	1.01556	6.4919	0.0002	TH
80812	300.53691	1.02451	6.4801	0.0002	TH
80851	302.08373	2.06913	6.4616	0.0005	TH
71452	303.34158	1.99485	6.5367	0.0004	TH
80852	304.15521	2.07383	6.4458	0.0003	TH
80853	306.23183	2.07941	6.4912	0.0002	TH
80881	308.30796	2.07285	6.4048	0.0002	TH
71492	309.30074	2.00009	6.5248	0.0002	GR
80882	310.36739	2.04601	6.4554	0.0001	TH
80911	312.42693	2.07308	6.5298	0.0001	TH
80912	314.50356	2.08018	6.5183	0.0001	TH
80941	318.67825	2.06475	6.5274	0.0001	TH