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Critical Behaviour of Gadolinium

by

Grzegorz Bednarz

A thesis

Submitted in partial fulfilment of the requirements
for the degree of Doctor of Philosophy

at

Department of Physics

Dalhousie University

Halifax, Nova Scotia

August, 1992

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ABSTRACT

A high-resolution, high-sensitivity, automated AC calorimeter capable of heat capacity measurements on very small samples ($m < 10$ mg) with a temperature resolution of a few mK in the AC mode is described. This calorimeter also can be operated in the relaxation mode to provide absolute heat capacity values with precision and accuracy of around 2%. A microprocessor was employed to generate a stable oscillatory heating signal and to control the heater power, in order to improve the sensitivity of the measurement over other designs. A new very sensitive and miniature temperature probe (a film flake of a thermistor material), which increased measurement resolution and minimized the heat contribution of the addenda relative to other methods, was used.

This calorimeter was tested by measuring the heat capacity of gadolinium (Gd) over its ferromagnetic phase transition for several single crystals of Gd. The results agree well with the literature data giving, however, better resolution of the heat capacity in the critical region.

The critical behaviour of Gd was analyzed in terms of power laws with critical exponents and the logarithmic form expected for uniaxial dipolar systems. The results of the analysis are discussed and compared with other studies.

LIST OF SYMBOLS AND ABBREVIATIONS

T	temperature
d	sample thickness
C	sample and addenda heat capacity
T_0	reservoir temperature
K	thermal conductance between sample and reservoir
ΔT	temperature difference between sample and reservoir
$P(t)$	sample heater power
P_0	amplitude of the sample heater power
ω	heating frequency
τ	thermal relaxation time
ϕ	phase shift
ΔT_{DC}	constant component of the temperature difference between sample and heat sink
ΔT_{AC}	amplitude of periodic temperature oscillations
τ_1	sample-reservoir thermal relaxation time
τ_2	sample thermal relaxation time
κ_s	sample thermal conductivity
c_s	sample heat capacity per unit mass
ρ_s	sample density
κ_g	exchange gas thermal conductivity
c_g	gas heat capacity per unit mass
ρ_g	gas density

l_1	distance from the reservoir to the temperature detector face of the sample
l_2	distance from the reservoir to the heater face of the sample
D_s	sample thermal diffusivity
D_g	gas thermal diffusivity
P_1	amplitude of the periodic component of the sample heating signal
k_{eff}	effective thermal conductance of gas per unit area
l_{eff}	effective distance between sample and reservoir
l_s	sample thermal diffusion length
l_g	gas thermal diffusion length
C_s	sample heat capacity
K_s	sample thermal conductance
K_{eff}	effective thermal conductance of gas
a	width of the unheated strip on sample surface
q_s	sample thermal diffusivity
T_c	critical temperature
M	magnetization
H	magnetic field
α	critical exponent α
β	critical exponent β
γ	critical exponent γ
δ	critical exponent δ
ρ_L	liquid critical density
ρ_G	gas critical density

p	pressure
p_c	critical pressure
C_H	magnetic heat capacity
χ	magnetic susceptibility
$\bar{s}(\underline{x})$	localized spin at site $\underline{x}$
$\sigma(\underline{x})$	spin density function
η	critical exponent η
F_{sing}	singular part of the free energy
F	free energy
H	Hamiltonian
LGW	Landau-Ginzburg-Wilson
RG	renormalization group
k_B	Boltzmann constant
J	spin exchange energy
L^d	integration volume in d dimensions
Z	partition function
$\underline{k}$	wave vector
σ_k	Fourier transform coefficient of spin density function
Λ	high momentum cut-off
R_s	renormalization group transformation
λ_i	Eigenvalue of the renormalization group transformation matrix
H_0^{PR}	primary part of the Hamiltonian
ΔH_0^{PR}	perturbation part of the Hamiltonian
Φ	crossover exponent

y_t	flow exponent of renormalization group transformation
t_t	scaling fields of the flow of the renormalization group transformation
g	spectroscopic splitting factor (Landé factor)
μ_B	Bohr magneton
α_D	critical exponent α for isotropic dipolar fixed point
γ_D	critical exponent γ for isotropic dipolar point
d^*	upper critical dimension
Γ_+, Γ_-	amplitude of magnetic susceptibility in uniaxial dipolar ferromagnet above and below T_c respectively
A_+, A_-	amplitude of heat capacity in uniaxial dipolar ferromagnets above and below T_c respectively
B_0	critical amplitude of magnetization in uniaxial dipolar ferromagnet
R_c	universal ratio of the amplitudes of magnetic susceptibility, heat capacity and magnetization
μ_i	random variable associated with impurities
α_p	critical exponent α for pure system
C_p	heat capacity at constant pressure
C_v	heat capacity at constant volume
H_{ex}	external magnetic field
U	internal energy
S	entropy

V	volume
σ_{ij}	stress tensor
ϵ_{ij}	strain tensor
C_σ	heat capacity at constant stress
C_ϵ	heat capacity at constant strain
α_{ij}	thermal expansion tensor
C_{ijkl}^T	isothermal elastic constant tensor
$D_{tot}(i)$	dipole sum
D	demagnetization factor
E_i	energy of i th stationary state of the crystal
a_w	domain thickness
L_z	sample thickness
L_x	sample length
L_y	sample width
$J_L(0)$	zeroth term of exchange energy expansion in momentum space
T_{c0}	mean field critical temperature
Ω_0	volume factor of the order of the volume of Gd unit cell
S_{Gd}	Gd spin number
V_{mol}	Gd molar volume
N_A	Avogadro's number
F_{tot}	total free energy of the single domain wall
κ	inverse of the correlation length
F_{qdr}	quadratic local contribution to the domain wall free energy

F_{grd}	gradient local contribution to the domain wall free energy
F_{qt}	quartic contribution to the domain wall free energy
V_i	volume of the domain plus the domain wall
F_{wall}	inhomogeneous demagnetization free energy of N domain walls
N_{Gd}	number of Gd atoms per m^3
P_{rms}	r.m.s. sample heater power
α_c, α_a	thermal expansion in the c-axis direction and a- axis direction, respectively
RRR	residual resistance ratio, $[R(293 \text{ K})/R(4.2 \text{ K})]$

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Chapter 1. INTRODUCTION

Calorimetry is one of the oldest and most extensively used research methods. Heat capacity data have a wide range of utility; for example they can be used to determine various thermodynamic quantities and to reveal and characterize phase transitions.¹

The progress made in the physics of critical phenomena in the two decades since Wilson² formulated the renormalization group (RG) approach to phase transitions in 1971, has created a need for data giving the temperature dependence of the heat capacity, $C(T)$, at temperatures extremely close to the critical value, T_c . The required heat capacity resolution can be of the order of a few mK, in order to give reduced temperatures, $t=(T-T_c)/T_c$, less than 10^{-3} . Such high-resolution heat capacity data can be used for testing and further development of existing RG models of phase transitions.

Despite impressive theoretical advances there is still a quite limited amount of experimental, high-resolution data available on the critical behaviour of heat capacity for various systems (this is particularly true for phase transitions in magnetic systems).³ This situation appears to reflect experimental difficulties involved in high-resolution measurements. The available data on critical

behaviour of heat capacity and other physical quantities often are not suitable for RG analysis and testing of RG predictions because they lack sufficient resolution around T_c .^{4,5}

The commonly used and well-known calorimetric methods are not very suited to high-resolution measurements. Adiabatic calorimetry, based on the heat-pulse method, is considered to be one of the most accurate calorimetric methods⁶, but its precision drops dramatically for very small temperature increments. This method, however, has been used successfully for high-resolution heat capacity studies at very low temperatures, when heat loss by radiation becomes negligible.⁷ The use of digital techniques of measurement also has led to the improvement of the precision of the heat-pulse method.⁸

Differential scanning calorimetry can be quite sensitive but it also lacks resolution and because of relatively high scanning rates there are problems with sample equilibrium when the heat capacity changes rapidly.^{9,10}

There have been several ingenious methods of high-resolution heat capacity measurement devised to remedy this situation. For example, in a continuous warming calorimeter, a thermally isolated sample is heated at a constant power and the heat capacity is derived from the rate of temperature increase.¹¹ The principal source of

error in this method is the uncertainty involved in determination of the temperature drift rate, which can be of the order of the actual drift rate for very slow temperature drift rates.

Another method appropriate for high-resolution measurements is the relaxation time method.¹² In this method, the sample temperature is increased by ΔT with respect to the heat sink temperature, and then the heat is turned off and the temperature relaxation curve is recorded. The heat capacity is determined from the temperature relaxation time constant and from the experimentally determined heat conduction between the sample and the surroundings. This method was used in this work to calibrate the measurements made in the AC mode and will be described in more detail in later sections.

In 1968 Sullivan and Seidel¹³ introduced a new method of measuring heat capacity which has subsequently been called "AC calorimetry". A number of publications have appeared since that time using this method in the study of phase transitions in solids^{14,15}, liquid crystals and fluids^{15,16} and biological materials.¹⁷ AC calorimetry offers very high (mK) resolution coupled with high sensitivity. This arises from the fact that this method measures amplitudes of periodic, millidegree temperature waves propagated through the sample. The changes in the temperature wave amplitude, which are caused by heat

capacity variations with temperature, can be very accurately measured with a lock-in amplifier. Advances of materials science and electronics have allowed the use of AC calorimetry in measurements on extremely small samples ($m \approx 25 \mu\text{g}$)¹⁸ and in noisy environments.¹⁹

In this thesis the design and the construction of an AC calorimeter for the study of phase transitions in solids is reported. This calorimeter also can be operated in the relaxation mode giving absolute values of heat capacity. In the following sections the theories of AC calorimetry and relaxation time calorimetry are described. The design of the electronics, which is crucial for the resolution of the calorimeter and which also allows one to run the calorimeter in the relaxation time mode, is described in detail. The designs of the cryostat and the sample assembly also are described in detail. Emphasis is put on the design of the sample heater and on the choice of the temperature probe, which allowed high-resolution heat capacity measurements while minimizing the heat capacity contribution of the addenda.

The physics of critical phenomena is reviewed in this thesis. The RG results for the systems whose critical behaviour is relevant to the critical behaviour of Gd is discussed. The discussion is concerned with ferromagnets with dipolar interactions and with phase transitions in disordered systems, including the phase transition in a

random dipolar Ising system.

The procedures employed to analyze experimental heat capacity data in terms of the RG theory are described.

The effect of an external magnetic field and a demagnetizing field on the heat capacity of a ferromagnet is discussed and mean field calculations of the contributions of demagnetization effects to the heat capacity of Gd are presented.

The literature results of experimental and theoretical studies of the critical behaviour of Gd are described and discussed.

The calorimeter presented here was used for high-resolution heat capacity measurements on several single crystals of gadolinium (Gd) in the vicinity of the ferromagnetic phase transition. These measurements tested the performance of the calorimeter. The results obtained agreed well with the literature data giving, however, better resolution of the heat capacity in the critical region.

The high-resolution heat capacity data around T_c were used to study the critical behaviour of Gd. The dependence of the heat capacity curve in the vicinity of T_c on sample preparation procedure, including sample annealing also was investigated. The results of this study are discussed and compared with results of other studies of the critical behaviour of Gd.

Chapter 2. THEORY OF AC CALORIMETRY AND RELAXATION TIME CALORIMETRY

2.1 Alternating current (AC) calorimetry

The theory of AC calorimetry has been discussed extensively in a number of publications^{13,20,21} and theses^{22,23}. Therefore only a brief review of the theory following the analyses given elsewhere^{20,22,23} and pertinent to the geometry of the apparatus used in this work will be given here.

Consider the simplified model of an AC experiment shown in Fig. 1. The sample is a thin slice of material of uniform thickness, d . This sample, which has a resistance heater attached to one face and a temperature sensor on the other face, is loosely coupled thermally to the reservoir at temperature T_0 via an exchange gas and connection leads. The thermal conductance of this thermal link is K and the heat capacity of the sample assembly is C . If the sample has infinite thermal conductivity and the thermal link has zero heat capacity, then the difference in temperature of the sample and the reservoir is given by Newton's law of cooling,

$$C\Delta\dot{T}(t) = P(t) - K\Delta T(t) , \quad (2.1)$$

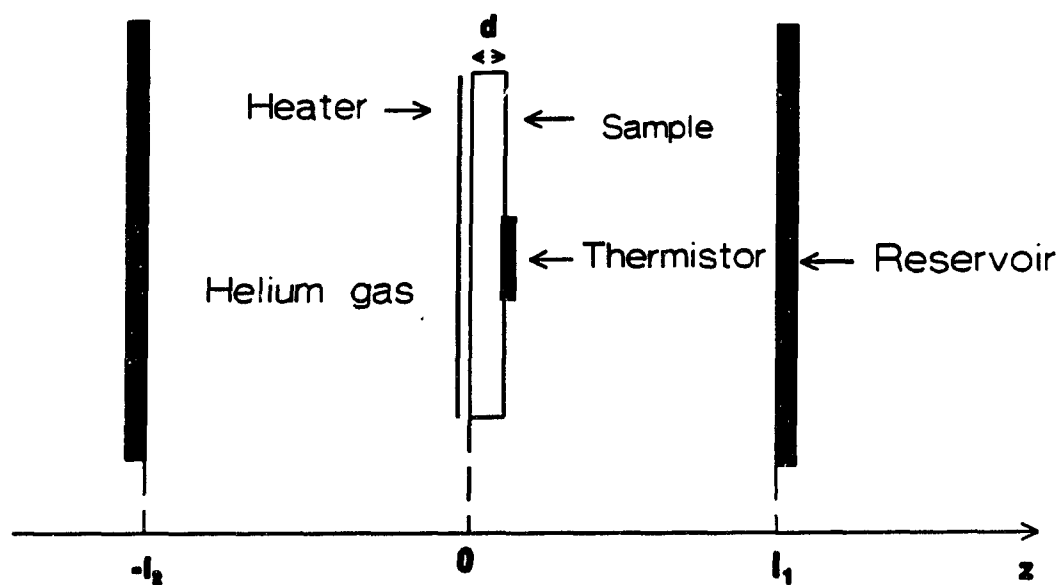


Fig. 1.1 Idealized one-dimensional heat flow problem.

where $\Delta T(t)$ is the temperature difference between the sample and the reservoir and $P(t)$ is the heater power.

For a phase-sensitive detection at the second harmonic the oscillatory power used is $P(t) = P_0 \cos^2 \omega t$ and the steady state solution to Eq.(2.1) is

$$\Delta T = \frac{P_0}{2K} + \frac{P_0}{4\omega C} \frac{1}{1 + \frac{1}{(2\omega\tau)^2}} \frac{\cos(2\omega t - \phi)}{\sin\phi}, \quad (2.2)$$

where $\tau = C/K$ is the external time constant and ϕ is the phase shift ($\tan\phi = 2\omega\tau$). If $(\omega\tau)^2 \gg 1$ the solution can be written in the form:

$$\Delta T \approx \frac{P_0}{2K} + \frac{P_0}{4\omega C} \cos(2\omega t - \phi) \equiv \Delta T_{DC} + \Delta T_{AC} \cos(2\omega t - \phi), \quad (2.3)$$

where ΔT_{DC} is the constant temperature difference between the sample and the heat sink and ΔT_{AC} is the amplitude of the AC temperature oscillations (the phase shift is around $\pi/2$). A lock-in amplifier detects the second harmonic of the temperature oscillation which is inversely proportional to C . Detection at the second harmonic is useful because of a built-in advantage of discrimination against leakage from the heater voltage.

In a real system two time constants serve to characterize the thermal dynamics of the system.^{22,23} One time constant, τ_1 , characterizes the thermal coupling between the sample and its surroundings. The other time

constant, τ_2 , characterizes the thermal relaxation within the sample and is determined by the thermal diffusivity, D , and thickness of the sample, d .

The effect of these time constants on the AC temperature oscillations can be investigated by solving the one-dimensional heat flow problem for the model situation described in Fig.1. For this purpose the sample is assumed to have thermal conductivity κ_s , density ρ_s , and heat capacity per unit mass c_s . The sample is surrounded by gas of thermal conductivity κ_g , density ρ_g , and heat capacity per unit mass c_g and the reservoir walls are at distances l_1 and l_2 from the sample, and are kept at temperature T_0 . The heat flux per unit area is given by $P(t) = P_0 + P_1 e^{i\omega t}$ producing a one-dimensional heat flow along z -axis. One has to solve the heat conduction equation²⁴:

$$\frac{\partial T(z, t)}{\partial t} = D_i \frac{\partial^2 T(z, t)}{\partial z^2}, \quad (2.4)$$

where $D_i = \kappa_i / \rho_i c_i$ is the thermal diffusivity of the gas ($i=g$) or of the sample ($i=s$). The boundary conditions are that the heat flux and the temperature are continuous on the interfaces and that at the reservoir walls

$T(l_1 + d, t) = T(-l_2, t) = T_0$. At the heater side of the sample the boundary conditions are:

$$T(0, t) \big|_{0^-} = T(0, t) \big|_{0^+}. \quad (2.5)$$

$$-\kappa_g \frac{\partial T}{\partial t} \Big|_{0^-} + P = -\kappa_s \frac{\partial T}{\partial t} \Big|_{0^+} \quad (2.6)$$

and those on the opposite side of the sample are:

$$T(d, t) \Big|_{d^+} = T(d, t) \Big|_{d^-} \quad (2.7)$$

$$-\kappa_s \frac{\partial T}{\partial t} \Big|_{d^+} = -\kappa_g \frac{\partial T}{\partial t} \Big|_{d^-} \quad (2.8)$$

The steady-state time-dependent solution to this problem inside the sample is of the form²⁴:

$$T(z, t) = T_0 + \Delta T_{DC}(z) + \Delta T_{AC}(z) e^{i\omega t}, \quad (2.9)$$

where $\Delta T_{DC}(z)$ can be written in the form:

$$\Delta T_{DC} = a_s + b_s z, \quad (2.10)$$

and $\Delta T_{AC}(z)$ is of the form:

$$\Delta T_{AC}(z) = A_s e^{q_s z} + B_s e^{-q_s z}, \quad (2.11)$$

where $q_s^2 = i\omega/D_s$ and D_s is the thermal diffusivity of the sample. Next the boundary conditions can be written explicitly and solved for the coefficients of the ΔT_{DC} and ΔT_{AC} parts of the solution. After algebraic manipulations one obtains for the DC part of the solution:

$$\Delta T_{DC}(z) = -\frac{P_0 l_2}{d\kappa_g + \kappa_s(l_1 + l_2)} z + \frac{P_0 l_2}{\kappa_g} \frac{d\kappa_g + \kappa_s l_1}{d\kappa_g + \kappa_s(l_1 + l_2)}. \quad (2.12)$$

If the thermal conductance of gas between the sample and the reservoir is much smaller than that of the sample, Eq.

(2.12) for $z=0$ reduces to:

$$\Delta T_{DC}(0) \approx \frac{P_0}{k_{eff}}, \quad (2.13)$$

where $k_{eff} = \kappa_g / l_{eff}$ is the effective thermal conductance of the gas per unit area and $l_{eff} = l_1 l_2 / (l_1 + l_2)$. In this case $\Delta T_{DC}(d) \approx \Delta T_{DC}(0)$, i.e., the sample has a single DC temperature.

The coefficients of Eq. (2.11) are:

$$A_s = \frac{P_1}{\kappa_s q_s} \left[(\gamma_1 - 1) + e^{2q_s d} \frac{(1 + \gamma_2)(1 + \gamma_1)}{(1 - \gamma_2)} \right]^{-1} \quad (2.14)$$

and

$$B_s = A_s e^{2q_s d} \frac{(1 + \gamma_2)}{(1 - \gamma_2)}, \quad (2.15)$$

where

$$\gamma_1 = \left[\frac{\rho_g C_g K_g}{\rho_s C_s K_s} \right]^{1/2} \coth(q_g l_2), \quad (2.16)$$

and

$$\gamma_2 = \left[\frac{\rho_g C_g K_g}{\rho_s C_s K_s} \right]^{1/2} \coth(q_g l_1). \quad (2.17)$$

The AC temperature at the back face of the sample is:

$$T_{AC}(d) = \frac{P_1}{\kappa_s q_s} \left(\sinh(q_s d) [1 + (\gamma_1 + \gamma_2) \coth(q_s d) + \gamma_1 \gamma_2] \right)^{-1}. \quad (2.18)$$

In order to extract useful information from Eq. (2.18) one can define an external relaxation time, τ_1 , by:

$$\frac{1}{i\omega\tau_1} \equiv (\gamma_1 + \gamma_2) \coth(q_s d) . \quad (2.19)$$

The external relaxation time, τ_1 , takes on a simple meaning if $l_1/l_g \ll 1$ and $l_2/l_g \ll 1$, and also $d/l_g \ll 1$ where $l_g = (D_g/\omega)^{1/2}$ and $l_s = (D_s/\omega)^{1/2}$ are the characteristic thermal diffusion lengths of the gas and the sample, respectively. In practice these conditions are satisfied by regulating the amount of thermal link between the sample and the surroundings, thinning the sample and adjusting the operating frequency of the AC power input. Making the approximations: $\coth(q_s d) \approx 1/(q_s d)$, $\coth(q_g l_1) \approx 1/(q_g l_1)$, and $\coth(q_g l_2) \approx 1/q_g l_2$, one obtains:

$$\tau_1 \approx \frac{\rho_s c_s d l_{eff}}{\kappa_g} = \frac{C_s}{K_{eff}} , \quad (2.20)$$

where $K_{eff} = \kappa_g (S/l_{eff})$ is the effective thermal conductance of the gas, S is the sample surface area, c_s is the sample heat capacity per unit mass and C_s is the total sample heat capacity. Thus τ_1 can be identified with the relaxation time from Eq. (2.2).

Eq. (2.18) can be simplified if one assumes that $\omega\tau_1 \gg 1$. In this case $\omega\tau_1 \gg 1$ then $\gamma_1\gamma_2 \ll \gamma_1 + \gamma_2$ and the $\gamma_1\gamma_2$ term can be neglected in Eq. (2.18).

At this point it is also convenient to introduce the internal relaxation time for the sample, τ_2 :

$$\tau_2 \equiv \frac{d^2}{D_s} = \frac{C_s}{K_s} , \quad (2.21)$$

where K_s is the thermal conductance of the sample.

Under the conditions that $(\omega\tau_1)^2 \gg 1$, and $(\omega\tau_2)^2 \ll 1$ and keeping two terms of the expansion of $\sinh(q_s d)$ in the Taylor series one obtains from Eq. (2.18):

$$T_{AC}(d) \approx \frac{P_1}{i\omega\rho_s c_s d} \left[1 + \frac{1}{i\omega\tau_1} + \frac{1}{6} i\omega\tau_2 + \frac{\tau_2}{6\tau_1} \right]^{-1}. \quad (2.22)$$

The amplitude of the temperature oscillations on the heater face of the sample is thus:

$$|T_{AC}(d)| \approx \frac{P_1}{\omega\rho_s c_s d} \left[1 + \frac{1}{(\omega\tau_1)^2} + \frac{1}{36} (\omega\tau_2)^2 + \frac{\tau_2^2}{36\tau_1^2} \right]^{-\frac{1}{2}}. \quad (2.23)$$

Eq. (2.23) can be written in more transparent form by expanding the square root in the Taylor series and keeping terms to the order of $(\tau_{1,2})^2$:

$$|T_{AC}(d)| \approx \frac{P_1}{\omega\rho_s c_s d} \left(1 - \frac{1}{2(\omega\tau_1)^2} - \frac{(\omega\tau_2)^2}{72} - \frac{\tau_2^2}{72\tau_1^2} \right). \quad (2.24)$$

For a sufficiently thin sample the heating frequency can be chosen so that the correction terms in the bracket in Eq. (2.24) contribute less than 0.1% to ΔT_{AC} .

If the sample is not heated uniformly (for instance, if the resistance heater leaves bare strips of the sample surface along its edges) then one has to consider the lateral heat flow in the sample. For this purpose assume that a strip of the sample from $x=0$ to $x=a$ in the direction of the x -axis is not heated. (The sample is assumed to be

infinite in the x-and y-directions with its surface perpendicular to the z-axis.) Then the amplitude of the AC oscillation at the back face in the heated part of the sample for $x > a$, $T(x)_{AC}$, is²²:

$$T(x)_{AC} \approx |T_{AC}(d)| (1 - \sinh(a/l_g) \exp(-x/l_g)) \quad (2.25)$$

For typical experimental conditions the lateral dimensions of the sample are much larger than the thermal diffusion length and the ratio $a/l_g \ll 1$, so the correction term for a temperature probe placed in the centre of the sample is very small (for samples described in this thesis it was of the order of 10^{-4}). The temperature probe senses the average AC temperature oscillations within the radius of the thermal diffusion length, the amplitude of which is determined by the local heating power and the heat capacity of the sample per unit of the sample surface area. Knowing the power density and the sample surface area one can calculate the total absolute heat capacity value from Eq. (2.3). However, because of the uncertainties involved in accurately determining the sample surface area and the heater surface area, and inhomogeneities in the heater coverage, this procedure can give only a rough estimate of the absolute heat capacity of the sample.

A much better way to calibrate data from AC calorimetry is by using the relaxation time method, which is the subject of the next section.

2.2 Relaxation time method

In the thermal relaxation method, the heat sink temperature is stabilized at some temperature T_0 . Current is then passed through the sample heater, dissipating power P and increasing the temperature of the thermometer-sample assembly to $T_0 + \Delta T$, where $\Delta T = P/K$, and K is the thermal conductance between the sample and the heat sink. The current in the sample heater is then turned off, and the sample temperature, T , relaxes exponentially,²⁵

$$T(t) = T_0 + \Delta T e^{(-\frac{t}{\tau})}, \quad (2.26)$$

to T_0 with the time constant

$$\tau = \frac{C}{K}, \quad (2.27)$$

where C is the total (sample plus addenda) heat capacity. The above expression assumes that the thermal link K has zero heat capacity. Bachmann et al.²⁵ showed that approximately 1/3 of the heat capacity of the thermal link should be included as addendum.

This simple model gives good results in many cases, but if the thermal conductance of either the sample or the sample-substrate bond is comparable to that of the heat leak or if the heat capacity of the connection wires is appreciable, $T(t)$ must be represented by a more complicated

sum of exponentials with different time constants.²⁶ The cooling curves in that case are characterized by an abnormally high initial slope compared to the rest of the decay. For experimental purposes, if the ratio τ_2/τ_1 of the time constants defined in the previous section is of the order of 10^2 or smaller then Eq. (2.26) is a reasonable approximation.

Near a phase transition the simple exponential decay becomes more complicated and one has to consider the full equation,

$$\frac{\dot{T}}{T-T_0} = -\frac{K}{C(T)} \quad , \quad (2.28)$$

from which Eq. (2.26) was derived, i.e., near transitions, not only must T be measured, but also its time derivative, $\dot{T}$, must be known. This one of the principal sources of error in this method and the source of its basic limitation for studies of phase transitions. However, the relaxation time method can be used for accurate absolute heat capacity measurements (to ca. 2%) and if the total heat input to the sample can be known accurately it is a very convenient way to calibrate AC calorimetry data.²⁷

Chapter 3. REVIEW OF THE PHYSICS OF CRITICAL PHENOMENA

3.1 Introduction

Changes of phase - the boiling of water, the melting of iron - have long fascinated scientists. In many cases, by varying the temperature or other thermodynamic parameters, two distinct phases can be made more and more similar in their properties until, at a certain critical point, all differences vanish²⁸. Beyond this point only one homogeneous equilibrium phase can exist. Familiar examples of such critical point are: the critical point which terminates the coexistence curve of a liquid and its vapour at a characteristic temperature, pressure and density; the critical point of phase separation in a binary fluid mixture (or a binary metallic alloy), which marks the temperature above which (or sometimes below which) the components mix homogeneously in all proportions; the Curie point or critical point of a ferromagnetic crystal at which the spontaneous magnetization, and hence the difference between two differently oriented magnetic domains, goes continuously to zero; the Néel point at which the alternating spin order of an antiferromagnet goes to zero; the critical point of a metallic superconductor below which the electrical resistance vanishes and a permanent current may flow.

It was noticed long ago that near a critical point the

behaviour of quite dissimilar systems exhibited many similar features. When Pierre Curie, in 1885, measured the magnetic equation of state of nickel, he was struck by the similarity between curves obtained by plotting magnetization as a function temperature, and density-temperature isobars of carbon dioxide near the critical point.²⁹ Since that time, it has been found that the richness and variety of critical behaviour can be understood and classified from a common point of view. Books by H.E. Stanley³⁰ and S.-K. Ma³¹ contain a general review of physics of critical phenomena; the Domb-Green-Lebowitz series gives detailed reviews of the theoretical and experimental progress in that field.³²

The phase below the critical point is an ordered phase; it can be characterized by an order parameter that goes to zero at the critical point. In ferromagnets, the order parameter is the magnetization vector, $\underline{M}$, and the magnetic susceptibility, χ , (change in magnetization induced by a small applied field) is its response function which diverges at the critical point, indicating that the system has reached a limit of stability. When the response function diverges, large-scale fluctuations of the order parameter can occur at low cost in free energy. (In liquids, these manifest themselves in an anomalous scattering of light called "critical opalescence", which gives a fluid near its critical point typical milky appearance³⁰). A way of describing this divergence is by means of the correlation

function, $G(r)$, which measures the extent to which local spin fluctuations a distance r apart are correlated. The correlation length, ξ , i.e. the range of $G(r)$, diverges in the vicinity of the critical point, which means that large-scale fluctuations extending over regions containing very many particles are present in the system. Because of those fluctuations the details of the particles' interactions are irrelevant and considerable similarity can be found in the critical behaviour of diverse systems.

Critical phenomena can be classified into two categories, static and dynamic. Static phenomena concern equilibrium properties such as magnetization, susceptibility and specific heat. Dynamic phenomena concern time-dependent phenomena such as relaxation times, heat diffusion and spin wave propagation. At present, the static critical phenomena are better understood than dynamic critical phenomena.

3.2 Definition of static critical exponents

A problem of central interest in physics of critical phenomena is the determination and explanation of the asymptotic laws describing the way in which various physical quantities (heat capacity, susceptibilities, etc.) diverge to infinity or converge to zero as the temperature or other variable approaches its critical value. Critical exponents are used to characterize the critical behaviour numerically.²⁸

The static critical exponents are conveniently discussed in the context of magnetic critical phenomena. The temperature dependence of the various magnetic quantities (such as magnetization) can be expressed by a series expansion about the critical temperature, T_c . For a quantity $L(T)$ the expansion can be written as^{28,30}:

$$L(T) = L_0 |t|^\lambda (1 + \sum_i a_i |t|^{\theta_i}), \quad (3.1)$$

for $T > T_c$, where L_0 and $\{a_i\}$ are constants, $t = (T - T_c)/T_c$ and the same function with primed coefficients for $T < T_c$. The critical exponent λ , for that quantity is defined as

$$\lambda = \lim_{t \rightarrow 0} \frac{\ln L}{\ln |t|} \quad (3.2)$$

so that sufficiently close to T_c , $L(T) \approx L_0 |t|^\lambda$, $t > 0$ and $L(T) \approx L_0' |t|^{\lambda'}$, $t < 0$.

3.2.a Magnetization as a function of t : the exponent β

When the external magnetic field $\underline{H}$ vanishes, the magnetization $\underline{M}$ below T_c decreases with increasing T , and vanishes at T_c . Very close to T_c , the power law behaviour is a common feature³¹:

$$M \propto |t|^\beta \quad (3.3)$$

with β being the critical exponent associated with the magnetization. The observed value of β for ferromagnets like Fe and Ni is around 0.37 and around 0.33 for anisotropic magnetic materials like MnFe_2 , CrO_2 and fluids.^{5,28,33,34,35} (For fluids the corresponding definition can be obtained by substitution of $\underline{M}$ by $\rho_L - \rho_G$, where ρ_L is the density at the liquid side of the coexistence curve and ρ_G is the density at the gas side of the coexistence curve).³⁰

3.2.b The magnetic susceptibility (order parameter susceptibility), χ , for $\underline{H} = 0$ as a function of t : the exponent γ

As T approaches T_c , χ diverges and its divergence is characterized by the exponents γ' and γ :

$$\begin{aligned} \chi &\propto t^{-\gamma}, & T > T_c \\ &\propto t^{-\gamma'}, & T < T_c. \end{aligned} \quad (3.4)$$

Data are usually consistent with $\gamma' = \gamma$ but the proportionality constants in the two cases are not the same.³¹

Experimentally observed values of γ are slightly larger than unity, e.g. $\gamma \approx 1.33$ for ferromagnets like Fe and nickel and $\gamma \approx 1.23$ for anisotropic magnetic materials such as CrBr_3 and for fluids.^{30,31,34,33} (For fluids γ describes the divergence of the isothermal compressibility.³⁰)

3.2.c Critical isotherm ($\underline{H}$ as a function of $\underline{M}$ at $T=T_c$): the exponent δ

One observes, for very small magnetic fields³¹:

$$H \propto M^\delta, \quad t=0. \quad (3.5)$$

The observed value of δ falls in the range from 4 to 4.4.³⁴

(For fluids one replaces $\underline{M}$ with $(\rho_L - \rho_G)$ and $\underline{H}$ with $(p - p_c)$ where ρ_L is the density at the liquid side of the coexistence curve and ρ_G is the density at the gas side of the coexistence curve and p and p_c are the pressure and the critical pressure respectively.³⁰)

3.2.d Heat capacity and the exponent α

The heat capacity C at $H = 0$ is observed to have a singularity at T_c , characterized by exponents α' and α :

$$\begin{aligned} C_M &= \frac{A}{\alpha} (t^{-\alpha} - 1), & T > T_c \\ &= \frac{A'}{\alpha'} ((-t)^{-\alpha'} - 1), & T < T_c, \end{aligned} \quad (3.6)$$

where A and A' are different proportionality constants and $\alpha \approx 0.1$ for uniaxial anisotropic magnets and for fluids, while $\alpha \approx 0$ for the lambda transition in ^4He , and $\alpha \approx -0.1$ for Ni, Fe and other isotropic magnets.^{30,31,34,35} Note from Eq. (3.6) that $\alpha = 0$ implies a logarithmic divergence as can be seen by taking the limit $\alpha \rightarrow 0$ in this equation. It is usually observed that $\alpha' = \alpha$ within experimental error.

3.2.e. Microscopic correlations

In addition to thermodynamic critical behaviour, the variations of microscopic correlations among magnetic moments with temperature are of particular interest in the critical region. These correlations are described by the spin-spin correlation function, $G(\underline{r})$:

$$G(\underline{x}) = \langle [\bar{s}(\underline{x}) - \langle \bar{s} \rangle] \cdot [\bar{s}(\underline{0}) - \langle \bar{s} \rangle] \rangle, \quad (3.7)$$

in which $\bar{s}(\underline{x})$ denotes a (localized) spin at site $\underline{x}$. The angular brackets indicate statistical averaging over all possible spin configurations. The spin density function, $\sigma(\underline{x})$ is also used in place of $\bar{s}(\underline{x})$. The average $\langle \bar{s} \rangle$ gives the magnetization, which is nonzero if $T < T_c$. The thermal average in Eq. (3.7) is thus the correlation function of the deviation from the average spin, i.e., spin fluctuation. One also can introduce a Fourier transform, $G(\underline{q})$, of the spin correlation function. There is an important identity, relating $G(\underline{q})$ to the susceptibility χ :

$$T\chi = G(\underline{q}=0). \quad (3.8)$$

Thus the susceptibility can be derived from neutron scattering experiments, which measure the correlation function.³¹

At the critical point, the correlation function involves the exponent η :

$$G(r) \propto r^{-(d-2+\eta)}, \quad t=0, H=0, \quad (3.9)$$

where d is the lattice dimensionality and the exponent η , which is difficult to measure experimentally, is observed to lie in the range 0.01-0.1.^{31,32}

The correlation length, ξ , is a measure of the range over which spin fluctuations are correlated (the degree of correlation being given by the correlation function) or the average size of the region in which a sizeable fraction of spins point in one direction. The correlation length enters the expression for the correlation function for $t \rightarrow 0$ (but $t \neq 0$):

$$G(r) \propto r^{-1} \exp(-\frac{r}{\xi}). \quad (3.10)$$

The correlation length diverges at T_c and the divergence, asymptotically, can be described by a power law:

$$\begin{aligned} \xi &\propto (-t)^{-\nu}, & T > T_c \\ &\propto t^{-\nu'}, & T < T_c, \end{aligned} \quad (3.11)$$

where ν and ν' are the associated exponents. The proportionality constants in the two cases generally are different. It is observed experimentally that $\nu = \nu'$ and the value of ν falls in the range from 0.6 to 0.7 for three dimensional magnets.³⁴

3.3 Scaling theory, critical exponents equalities, critical point universality

The first successful attempt to bring order into a variety of critical exponents and power laws was based on the static scaling hypothesis which asserts that the singular part of the free energy is a generalized homogeneous function of its two independent variables (t and H in the magnetic case) such that:

$$F_{sing}(\lambda^p t, \lambda^q H) = \lambda^d F_{sing}(t, H) , \quad (3.12)$$

where p and q are two critical exponents, d is the dimensionality and λ is an arbitrary constant.³⁰

The alternative and original formulation of the scaling hypothesis was due to Widom³⁶, Kadanoff³⁷ and Griffiths³⁸. In this formulation, which is often used in the literature, the homogeneity relation for the free energy, $F_{sing}(t, H)$, is written as

$$F_{sing}(t, H) = t^{2-\alpha} F_{sing}(t^{\beta\delta}/H) , \quad (3.13)$$

where the exponents α, β and δ are defined in the preceding section.

The scaling form of the magnetic equation of state is³⁸

$$H(M, T) = M |M|^{\delta-1} h(t | M|^{-1/\beta}) . \quad (3.14)$$

All critical exponents defined in the preceding section now may be expressed as combinations of p , q , and d . This can

be done by taking various partial derivatives of the free energy in the scaling form given in Eq. (3.12) in order to obtain corresponding thermodynamic quantities and then equate them to their power law counter-parts. In the next step, relations among various critical exponents are obtained.³⁰ A list of scaling relations is shown in Table 3.1. It should be noted that many scaling relations can be proven in the form of rigorous inequalities without making the scaling assumption.³⁰

The physical basis for the homogeneity property of the free energy was initially unknown. However, it became clear later that the homogeneity property follows from the role which the correlation length plays in critical phenomena.³²

In this context the scaling hypothesis asserts that the correlation length, ξ , is the longest and the only relevant length in explaining critical phenomena.³¹ Other lengths, such as the interatomic distances, are too short to play a role. In other words, physical quantities depend on t only through their dependence on the correlation length. Thus, the divergence of ξ is responsible for the singular behaviour of physical quantities.

Table 3.1 Relations among the critical-point exponents predicted by the scaling hypothesis.

(1)	$\alpha + 2\beta + \gamma = 2$
(2)	$\gamma = (2 - \eta)\nu$
(3)	$\alpha = 2 - \nu d$
(4)	$\beta\delta = \beta + \gamma$
(5)	$\delta = (d + 2 - \eta) / (d - 2 + \eta)$
(6)	$\alpha' = \alpha$
(7)	$\gamma' = \gamma$

Under a scale change, the correlation length changes and since the correlation length is proportional to $|t|^{-\nu}$ this change corresponds to a change in temperature. Therefore, near T_c the temperature dependence of a physical quantity can be deduced from the way it behaves under a scale change. One of the implications of the scaling hypothesis formulated in this way is the scaling form of the free energy (Eq. (3.12)). A simple example applying this idea follows. The free energy per unit volume $F_{\text{sing}}(\xi)$ becomes $s^d F_{\text{sing}}(\xi)$ when the volume of the system is shrunk by a factor of s ; d is the dimension. Therefore one has $F_{\text{sing}}(\xi/s) = s^d F_{\text{sing}}(\xi)$. Since s is arbitrary, one sets $s = \xi$. Thus:

$$F_{\text{sing}}(\xi) = s^{-d} F_{\text{sing}}\left(\frac{\xi}{s}\right) = \xi^{-d} F_{\text{sing}}(1) \propto |t|^{-d}. \quad (3.15)$$

By taking the second derivative with respect to temperature

of this scaled free energy scaling relation (3) from Table 3.1 can be obtained.

The important feature of critical phenomena highlighted by current theories and experiments is the concept of universality introduced by Kadanoff.³⁷ According to the universality principle, the variety of systems that show critical behaviour can be divided into equivalence classes called universality classes. At present, the following factors are thought to distinguish the various universality classes: d , the spatial dimensionality of the system; n , the number of components of the order parameter; the symmetries of the Hamiltonian of the system; the range of the microscopic interactions responsible for the phase transition; the presence of disorder. These features of critical phenomena has been emphasized by the renormalization group theory described in subsequent sections.

3.4 Classical theories of critical behaviour

In an attempt to understand critical behaviour, there have been many theoretical models proposed that have critical-point phase transitions.^{28,30} The earliest models, i.e. the van der Waals theory and the Weiss molecular-field theory, are mean field theories. The classical predictions of the van der Waals theory and the Weiss molecular field theory are derived by an approximate theoretical treatment in which the crucial assumption is that the fluctuating forces acting on a single element of the system, i.e. spin, may be replaced by an effectively constant average field due to the rest of the system. Those models have a critical point for which critical exponents are integers or simple fractions independent of dimension. The mean-field exponents differ, however, from those found in real systems with short-range interactions.^{28,30}

Alternatively, the classical predictions follow from the phenomenological equation of state derived under two assumptions: (1) that the relevant thermodynamic potentials may be expanded in Taylor series about the critical point in powers of some order parameter, and (2) the expansion coefficients may be expanded in powers of $(T-T_{c0})$, where T_{c0} is the mean field critical temperature (the coefficients may vanish at T_{c0} to yield, e.g., an infinite susceptibility).²⁸ The order parameter is a thermodynamic variable selected so

that its equilibrium value is zero above T_{c0} and one of several non-zero values related by symmetry below T_{c0} . These assumptions were first introduced and discussed by Landau³⁹ and led to a subsequent development of the Landau theory of phase transitions.^{30,40} Some of the concepts of the Landau theory are present in the modern theories of phase transitions and because of that this theory will be illustrated here, using the example of a ferromagnetic phase transition. The order parameter in this case is the magnetization M and the free energy after expanding in powers of M will take the form:^{30,28}

$$F(T, H, M) = F_0(T, H) + F_2(T, H)M^2 + F_4(T, H)M^4 + \dots \quad (3.16)$$

Coefficients of odd powers must vanish because the free energy is an even function of the magnetization. The equilibrium value is found by minimizing $F(T, H, M)$ with respect to M . Assuming now that $F_4(T, H)$ is positive, and $F_2(T, H) = A(T - T_c)$ with $A > 0$ (these assumptions ensure a single minimum above T_c and a double minimum below T_c) one obtains:

$$M_{eq} = \left[\frac{1}{2} \frac{A}{F_4} (T_c - T) \right]^{\frac{1}{2}}, \quad T \leq T_c. \quad (3.17)$$

This relation gives the classical $\beta = 1/2$ result. The other classical values of critical exponents which can be obtained from the Landau theory are: $\gamma = \gamma' = 1$, $\delta = 3$ and the heat capacity has a discontinuity at T_c corresponding to $\alpha = \alpha' = 0$.

These values of the critical exponents do not agree with experimental observations (Sec. 3.2). The reason for the quantitative failure of mean-field theories is not hard to identify. In all these theories the state of any selected particle (spin) is determined by the average properties of the system as whole. In effect all spins in the systems contribute equally to the force exerted on each spin, which is equivalent to assuming that the interaction forces have infinite range. This is a serious approximation; the nearest neighbours are much more important than any other spins. The same objection can be expressed another way: the main approximation made in the classical theories is that they do not account for the local fluctuations and correlations. One may estimate within the mean field theory how important the fluctuations are by computing the relationship between the deviation of the spontaneous magnetization from its average at one point in the material, and similar deviations in the neighbouring region.³⁴ This deviation can be described in terms of the correlation function given by Eq. (3.10).³⁴ Thus the fluctuations turn out to be very large close to the critical point. This implies that the mean field theories should be accurate far enough from the critical point (outside some critical region). Fisher²⁸ estimated the size of this critical region by:

$$\frac{|T - T_c|}{T_c} \approx \left(\frac{a}{b}\right)^d, \quad (3.18)$$

where a is the radius of the sphere occupied by the interacting particle, b is the interaction range and d is the dimensionality. In the limit $a/b \rightarrow 0$ the critical region shrinks to zero, that is the mean-field theory becomes exact. Because the interaction potential also has to be scaled so that its mean-field value remains constant it follows that the mean-field theory should be valid for an infinitely weak and infinitely long-range potential. Eq.(3.15) also implies that the mean field predictions should become correct as $d \rightarrow \infty$. Ginzburg⁴¹ proposed a criterion in which the Landau theory is used to predict its own range of validity. This criterion estimates the size (on the reduced temperature scale) of the critical region where the Landau theory fails, by comparing the size of the discontinuity in the heat capacity predicted by the Landau theory to the size of the divergent term as given by the power law for heat capacity. For instance, the width of the critical region for the magnetic transition for iron from the Ginzburg criterion is $|t| < 10^{-2}$. The Ginzburg criterion also indicates that as the range of interaction forces increases the size of the critical region decreases.

In the early 1920's Wilhelm Lenz⁴² and Ernest Ising⁴³ constructed the first statistical model for a lattice system

with short-range forces. The Ising system, as that model is now called, is an array of up and down spins. The Ising, XY and Heisenberg models represent lattice systems with, respectively, one-, two-, and three-component magnetic spins. None of the models predicts a phase transition in one dimension but all do in three dimensions. For the two-dimensional Ising system, which exhibits a phase transition in zero field, the critical exponents are known from Onsager's⁴⁴ and Yang's⁴⁵ exact calculation. The correct values are^{44,45}: $\beta = 1/8$, $\gamma = 7/4$ and $\nu = 1$. The heat capacity has a logarithmic singularity, $C \propto \ln|t|$. For the three-dimensional Ising and other models exact solutions are not available and approximate solutions have been obtained by a variety of methods, e.g. by series expansion (the Boltzmann factor $\exp(-H/k_B T)$ is expanded in powers of $1/T$ and the trace is taken term by term²⁸) and by renormalization group theory methods such as described in the next section.

3.5 Renormalization group theory

An approach which can account for large length scale fluctuations is the renormalization group (RG) theory.^{46,47} This approach to understanding phase transitions was developed by Kenneth Wilson and can be viewed as an extension and implementation of Kadanoff's ideas of scale transformation and of the block of spins Hamiltonian.³⁴ The renormalization group theory studies the transformation under repeated change of scale of $H/k_B T$, where H is the Hamiltonian of the system, k_B is the Boltzmann constant and T is the temperature. This transformation has three basic steps which can best be illustrated with the Ising model.^{40,31}

Consider a spin system in which only nearest-neighbours interact and the coupling strength, J , is assumed to be proportional to $1/T$. The first idea in the RG theory is to remove from the problem a finite fraction of the degrees of freedom by averaging over them. This can be done by dividing the lattice into blocks of s^d spins each, where d is the dimensionality. Next all the spins in the block are averaged in some way and the entire block is replaced by a single new spin. The result of these two operations is to create a new lattice whose fundamental spacing is s times as large as that of the old lattice. In the third step the original scale is restored by reducing all dimensions by s . The calculation ends by expressing the coupling strength,

J' , between adjacent spins of the new lattice as a function of J in the hope that if that step is possible, a recursion relation, $J' = R_s(J)$, can be developed. The renormalization group calculation then proceeds by starting all over again, and iterating with the new system of block spins as the starting lattice. Each new system created is distinguished by a different coupling J_i . Its behaviour is that of the original lattice but at a different temperature. The iterations may drive the system towards or away from the critical temperature. The transformation of the system from one state to the next can be represented by motion of J in its parameter space under application of the RG transformation $J_{i+1} = R_s(J_i)$. When the system reaches the point when $J^* = R_s(J^*)$, i.e. the RG transformation leaves all essential properties of the lattice unchanged, the system is said to be at a fixed point.

There is an analogy between a fixed point and a critical point. At the critical point the correlation length is infinite so it does not change under the scale change, i.e. $\xi^* = R_s(\xi^*)$. Therefore one of the fixed points in the parameter space of J (there can be, in general, many fixed points) may correspond to the critical point of the system. The information about the critical exponents of the system can be obtained from the shape of the parameter surface in the vicinity of the critical point. The slope near the fixed point determines the rate at which properties

of the system change as the temperature changes; thus a connection can be drawn between the slope and the critical exponents which also describe the change of the system with temperature.

Practical RG calculations have been performed for a number of model systems.^{3,48,49} The calculations start by defining a probability distribution P for the system and the RG transformation for that system which takes the probability distribution P to another probability distribution P' .

This procedure will be demonstrated here for the Ising model in the Gaussian approximation in which spin fluctuations around the most probable value are treated as independent modes with Gaussian probability distribution. The Hamiltonian for the system is derived from the Landau-Ginzburg-Wilson Hamiltonian (LGW)³¹:

$$\frac{H}{k_B T} = \int d^d \underline{x} \left[\frac{r_0}{2} (\sigma(\underline{x}))^2 + \frac{c}{2} (\nabla \sigma(\underline{x}))^2 + \frac{u}{8} (\sigma(\underline{x}))^4 \right], \quad (3.19)$$

where $(r_0, c, u) = \mu$ is the set of parameters describing the initial probability distribution and $\sigma(\underline{x})$ is the spin density function. The Gaussian case is obtained by setting $u=0$.

A discrete set of integration variables is introduced by Fourier transforming $\sigma(\underline{x})$

$$\sigma(\underline{x}) = \sum_k \frac{e^{i \underline{k} \cdot \underline{x}}}{L^{\frac{d}{2}}} \sigma_k, \quad (3.20)$$

where L^d is the integration volume and Λ is the short wavelength cut-off. The partition function is

$$Z = \prod_{k < \Lambda} \int d\sigma \exp\left(-\frac{1}{2} \sum_k (r_0 + ck^2) |\sigma_k|^2\right). \quad (3.21)$$

The RG operations are as follows: (1) integrate over $\underline{k}$ in the shell $\Lambda/s < k < \Lambda$ where $s > 1$ (this step is elementary only for $u=0$), giving

$$Z = e^{-\Lambda L^d} \prod_{k < \frac{\Lambda}{s}} \int d\sigma^< \exp\left(-\frac{1}{2} \sum_k^{\frac{\Lambda}{s}} (r_0 + ck^2) |\sigma_k|^2\right), \quad (3.22)$$

where the factor $\exp(-\Lambda L^d)$ comes from the integration over the shell $\Lambda/s < k < \Lambda$ and $d\sigma^<$ are the remaining integration variables; (2) rescale $\underline{k}$'s to restore the Λ cut-off ($\underline{k}' = s\underline{k}$); (3) rescale σ 's by defining a new integration variable ($\sigma_{k'/s}^< = Z_s \sigma_{k'}^<$). The last two operations restore the initial form of the Hamiltonian and allow formulation of the recursion relation for the RG transformation ($R_s(\mu) = \mu'$):

$$Z \propto \prod_{k < \Lambda} \int d\sigma \exp\left(-\frac{1}{2} \sum_k^{\Lambda} \left(r_0 Z^2 + \frac{c Z^2 k^2}{s^2}\right) |\sigma_k|^2\right). \quad (3.23)$$

where $\mu' = (r'_0, c') = (Z^2 r_0, (Z/s)^2 c)$.

There exist two fixed points for this transformation.

If Z is set to one then after n iterations $r_0^n = r_0$ and $c^n = c/(s^{2n}) \rightarrow 0$, i.e. $R_c(\mu^*) = \mu^*$ where $\mu^* = (r_0, 0, 0)$. This case corresponds to very disordered situation (the correlation function is proportional to $(1/r_0)\delta(\mathbf{x})$ where $\delta(\mathbf{x})$ is the delta function), i.e. infinite temperature. The other critical point is obtained by setting $Z = s^2$. Then $\mu' = (s^2 r_0, c)$ and if $r_0 = 0$ (this a logical choice since $T = T_c$ at the critical point and $r_0 \propto (T - T_c) = 0$ at T_c) the fixed point is $\mu^* = (0, c, 0)$. This fixed point is called a Gaussian fixed point.

As was mentioned in the beginning of this section, critical properties, in particular the critical exponents, are related to the properties of R_s near the critical point. If μ is near μ^* , one can write

$$\mu = \mu^* + \delta\mu, \quad (3.24)$$

where $\delta\mu$ transforms under R_s giving $\delta\mu'$ ($R_s(\delta\mu) = \delta\mu'$). R_s becomes a linear operator when $O((\delta\mu)^2)$ terms are dropped in calculating $\delta\mu'$ from $\delta\mu$. This linearized R_s should, in principle, show qualitative features of the full RG transformation, assuming that the system is very close to the critical point and $O((\delta\mu)^2)$ terms are very small. The analysis proceeds by expressing R_s as a matrix, R_s^L , and determining the Eigenvalues, λ_i , and Eigenvectors, e_i , of this matrix. Since $R_s R_s = R_s$, the Eigenvalues, λ_i , are of the form:

$$\lambda_i = s^{y_i}, \quad (3.25)$$

where y_i are constants. Also writing $\delta\mu$ as a linear combination of the e_i 's, one obtains:

$$\delta\mu = \sum_i t_i e_i, \quad (3.26)$$

where the coefficients t_i are called the scaling fields. The linearized R_s can now be written as follows:

$$\delta\mu' = \sum_i t_i s^{y_i} e_i. \quad (3.27)$$

If, for the purpose of discussion, one assumes that only $y_1 > 0$ and all other y_i 's are negative then after many iterations Eq. (3.27) becomes:

$$\delta\mu' = t_1 s^{y_1} e_1 + O(s^{y_1}, s^{y_1}, \dots). \quad (3.28)$$

As s increases the correction term goes to zero. In this context t_1 is called a relevant variable (relevant scaling field) and the other t_i 's are irrelevant variables (irrelevant scaling fields) for the critical behaviour of the system³¹. (If some of Hamiltonian flow exponents y_i 's are equal to zero the corresponding t_i 's are called marginal variables.) At a temperature T which is very close to T_c the distance from $\mu(T)$ to μ^* is given by t_1 , which should then be approximately proportional to $T - T_c$. A near critical form of the free energy density can now be written as

$$F_{sing}(\mu(T)) = s^{-d} F_{sing}(\mu + s^{y_1} t_1 e_1 + s^{y_2} t_2 e_2 + s^{y_3} t_3 e_3 + \dots) \quad (3.29)$$

Since s is arbitrarily large it may be chosen to be equal to t_1^{-1/y_1} , if $T - T_c$ is very small. Eq. (3.29) will then read

$$F_{sing}(\mu(T)) = t_1^{d/y_1} (\mu + e_1 + \frac{t_2}{t_1^{y_2/y_1}} e_2 + \frac{t_3}{t_1^{y_3/y_1}} e_3 + \dots) \quad (3.30)$$

Comparison with the phenomenological scaling relation $F \propto |T - T_c|^{2-\alpha}$ yields the identification of the exponent α :

$$2 - \alpha = d/y_1 \quad (3.31)$$

Further analysis in the same spirit of the form of the free energy and of the form of the correlation function near the critical point yields other scaling relations and exponent identifications.³¹

If the magnetic field, H , is non-zero it becomes another relevant variable (besides $t_1 \propto |T - T_c|$). Conventionally, a fixed point is called unstable if there are relevant parameter(s) other than the reduced temperature and the magnetic field. If $d < 4$ the Gaussian critical point is unstable with respect to the u parameter in the LGW Hamiltonian^{31,3}. The critical exponents in the Gaussian approximation are: $\alpha = 1/2$, $\beta = 1/2$, $\gamma = 1$, i.e. the same as in the mean field theory. This implies that the mean field theories describe the critical behaviour correctly provided that the system's dimensionality is larger than four.

Three conclusions follow from the above analysis: (1)

the linearization of the RG recursion relations about the fixed point implies the scaling of the near-critical free energy. i.e. free energy homogeneity; (2) the values of the critical exponents are given by the Eigenvalues of the linearized RG; (3) because only some scaling fields are relevant for critical behaviour a universality class can be formed which contains all Hamiltonians with the same relevant scaling fields and different sets of irrelevant scaling fields.

For $d < 3$ a non-trivial fixed point, i.e. for $u \neq 0$, can be found if the quartic term (u -term) is included in the calculations. In this case performing step (1) of the RG group calculations becomes very difficult and approximate calculational methods have to be employed in order to obtain the recursion relation.^{47,31} For this purpose the LGW Hamiltonian can be treated with the use of the perturbation theory methods. The Hamiltonian is divided into two parts: $H_{\text{LGW}} = H_0 + H_1$, where H_0 is the Gaussian term and H_1 is the quartic term (see Eq. (3.17)). The H_1 is treated as a perturbation and the partition function is expanded in powers of H_1 :

$$e^{-H} = e^{-H_0} e^{-H_1} = e^{-H_0} \sum_{m=0}^{\infty} \frac{(-1)^m}{m!} H_1^m. \quad (3.32)$$

The calculations proceed by taking the Gaussian trace over consecutive powers of H_1 . Working to first order only the

Gaussian critical point is retained; a non-trivial fixed point is obtained when the second-order terms in the perturbation expansion are kept. The perturbation approach will be practical if u (or other parameters in K_1) are small enough to justify keeping only a few terms in the perturbation expansion. Such a small parameter can be a parameter $\epsilon = 4 - d$ where the dimension d is assumed to be a non-integer number, very close to but smaller than four. The ϵ -expansion was carried out to high order in ϵ using field theoretical methods.⁵⁰ The perturbation expansion calculations also can be carried out using $1/n$ where n is the number of the spin components as a perturbation parameter.⁵⁰ Table 3.2 presents estimates of two- and three-dimensional exponents from the ϵ -expansion at order ϵ^5 after Le Guillou and J. Zinn-Justin.⁵¹

Table 3.2 Estimates of two- and three-dimensional exponents by the ϵ -expansion of the 5th order.⁵¹ (Exact results for $d=2$ are also included for comparison.)

$d=2$					
	γ	ν	β	η	ω
$n=1$	1.73 ± 0.06	0.99 ± 0.04	0.120 ± 0.015	0.26 ± 0.05	1.6 ± 0.2
Onsager	7/4	1	1/8	1/4	-
$d=3$					
$n=1$	1.239 ± 0.004	0.6305 ± 0.0025	0.3265 ± 0.0025	0.037 ± 0.003	0.81 ± 0.04
$n=2$	1.315 ± 0.007	0.671 ± 0.005	0.3485 ± 0.0035	0.040 ± 0.003	0.80 ± 0.04
$n=3$	1.390 ± 0.010	0.710 ± 0.007	0.368 ± 0.004	0.040 ± 0.003	0.79 ± 0.04

3.6 The approach to criticality: corrections to scaling and crossover behaviour

In the asymptotic critical region the effects of all irrelevant scaling fields associated with a fixed point become negligible, leaving only a homogenous dependence of observables on t . The range of $|t|$ in which this true asymptotic behaviour will be displayed reflects the extent to which the irrelevant (or marginal) parameters of the system differ from their fixed point values.³ One may allow for the non-asymptotic behaviour observed when t approaches the asymptotic regime by taking into account the residual temperature dependence associated with the leading irrelevant scaling fields, i.e. with the scaling fields t_2 and t_3 in Eq. (3.30). The leading singularity of a physical observable L thus has a correction to scaling factor

$$L((T)) = L_0 t^\gamma (1 + L_1 t^\Delta + \dots) , \quad (3.33)$$

where γ is the leading critical exponent and Δ is the correction to scaling exponent which can be identified using Eq. (3.30) as: $\Delta = -\gamma_2/\gamma_1 = \omega\nu$. The exponent $\omega = -\gamma_2$ is listed in Table 3.2. The amplitudes of L_0 and L_1 are non-universal and depend on the details of the physical system. (They are also different below and above the phase transition.) However, the ratios of those amplitudes, L_i^+/L_i^- , where (+) and (-) are the values of the amplitudes

above and below T_c respectively, are universal and have been calculated for the basic thermodynamic functions for most of the universality classes.^{52,53}

The diversity of the critical region is fully displayed in the context of the crossover behaviour^{3,48}. A system which exhibits a crossover behaviour is characterized by an effective Hamiltonian of the form

$$H_0 = H_0^{PR} + g\Delta H_0, \quad (3.34)$$

where H_0^{PR} is the primary part, representative of a universality class, and ΔH_0 is a perturbation, the strength of which depends on g . The symmetry of ΔH_0 implies its universality class is different from the universality class of H_0^{PR} . For instance, the primary Hamiltonian may be the Landau-Ginzburg-Wilson (LGW) Hamiltonian and the perturbation term may represent the effects of long-range dipolar interactions. The scaling hypothesis for this system can be written (using the susceptibility of the order parameter as an example):⁴⁸

$$\chi(T, g) = Ct^{-\gamma} X\left(\frac{g}{t^\phi}\right), \quad (3.35)$$

where $X(z)$ is the crossover scaling function and ϕ is the crossover exponent ($\phi = \gamma_g/\gamma_1$, where γ_g is the flow exponent of the scaling field introduced by the perturbation g). If the ratio g/t^ϕ is small compared to unity, the observed critical behaviour will be that of the universality class of

the leading part of the total Hamiltonian. When this ratio grows larger, i.e. t becomes smaller, the observed behaviour crosses over to the universality class of the perturbation Hamiltonian. The crossover temperature, t_c , is defined as

$$t_c = g^{\frac{1}{\Phi}}. \quad (3.36)$$

In general, there can be several relevant variables present in the Hamiltonian of a system, which then will exhibit a sequence of crossovers characterized by the crossover exponents $\Phi_i = \gamma_i/\gamma_1$ and the critical behaviour observed will change on approaching the critical point.

The Hamiltonian of any real system is made up of many terms describing interactions of different symmetry, spatial form and magnitude. From the above discussion of crossover scaling it follows that it may be difficult experimentally to see truly asymptotic critical exponents. In practice, with the restricted range of experimentally accessible reduced temperature, one may instead observe effective, or apparent critical exponents taking some intermediate values which vary with the reduced temperature and the coupling parameter between the values of the relevant universal exponents.

The renormalization group approach is a powerful method to study the effects of different types of magnetic interactions on critical behaviour.⁴⁸ The important types of magnetic interactions are⁴⁸: (1) isotropic, short-range n -

vector exchange; (2) single-ion anisotropy with reduced symmetry index $m < n$, i.e. m of n spin components interact with a different coupling strength and also anisotropic short range exchange; (3) isotropic dipolar $n=d$; (4) anisotropic dipolar - symmetry index $m < n$; (5) cubic short range; (6) long-range isotropic exchange.

The short-range interactions are always present in the Hamiltonian, thus the Gaussian fixed point which is unstable below four dimensions crosses over for $d=3$ to the isotropic Heisenberg fixed point ($n=3$) or the anisotropic, XY ($n=2$), or Ising ($n=1$) fixed points. The Heisenberg fixed point is unstable with respect to the single-ion anisotropy or the anisotropic short-range exchange with the corresponding crossover exponent $\Phi_s \approx 1.25$ for $d=3$.^{54,55}

The addition of dipolar forces results in other crossovers and new critical points. Magnetic systems with dipolar interactions will be discussed in more detail in the next section.

3.7 Ferromagnets with dipolar interactions

A magnetic dipole-dipole coupling between spins exists in all real magnetic materials and it is essential to include this interaction for their correct description.^{56,57 58 59 60} In most magnets with high Curie temperatures ordering is caused by exchange coupling which strongly dominates the dipolar coupling. The effects of the dipolar forces become apparent only very close to T_c .⁵⁹

Normal isotropic Heisenberg behaviour⁴⁸ is retained for $t \gg (g\mu_B)^2 / J a^d = \hat{g}$ where $(g\mu_B)^2$ measures the strength of the dipole-dipole interactions in terms of the Bohr magneton (μ_B) and the spectroscopic splitting factor (Landé factor) (g), J is the exchange energy, a is the lattice spacing, and $\hat{g}$ denotes the dimensionless coupling parameter.⁵⁶ The crossover exponent from the isotropic short-range behaviour to the isotropic dipolar behaviour is $\Phi = \gamma_H \approx 1.365$ ($d=3$), where γ_H is the susceptibility exponent in the Heisenberg $d=n=3$ model.^{56 58} When $t_D \approx \hat{g}^{1/\Phi}$, crossover occurs to a characteristic dipolar behaviour described by a new fixed point. This new isotropic dipolar fixed point has critical exponents which are numerically very close to their isotropic counterparts, i.e. $\alpha_D = -0.135$, $\gamma_D = 1.372$, according to the second-order ϵ expansion calculations of Bruce and Aharony.⁵⁸

For ferromagnets like Ni, EuO and EuS, with $T_c \approx 627$,

69.3 and 16.3 K, respectively, and the crossover temperatures were estimated by Fisher and Aharony⁵⁹ to be $t_D \approx 3 \times 10^{-4}$, 4×10^{-2} and 9×10^{-2} respectively. Thus the dipolar behaviour dominates only very close to T_c , in the temperature range which is difficult to access experimentally. Furthermore, the isotropic dipolar exponents also may be difficult to observe because of very small differences between them and the isotropic short-range exponents. Some experimental evidence for the existence of a crossover to the asymptotic dipolar behaviour in EuO was provided by Kornblit et al.⁶¹ Their range-of-fit analysis of the heat capacity of EuO suggested a crossover from short-range to dipolar critical behaviour for $t < 0.03$. Dunlap and Gottlieb⁶², based on their zero-field electron-spin resonance measurements of the relaxation time in EuO, showed that the asymptotic behaviour of EuO for $t < 0.02$ is consistent with theoretical predictions for the dipolar critical behaviour. The crossover to an asymptotic dipolar regime was observed experimentally in EuS by Kötzler et al.⁶³

Aharony and Bruce⁶⁴ derived the scaling equation of state and the scaling relations to the first order in ϵ for isotropic ferromagnets with both isotropic exchange and dipolar interactions in a very small external magnetic field in the temperature region below T_c . Their derivation was restricted to a single magnetic domain. They remarked⁶⁴ that

the complete solution of a multi-domain case would be very difficult as it would involve simultaneous consideration of the equations governing the macroscopic variation of magnetization inside the sample together with the spin fluctuations. Their results are thus strictly applicable only to needle-shaped samples with a magnetic field directed along the long axis of the sample. For other sample geometries demagnetization effects have to be considered. These effects will be discussed in the next chapter.

The uniaxial dipolar ferromagnet is an interesting special case. The RG analysis predicts that mean-field theory describes the correct critical behaviour for dimensionalities $d > d^*$, where $d^* = 4$ is the upper critical dimension for the systems with short-range interactions (Sec. 3.5) and $d^* = 3$ is the upper critical dimension for uniaxial dipolar ferromagnets or ferroelectrics^{57,65} and for tricritical behaviour.⁶⁶ At $d = d^*$, the solution to RG equations yields logarithmic corrections to the mean-field behaviour.^{57,65,66} In fact, the leading logarithmic corrections at $d = 3$ are the same as those of the short-range Ising model at $d = 4$.⁶⁶ There are differences if the higher-order correction terms are included⁶⁷, but numerically those differences are very small. In particular the susceptibility of the uniaxial dipolar ferromagnet behaves as:^{65,68}

$$\chi = \Gamma_{\pm} |t|^{-1} |\ln|t||^{\frac{1}{3}}, \quad (3.37)$$

where Γ_+ and Γ_- are for $T > T_c$ and $T < T_c$ respectively and $\Gamma_+/\Gamma_- = 2$. The heat capacity, $C_{H=0}$, has a similar form^{3,52}:

$$C_{H=0} = A_{\pm} |\ln|t||^{\frac{1}{3}}, \quad (3.38)$$

with the amplitude ratio $A_+/A_- = 1/4$ (A_+ and A_- are for $T > T_c$ and $T < T_c$ respectively).

The spontaneous magnetization, M_s , is also modified with a fractional power⁶⁸:

$$M_s = B_0 (-t)^{\frac{1}{2}} |\ln|t||^{\frac{1}{3}}, t=0, H=0. \quad (3.39)$$

The normalized amplitudes A_+ , B_0 , Γ_+ form the universal ratio given by⁵²

$$R_c = A_+ B_0^{-2} \Gamma_+ = \frac{1}{6}. \quad (3.40)$$

The logarithmic corrections at $d^*=3$ provide a direct check of RG theory. The best chance of observing the logarithmic corrections exists in heat capacity measurements because they are not masked by a stronger power law singularity at T_c . The measurements of the heat capacity of the dipolar Ising ferromagnet LiTbF_4 confirmed the predicted asymptotic behaviour.⁷ It was also found that the logarithmic corrections very well described the spontaneous magnetization and magnetic susceptibility of LiTbF_4 .^{69,70} Beauvillain et al.⁷⁰ tested the value of the universal ratio

R_c for LiTbF_4 and found it to be close to the theoretical value $1/6$. Kötztler and Eiselt⁷¹ measured the magnetic susceptibility of GdCl_3 above T_c and found that the data close to T_c were well described by Eq. (3.37). However the power law fit also gave a good representation of the data in the same temperature range. Using the available data on the heat capacity and the magnetization of GdCl_3 , Kötztler and Eiselt⁷¹ found that the ratio R_c is very close to $1/6$.

3.8 Critical phenomena in disordered systems

Any real system has impurities and defects such as dislocations and vacancies, and other types of disorder. For example, in a ferromagnetic crystal, a fraction of sites may be occupied randomly by non-magnetic atoms. If this fraction is larger than certain threshold value the ferromagnetism is suppressed.

Experiments also show that phase transitions display rounding in the proximity of T_c , even though model systems have singularities, such as cusps, at T_c , Fig. 3.1. The purer a sample is, i.e. the fewer impurities, defects and strains it has, the sharper the phase transition becomes. The observed smearing appears to be correlated with the amount of disorder in the sample.⁷²

Conventionally, impurities are classified according to the way they are distributed in the host system.^{73,74} Impurities which are in thermodynamic equilibrium with the host system within the relevant time scale, i.e. the relaxation time of impurity redistribution processes is short compared to the observation time, give rise to annealed disorder. In a magnetic system with nonmagnetic ions at random sites experiments will thus measure averages over all possible spin configurations and positions of the nonmagnetic ions, and the system behaves like a pure system

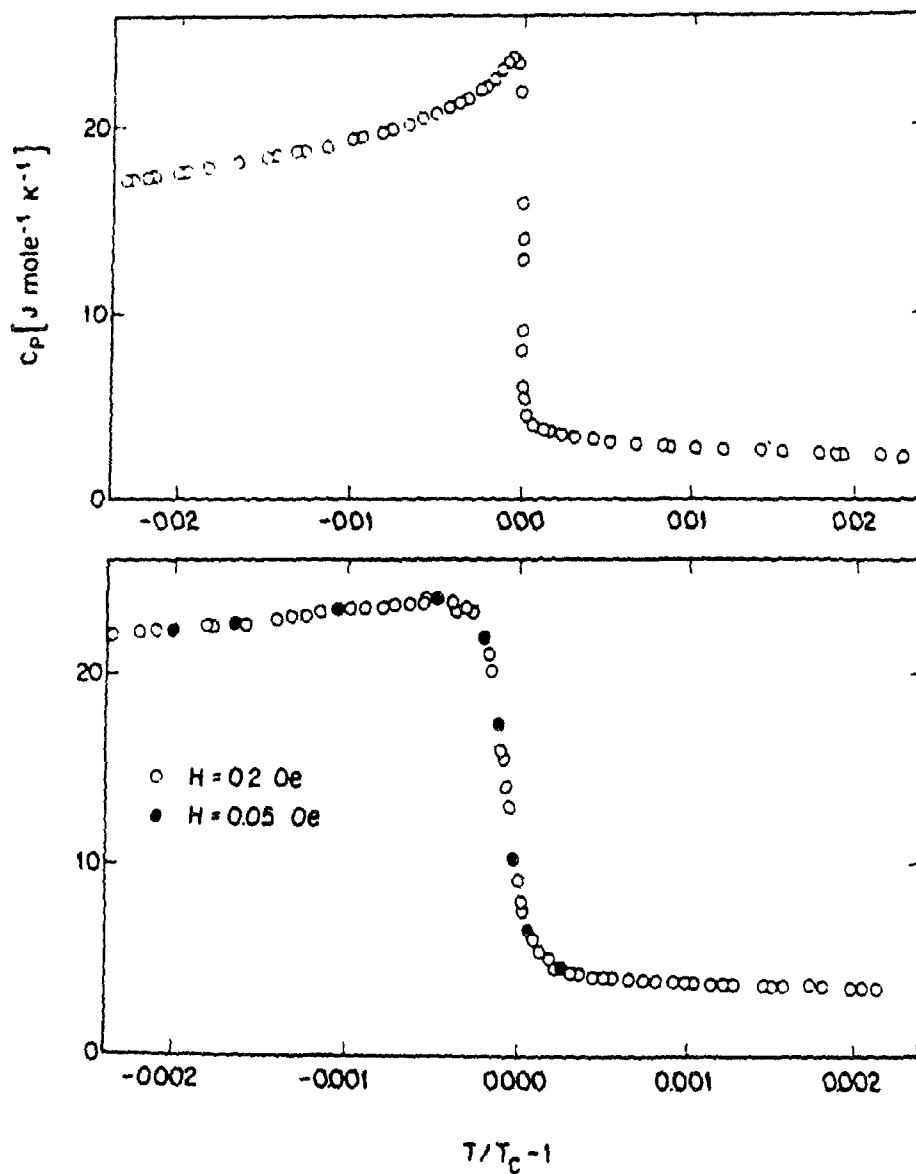


Fig. 3.1 The heat capacity of dipolar Ising ferromagnet LiTbF_4 as a function of the reduced temperature (ref. 7). The transition exhibits rounding in the proximity of T_c .

with the random variables as an extra set of dynamic variables.

In reality one mostly has to deal with quenched disorder in which the impurities are considered fixed, with the distribution prescribed by the mechanism by which they were introduced. The spins distribute themselves to fit the imposed distribution of impurity sites, which makes the analysis of quenched disorder much more complicated than the analysis of annealed disorder.^{31,73,74} Within the quenched disorder one also distinguishes systems whose impurities are correlated or have clustered structure over long distances (inhomogeneous disorder) and systems with purely short-range, or homogenous disorder.⁷⁵

McCoy and Wu⁷⁶ carried out an early study of quenched disorder through exact analysis of the two-dimensional Ising model with rows of differing bonds. They found a smeared phase transition, which exhibited a continuous heat capacity throughout the transition region.

A general argument due to Harris⁷⁷, showed that one should expect a new type of critical behaviour for the random system, distinct from that of a pure one, if the heat capacity of the pure system diverges at the transition temperature. In terms of critical exponents, the Harris criterion can be expressed as

$$\alpha_p = 2 - \nu d > 0, \quad (3.41)$$

where α^p is the heat capacity critical exponent of the pure system. The Harris criterion has been confirmed by renormalization group calculations for quenched random systems.^{55,73}

The main difficulty in calculating thermodynamic properties of a quenched random system is that one has first to calculate the free energy of a given random configuration and then average over all possible configurations. If the random variables $\{\mu_i\}$ have the probability distribution $P(\{\mu_i\})$, then the average free energy is:⁷³

$$F_{Av} = -k_B T \sum_{\mu_i} P(\mu_i) \ln Z(\mu_i), \quad (3.42)$$

where Z is the partition function. Since the average over the logarithm of the partition function would be very difficult to calculate one can employ a replica procedure based on the identity:

$$\ln Z = \lim_{n \rightarrow 0} \frac{Z^n - 1}{n}. \quad (3.43)$$

The averaging over $\ln Z$ is now replaced by averaging over Z^n , which is written in terms of n replicas of the original Hamiltonian. The average free energy of the original system is obtained in the $n \rightarrow 0$ limit of the replica Hamiltonian.⁷⁴ The presence of disorder introduces a new parameter into the replica Hamiltonian describing a coupling among n replicas.

The scaling fields which describe the critical properties of the system now include the scaling field of the new parameter which may turn out to be a relevant scaling field and lead to a new fixed point.^{55,73} This new parameter is the root mean square deviation of the local fluctuations in the critical temperature.

The results obtained using the replica procedure show that the pure fixed point is stable only when the heat capacity exponent of the pure system, α_p , is negative^{75,78}, i.e. a small amount of disorder does not alter the critical behaviour.

When α_p is positive the pure fixed point is unstable but a new random fixed point becomes stable instead, and the transition remains sharp and second-order. The exponents associated with the new fixed point differ from those of the pure system. In particular the new α is small and negative. At $d=3$, α_p is negative only in the Ising case. For the Ising case, one thus has a crossover to a new random fixed point⁷⁴ with $\alpha = -(6\epsilon/53)^{1/2} + O(\epsilon)$.

The heat capacity of the pure dipolar Ising model at $d=3$ diverges when $t \rightarrow 0$ although it is not a simple power law (see Sec. 3.6). Following the general argument by Harris⁷⁷ a new type of critical behaviour should be expected for a random dipolar Ising system. Aharony⁷⁹ analyzed the random Ising model with weak, homogeneous disorder. He found a new random fixed point for this model with short range

interactions at $d=4$ and with dipolar interactions at $d=3$. In both cases the leading singularity of the heat capacity was of the form:

$$C \propto -| \ln t |^{1/2} e^{[-2(D| \ln t |)^{1/2}]}, \quad T > T_c \quad (3.44)$$

where D is a universal constant, equal to $6/53 \approx 0.11321$ in the short-range case and to $9/(81 \ln(4/3) + 53) \approx 0.11795$ in the dipolar case. The numerical difference between the two forms is very small and for practical purposes the calculations for the short-range Ising model with $d=4$ are sufficient for obtaining very good estimates of the behaviour of the dipolar Ising system with $d=3$. A similar calculation was also reported by Schuster.⁸⁰

Shalaev⁸¹ extended the result of Aharony⁷⁹ and suggested that the singular part of the heat capacity is:

$$C \propto -| \ln t |^{1/2+2\omega} e^{[-2(D| \ln t |)^{1/2}]}, \quad T > T_c, \quad (3.45)$$

where $\omega = (580.5 + 378\zeta(3)) / (53^2) \approx 0.368$ and $\zeta(3) = 1.202$ is the Riemann zeta function. The exponent ω also enters the expression Shalaev obtained for the susceptibility. Geldart and De'Bell⁸² showed that this identification was not correct and the correct exponent in Eq. (3.45) is $1/2 + 2\omega_1$, with $\omega_1 \approx 0.373$.

The singularity given by Eq. (3.45) may be very difficult to see in practice, due to the crossover effects. First, there will be a crossover region from non-random to random behaviour which can be very wide owing to the weak

divergence of the non-random heat capacity.⁸³ Another relevant crossover is the crossover between the asymptotic critical region and the mean field region.

Aharony⁷⁹ suggested that a dipolar Ising system such as LiTbF_4 with controlled impurities of nonmagnetic ions might be a good candidate for experimental studies of the random critical point.

The RG calculations carried out thus far indicate that the phase transition in a broad class of quenched disordered systems is sharp and second-order. This result does not account for the rounding which is observed in so many experiments in critical phenomena.

One explanation is that even high quality crystals still have a certain amount of inhomogeneous disorder such as macroscopic gradients of impurities and macroscopic strains and this inhomogeneous disorder inhibits the growth of the correlation length and gives rise to rounding. If the crystal's imperfections limit the growth of the correlation length this may result in breaking up the crystal into an array of microcrystals with slightly different ordering temperatures. In this case the rounding in the heat capacity curve may be represented by a convolution of the distribution function of the critical temperature and the asymptotic heat capacity.^{84 14}

It is unclear how to explicitly detect rounding of the transition using the RG methods. Weinrib and Halperin⁸⁵

considered a model system with long-range-correlated quenched disorder with a correlation function for the spatially-variable transition temperature obeying a power law ($\sim x^c$ for large separations x , where c is a parameter). They found a new long-range random fixed point in addition to the short-range random fixed point. They also found a region in the parameter plane ($\epsilon=4-d, \delta=4-c$) in which the long-range random fixed point becomes unstable without any other fixed point becoming stable. Weinrib and Halperin⁸⁵ suggested that this runaway region might be a crossover to a smeared transition (the parameter describing coupling among replicas flows to infinity, indicating a wide range of possible local transition temperatures). However, Aharony⁷⁴ pointed out that there are several possible explanations for such a runaway, i.e. it may indicate that the transition is first-order as it is for some model systems without stable fixed points.

It is also not clear that all the rounding can be accounted for only on the basis of inhomogeneous disorder. Källbäck⁸⁶ analyzed literature data on the heat capacity and resistivity of nickel around the Curie point and suggested that part of the observed rounding can be well described in terms of the critical slowing down (increasingly slow relaxation towards new equilibrium values of resistance and heat capacity as T_c is approached). Källbäck⁸⁶ estimated that the relaxation time for Ni was of the order of few

hours at a few tens of mK from T_c .

3.9 Analysis of the critical behaviour of heat capacity

An analysis of the heat capacity near T_c can provide information about the critical exponents below and above a phase transition (α' and α respectively) and the magnitude of the leading singularity below and above T_c (A' and A respectively). The exponent $\alpha=\alpha'$ has been calculated for a number of systems (Sec. 3.2) and the universal ratio A/A' is equal to 0.524, 1.029 and 1.521 for $n=1, 2$ and 3 respectively, for systems with short range interactions, by the ϵ -expansion.⁵³ The experimental values of the critical exponents and the A/A' ratio provide checks for various scaling relations and information about the universality class of a given system.

A number of analytical expressions have been used in the literature to represent the critical heat capacity. They range from simple power law functions to more complicated fitting functions with several singular and regular terms. A general fitting function for the critical heat capacity for the systems with short range interactions can be written:^{87 88 61}

$$C_p = \frac{A}{\alpha} |t|^{-\alpha} (1 + D|t|^{\tau}) + B + Et, \quad (3.46)$$

for $T > T_c$, and the same function with primed coefficients for $T < T_c$. The constant B contains a contribution associated with the phase transition and it may not have the same value

above and below T_c . The major contribution to B is from the lattice degrees of freedom for which the temperature dependence is taken into account by including the term Et into the fit. For $D=D'=0$ Eq. (3.46) reduces to a pure power law representation with regular background. The confluent singular term $D|t|^x$ represents the correction to the asymptotic scaling term (Sec. 3.6, Eq. (3.33)). The value of D is not given by the theory. However the ratio D/D' is universal and is estimated to be 0.96, 1.6 and 1.4 for $n=1$, 2 and 3, respectively, by field theoretical methods and 1.17 for $n=2$ by the ϵ -expansion.⁵³ The value of the exponent x is around 0.5 in 3d for short-range interactions (Table 3.2 and Eq. (3.33)). Equation (3.46) can be extended to account for the possibility of the logarithmic singularity at T_c :⁸⁸

$$C_p = \frac{A}{\alpha} (|t|^{-\alpha} - 1) (1 + D|t|^x) + B + Et, \quad (3.47)$$

for $T > T_c$, with the same function with primed coefficients for $T < T_c$. (The logarithmic singularity is obtained by taking the limit $\alpha \rightarrow 0$.)

It is truly nontrivial to extract useful information and meaningful parameters from a fit of experimental data to such complicated functions as Eq. (3.46) and Eq. (3.47)⁸⁹. Without any constraints each equation contains 14 adjustable parameters, and convergence of iterative nonlinear least-squares fit may be very difficult to obtain. In many cases the statistical errors may be so large that the fitted

values of parameters will not provide useful information; also the improper choice of the initial values of the parameters may lead to spurious results.⁹⁰

In this situation one proceeds by imposing constraints on some of the fitted parameters (some of the constraints may be imposed or suggested by the theory) and by inquiring if imposition of these constraints leads to reasonable values for adjusted parameters and acceptable statistical errors. In subsequent steps the effect of relaxing some of the constraints on the quality of the fit can be investigated.⁸⁸

An analysis may start by initially assuming that $D=D'=0$, i.e., that singular higher-order corrections to the leading singularity are negligible. Another reasonable constraint is that $T_c=T_c'$. One also may require that $E=E'$ so that the term Et will indeed be regular at T_c and $B=B'$, i.e., there is no discontinuity in the heat capacity at T_c .⁸⁹ The data can then be fitted with the other parameters varying freely in order to test if $\alpha=\alpha'$ within statistical error. The fit can be repeated for different temperature ranges.

In the next stage a confluent singular term can be included in the analysis by letting D and D' be different from zero and assuming that $x=x'$ (one also assumes initially that $x=x'=0.5$ in 3d).

A dipolar uniaxial ferromagnet is a special case as its heat capacity near the Curie point is described by a

fractional power of $\ln|t|$ (Sec. 3.6). Ahlers et al.⁷ fitted the critical heat capacity of the dipolar Ising ferromagnet LiTbF_4 (See Fig. 3.1) with the functions

$$C = \frac{A}{b^z} \left[\left(1 + b \ln \frac{a}{|t|} \right)^z - 1 \right] + B, \quad T > T_c \quad (3.48)$$

and

$$C = \frac{A'}{b'^{z'}} \left[\left(1 + b' \ln \frac{a'}{|t|} \right)^{z'} - \frac{1}{4} \right] + B', \quad T < T_c, \quad (3.49)$$

with the constraints $a=a'$, $b=b'$, $z=z'$, and $B=B'$ in the temperature range from $t=10^{-3}$ to $t=10^2$. They found $A/A'=0.244 \pm 0.009$ and $z=z'=0.336 \pm 0.024$, in very good agreement with the theoretical values $A/A'=1/4$ and $z=z'=1/3$.⁶⁵

Chapter 4. HEAT CAPACITY OF MAGNETIC SYSTEMS WITH DIPOLAR INTERACTIONS

4.1 Thermodynamic relations for the heat capacity of a magnetic system in an external magnetic field

The free energy, $F(T, V, H_{ex})$, of a magnetic sample in an external magnetic field, H_{ex} , can be expressed as³⁰

$$F(T, V, H_{ex}) = U - TS, \quad (4.1)$$

where U is the internal energy, T is the temperature, V is the sample volume and S is the entropy. The dependence of the free energy on the magnetic field follows from the first law of thermodynamics⁹¹:

$$dU = TdS - MdH_{ex} - pdV, \quad (4.2)$$

where M is the magnetization and p is the pressure. The differential expression for the free energy is:

$$dF = -SdT - MdH_{ex} - pdV. \quad (4.3)$$

The heat capacity at constant external field and constant volume, $C_{V,H}$ can now be defined as³⁰

$$C_{V,H_{ex}} = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_{V, H_{ex}}. \quad (4.4)$$

For an isotropic material, the isochoric heat capacity, C_V ,

is related to the isobaric heat capacity, C_p , as follows⁹²:

$$C_p - C_v = V \alpha_v^2 T / K_T , \quad (4.5)$$

where α_v is the volume thermal expansion coefficient and K_T is the isothermal compressibility. For an anisotropic crystal the work per unit volume is determined from the more general expression

$$\delta W = \sum_{ij} \sigma_{ij} d\epsilon_{ij} , \quad (4.6)$$

where σ_{ij} is the stress tensor and ϵ_{ij} is the strain tensor. The difference between the heat capacities at constant stress, C_σ , and constant strain, C_ϵ is⁹³

$$C_p - C_\epsilon = C_\sigma - C_\epsilon = VT (c_{ijkl}^T \alpha_{ij} \alpha_{kl}) , \quad (4.7)$$

where c_{ijkl}^T is the isothermal elastic constant tensor and α_{ij} is the thermal expansion tensor. If the stress is due to isotropic pressure then $C_\sigma = C_p$. For cubic symmetry one also has $C_\epsilon = C_v$ and Eq. (4.7) gives Eq. (4.5) as a special case. For either trigonal or hexagonal symmetry Eq. (4.7) becomes⁹⁴

$$C_p - C_\epsilon = VT [2 (c_{11} + c_{12}) \alpha_a^2 + 4 c_{13} \alpha_a \alpha_c + c_{33} \alpha_c^2] , \quad (4.8)$$

where the Voigt notation is used.

The heat capacity at constant magnetization is related to the heat capacity at constant external field by

$$C_{V,H_a} - C_{V,M} = \frac{T \alpha_M^2}{\chi_T} , \quad (4.9)$$

where $\chi_T = (\partial M / \partial H)_T$ is the isothermal susceptibility and $\alpha_H = (\partial M / \partial T)_H$. One has to bear in mind that Eq. (4.9) is a macroscopic equation, i.e. it is given only after assuming that the magnetization and the magnetic field are essentially uniform over the sample volume and are well represented by their average values. For a ferromagnet below T_c in a vanishingly small external magnetic field the local magnetization is strong but the net magnetization is zero (or nearly zero) due to coexistence of oppositely magnetized domains.⁹⁵ This point is further discussed in the next two sections.

Finally the connection between the theory and experiment is given by the general quantum-statistical result for the heat capacity at constant volume⁹⁶:

$$C_V = \left(\frac{dU}{dT} \right)_V = V \frac{\langle E_i^2 \rangle - \langle E_i \rangle^2}{k_B T^2}, \quad (4.10)$$

where V is the sample volume, E_i is the energy of the i th stationary state of the crystal and the brackets denote averages over the all states.

Experiments usually measure the heat capacity at constant pressure but theory gives the heat capacity at constant volume. In a gas these differ substantially, but in solids they are more nearly identical. However the difference in solids may be quite large if the coefficients of thermal expansion become divergent, which may occur at

the critical point and then this difference should be taken into account in an analysis of the critical heat capacity.

4.2 Effect of an external magnetic field and the demagnetizing field on the heat capacity of a ferromagnet

4.2.a Heat capacity of a ferromagnet in an external magnetic field

Magnetostatic considerations show that the free energy and hence the heat capacity of a sample of magnetic material placed in an external magnetic field will depend on the sample's shape.^{97,98} The origin of this dependence lies in the long-range nature of dipolar forces present in all magnetic materials. The shape of the external boundary of a sample enters the thermodynamic properties of the sample in the dipolar sum in the dipolar contribution to the total Hamiltonian, H_{dip} ,

$$H_{\text{dip}} = \frac{(g\mu_B)^2}{2} \sum_i D_{\text{tot}}(i) , \quad (4.11)$$

where g is the Landé factor, μ_B is the Bohr magneton. The dipolar sum is:

$$D_{\text{tot}}(i) = \sum_{j, j \neq i} \left[\frac{\bar{s}_i \cdot \bar{s}_j}{r_{ij}^3} - \frac{3(\bar{s}_i \cdot \bar{r}_{ij})(\bar{s}_j \cdot \bar{r}_{ij})}{r_{ij}^5} \right] , \quad (4.12)$$

where $\bar{s}_i$ and $\bar{s}_j$ are the spins at sites i and j , and $\bar{r}_{ij}$ is the vector connecting the sites.

The magnetic field on the spin i is the sum of the

external applied magnetic field H_x and the field due to the other spins in the crystal which depends on $D_{\text{tot}}(i)$. The standard method of summing the dipole fields of the other spins is to break up the dipolar sum, $D_{\text{tot}}(i)$, into a sum, D_0 , over a moderate number of neighboring spins inside an imaginary sphere centred on the reference spin plus an integral over the rest of the sample.⁹⁹ The contribution of the integral to the field at the reference spin is made up of the contribution from the surface integral over the spherical cavity (D_1) which gives rise to the Lorentz field, and the contribution from the integral over the sample surface, which is the demagnetization factor D . The value of factor D lies between zero for a long circular cylinder parallel to the external field and one for a thin slab perpendicular to the external field.

An example of a system for which shape dependent effects are important is dysprosium aluminum garnet (DAG) where the dipolar interactions account for ca. 70% of the energy.⁹⁸ Levy and Landau⁹⁸ measured the heat capacity for several ellipsoidal samples of DAG at constant external field. They found that the maximum in the heat capacity decreased by as much as 40% for the sample with a large demagnetization factor compared to the sample with $D \approx 0$. Also the temperature of the maximum was shifted. Defining the internal, shape independent magnetic field, H_i , as⁹⁷

$$\underline{H}_i = \underline{H}_e - D\underline{M} , \quad (4.13)$$

where $(-D\underline{M})$ is the demagnetizing field, Levy and Landau⁹⁸ showed that the heat capacity at constant internal field is shape-independent.

Griffiths¹⁰⁰ argued that the demagnetizing effects should lead to a singularity (nonanalytic behaviour) in the heat capacity in an external field at the temperature $T_0 < T_c$ where the spontaneous magnetization M_s equals the external field divided by the demagnetization factor, that is, where the internal field equals zero. Below T_0 the internal field is zero and the heat capacity in the external field is identical to the heat capacity in zero applied field. Above T_0 two limiting behaviours can occur. In low fields the heat capacity in the field will resemble the heat capacity at constant magnetization and in the high-field limit the heat capacity will look like the heat capacity at constant internal field.

Simons and Salamon¹⁰¹ reported a kink in the heat capacity of Gd in the external magnetic fields between 165 and 585 Oe a few K below T_c which they attributed to the Griffiths-type singularity.

4.2.b Magnetic domains and demagnetization heat capacity

In the renormalization group theory of magnetic systems with dipolar interactions the contribution to the free energy of the system from the demagnetization effects is neglected by assuming that the sample consists of one magnetic domain and that the bulk magnetization is uniform.⁶⁴ This requirement is satisfied by needle-shaped samples. (If an external magnetic field is present it has to be parallel to the long axis of the sample). However for samples of other shapes the free energy and hence the heat capacity will have a contribution from the demagnetization effects. In such cases the experimental heat capacity data may need to be corrected for these effects. Knowledge of the magnitude of such a correction term is particularly important close to T_c because of the possible effect of this correction on the critical behaviour of the heat capacity. Calculation of the demagnetization free energy and the demagnetization heat capacity in the mean field approximation is the subject of this section.

In a zero or vanishingly small external magnetic field the spontaneous magnetization of a ferromagnetic sample below T_c is not uniform; the sample is composed of a number of small regions called domains, and within each the local magnetization is uniform.^{95,102} The directions of magnetization of different domains need not be parallel.

The magnetic domains are a natural consequence of contributions to the total energy from the demagnetization field and from the exchange and the anisotropy energy. If a saturation configuration of a ferromagnetic single crystal consists of a single domain then this configuration has a high value of demagnetizing energy. Dividing the crystal into a number of oppositely magnetized domains reduces the demagnetization energy.⁹⁵ This process results in a zero or nearly zero macroscopic magnetization. The division process continues until the energy required to establish the interface separating oppositely magnetized domains is greater than the reduction in the demagnetization energy. The final domain structure is the structure which minimizes the total energy of the structure. This total energy will generally consist of two parts: the energy of the walls separating the domains and the magnetic energy associated with the demagnetizing field or with the anisotropy energy.⁹⁵

The domain structure of most crystals falls into two classifications: a superficial domain structure which often assumes a very complicated pattern, and the underlying bulk domain structure running throughout the sample which is believed to be fairly simple in most cases.^{95,103}

The magnetic energy, F_{dom} , for a ferromagnetic plate (magnetized along the normal) was calculated by Kittel⁹⁵ for stripe domains with narrow walls, in a thick slab (Fig. 4.1):

$$F_{dom} = V \frac{C_1 M_s^2 a_w}{L_z} , \quad (4.14)$$

where V is the slab volume, M_s is the spontaneous magnetization, a_w is the domain width, L_z is the slab thickness and C_1 is a numerical factor equal approximately 0.85.

It is possible to devise a domain arrangement for the rectangular slab from Fig. 4.1 which will have no demagnetizing field.^{95,102} In Fig. 4.2 the boundaries of the triangular prisms domains (termed "the domains of closure") make equal angles (45°) with the magnetization in the volume domains and with the domains of closure. The magnetic flux circuit is completed within the crystal and no magnetic "poles" are formed on the crystal surface. The magnetic energy associated with the demagnetization field is zero, but the anisotropy energy is not zero.

In a uniaxial crystal the magnetization within the domains of closure is oriented in a direction of hard magnetization; this involves the anisotropy energy^{95,102}

$$F_{anis} = V \frac{a_w \sum_i K_i}{2L_z} , \quad (4.15)$$

where V is the sample volume, K_i are the anisotropy constants, a_w is the domain width and L_z is the sample thickness.

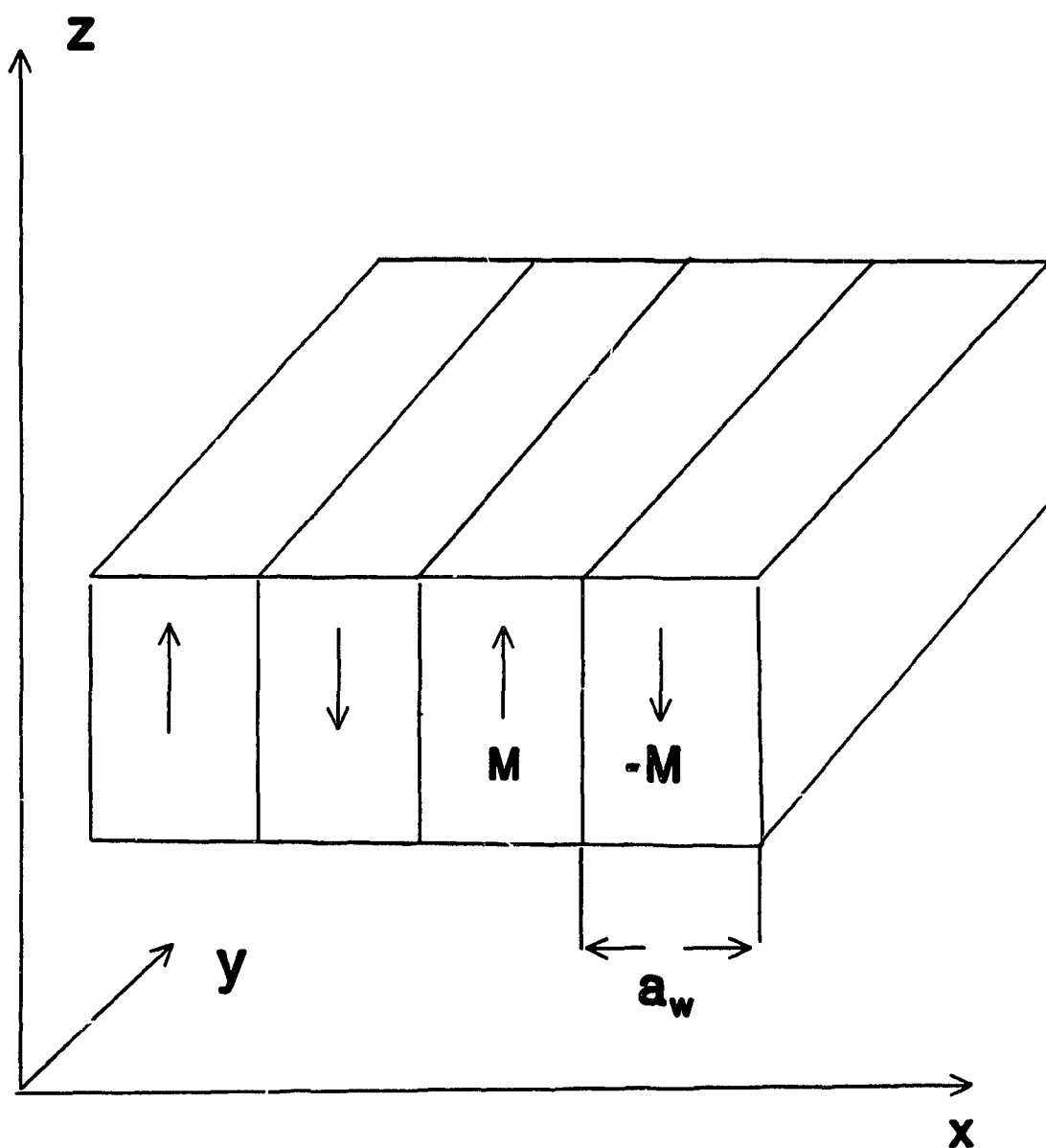


Fig. 4.1 Model for calculation of the magnetic field energy of coplanar strip-domains of alternate sign.

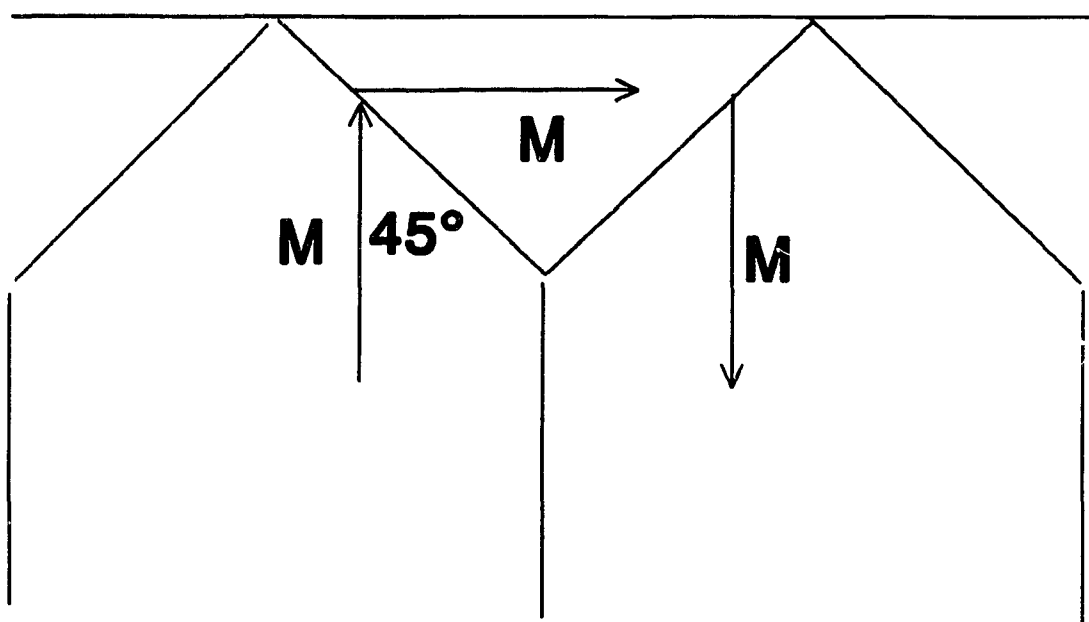


Fig. 4.2 Details of flux closure with the domains of closure.

The ratio of the energy of a domain structure with the domains of closure to the energy of a slab-like structure is determined primarily by the ratio of the sum of the anisotropy constants to the square of the spontaneous magnetization, M_s^2 . If the ratio $4\pi(\sum K_i)/\mu_0 M_s^2 \ll 1$, where μ_0 is the permeability of free space then the flux closure configuration gives the lower energy but with the increasing value of the ratio the domains of closure will gradually open.

In order to estimate the total energy associated with the domain structure one also has to estimate the domain walls' contribution to that energy. Usually, the walls are described by rotation of the magnetization vector, $\underline{M}$, at constant magnitude, M , within the wall. This magnetization profile is known as a rotational solution.¹⁰⁴ Another possible wall structure (linear solution) is given by a varying magnitude of $\underline{M}$ with the magnetization always either parallel or antiparallel to the easy axis of the magnetization.^{104,105} The latter magnetization profile is expected to occur near T_c .

Bulaevskii and Ginzburg¹⁰⁴ analyzed a single wall structure near T_c using the free energy expansion in powers of magnetization under assumption that the domain width, a_w , is much larger than the wall thickness. They showed that close to T_c the linear solution for the magnetization profile was given by $M_s(x) = M_s \tanh(x/\lambda)$ where x is the

distance perpendicular to the wall and λ is of the order of both the wall thickness and the correlation length.

The solution of Bulaevskii and Ginzburg¹⁰⁴ for one domain wall can be used to estimate the domain wall energy of N walls close to T_c in the mean field approximation. This is the subject of the remainder of this chapter.

The free energy of the domain walls of the slab-like structure (Fig. 4.1) with $N=L_x/a_w$ can be obtained by integrating the free energy functional derived from the exchange Hamiltonian of the LGW form⁵⁰:

$$\frac{H_{ex}}{2J_L(\underline{0})} = \int d^3\underline{x} \left[\frac{1}{2} \frac{T-T_{c0}}{T_{c0}} (\sigma(\underline{x}))^2 + \frac{c}{2} (V\sigma(\underline{x}))^2 + u(\sigma(\underline{x}))^4 \right], \quad (4.16)$$

where c and u are constants defined later, $\sigma(\underline{x})$ is the spin density function and the integration is over the sample volume. The zeroth term, $J_L(\underline{0})$, of a series expansion of the exchange energy, J_L , in momentum space is related to the mean field critical temperature, T_{c0} , by

$k_B T_{c0} = 2/3 S_{Gd}(S_{Gd}+1)J_L(\underline{0})$, where $S_{Gd}=7/2$ is the Gd spin number.²⁸

The spin density can be related to the magnetization by

$$\sigma(\underline{x}) = M(\underline{x}) \frac{\Omega_0^{\frac{1}{2}}}{g\mu_B}, \quad (4.17)$$

where μ_B is the Bohr magneton, g is the Landé factor and Ω_0 is the volume factor of the order of the volume of the unit cell ($\Omega_0=V_{mol}/N_A$, where V_{mol} is the molar volume of Gd and N_A is the Avogadro's number).

The total free energy of a single wall, F_{tot} , is

$$F_{\text{tot}} = \tau \int d^3\mathbf{x} \left[-\frac{1}{2} \frac{\kappa^2}{\kappa_0^2} (\mathbf{M}(\mathbf{x}))^2 + \frac{a}{2\kappa_0^2} (\nabla \mathbf{M}(\mathbf{x}))^2 + u'(\mathbf{M}(\mathbf{x}))^4 \right], \quad (4.18)$$

where the new symbols are defined as follows:

$\kappa = \xi^{-1} = \xi_0^{-1}(-t)^{\nu/2} = \kappa_0(-t)^{\nu/2}$ where ν is the correlation length critical exponent equal to 1/2 in the mean field theory, and $c = a/\kappa_0^2$ (a is a dimensionless constant), and $u' = u\Omega_0/(g\mu_B)^2$.

The constant τ is defined as

$$\tau = \frac{2J_L(\underline{0})}{(g\mu_B)^2/\Omega_0}. \quad (4.19)$$

Assuming that for Gd, $T_c \approx 300$ K and estimating $J_L(\underline{0})$ using the relation given in Eq. (4.16) with $T_{c0} \approx 1.5T_c$ one obtains $\tau \approx 12 \times 10^2$.

The coefficient, a , was obtained using the data of Mackintosh and Møller on the exchange function $J_L(\mathbf{k})$ for Gd as a function of the reduced wave vector $\mathbf{k}/\mathbf{k}_{\text{max}}$ in the c-axis direction.¹⁰⁶ The coefficient, a , was identified using the relationship

$$\frac{J_L(\mathbf{k}) - J_L(\underline{0})}{J_L(\underline{0})} \approx \frac{m}{J_L(\underline{0})} \left[\frac{k^c}{k_{\text{max}}^c} \right]^2 - \frac{a(k_{\text{max}}^c)^2}{2\kappa_0^2} \left[\frac{k^c}{k_{\text{max}}^c} \right]^2, \quad (4.20)$$

where the coefficient $m \approx -12$ meV was estimated from the fit to the data in Fig. 5.8 of Mackintosh and Møller. Taking $k_{\text{max}}^c \approx 2\pi/c$ where $c \approx 5.8$ Å and $\kappa_0 = \xi_0^{-1} \approx 0.5$ Å⁻¹ for an estimate of

the inverse of the correlation length at $T = 0$ K one obtains $a \approx 0.59$.

If the domain wall lies in the y - z plane and the origin of the coordinate system is in the centre of the wall then the Bulaevskii and Ginzburg¹⁰⁴ solution $M_z(x) = M_s \tanh(x/\lambda)$ minimizes the functional given by Eq. (4.18) with $\lambda = (2a)^{1/2}\xi$ under the constraint that $M_s = 1/(4u')(\kappa^2/\kappa_0^2)$.

F_{tot} can be expressed as a sum of several integrals resulting from the integral given by Eq. (4.18),

$$F_{tot} = -\frac{1}{4} \tau \frac{\kappa^2}{\kappa_0^2} M_s^2 V_1 + F_{qdr} + F_{grd} + F_{qri} , \quad (4.21)$$

where V_1 is the volume of the wall plus the domain, the first term is the homogeneous background magnetization energy and the contributions F_{qdr} , F_{grd} and F_{qri} are defined below.

The quadratic term, F_{qdr} , is given by

$$F_{qdr} = -\tau L_y L_z \frac{\kappa^2}{\kappa_0^2} \frac{M_s^2}{2} \int_{-a_w/2}^{a_w/2} dx (\tanh^2(\frac{x}{\lambda}) - 1) . \quad (4.22)$$

where L_y is the width of domain wall, L_z is the domain wall height and a_w is the domain width. Because $\tanh(x) \rightarrow 1$ when $x \rightarrow \infty$ and $a_w \gg \xi$ the integration limits in Eq. (4.22) may be extended to $\pm\infty$ to give

$$F_{qdr} = \sqrt{2a} \tau L_y L_z \frac{M_s^2}{\xi \kappa_0^2} . \quad (4.23)$$

For the contribution of the gradient term, F_{grd} , one obtains

$$F_{grd} = \tau \frac{a}{2\kappa_0^2} L_z L_y M_s^2 \int_{-a/2}^{a/2} dx \left(\frac{d}{dx} \left(\tanh\left(\frac{x}{\lambda}\right) \right)^2 \right) . \quad (4.24)$$

After changing the integration limits and evaluating the integral F_{grd} becomes

$$F_{grd} = \frac{\sqrt{2a}}{3} \tau L_y L_z \frac{M_s^2}{\xi \kappa_0^2} . \quad (4.25)$$

The contribution from the quartic term, F_{qtr} , is

$$F_{qtr} = -\tau U' L_y L_z M_s^4 \int_{-a/2}^{a/2} dx \left(\tanh^4\left(\frac{x}{\lambda}\right) - 1 \right) . \quad (4.25)$$

After changing the integration limits and evaluating the integral it becomes

$$F_{qtr} = -\frac{2\sqrt{2a}}{3} \tau L_z L_y \frac{M_s^2}{\xi \kappa_0^2} . \quad (4.27)$$

The contribution from $N=L_x/a_w$ walls, F_{wall} , is given by the product of N and the sum of F_{qdr} , F_{grd} and F_{qtr} :

$$F_{wall} = \frac{2\sqrt{2a}}{3} \frac{V \tau M_s^2}{\xi \kappa_0^2 a_w} , \quad (4.28)$$

where V is the sample volume.

The total free energy associated with the demagnetization effects is obtained by adding to F_{wall} either the magnetic energy of the N volume domains or the anisotropy energy of the N domains of closure, depending on the domain structure, i.e. the ratio $4\pi K_2(T)/\mu_0 M_s^2$ close to T_c .

For Gd the saturation magnetization at $T=0$ K is $M_{s0} = g\mu_B S_{\text{Gd}} N_{\text{Gd}} \approx 196 \times 10^4 \text{ A m}^{-1}$, where N_{Gd} is the number of Gd atoms per m^3 .

The temperature dependence of the spontaneous magnetization is given for small t by the power law $M_s(t) = M_{s0}(-t)^\beta$ where $\beta \approx 0.39$ for Gd.¹⁰⁷ The anisotropy constants K_2 and K_4 were measured by Graham¹⁰⁸ as a function of temperature. The anisotropy constant K_2 reaches a maximum at around 285 K ($K_2 \approx 2 \times 10^4 \text{ J m}^{-3}$) and decreases to zero at around 350 K ($K_2 \approx 1.5 \times 10^4 \text{ J m}^{-3}$ in the region of the Curie temperature). The anisotropy constants K_4 and K_6 vanish at around 240 K.^{108,109} Thus the ratio $4\pi K_2(T)/\mu_0 M_s^2(T)$ is much less than unity far below T_c and the flux closure configuration is favoured. However sufficiently close to T_c , $M_s^2(T)$ is much less than $K_2(T)$ and the domain structure is approximated by that in Fig. 4.1 ($\mu_0 M_s^2(T) = 4\pi \times 1.5 \times 10^4 \text{ J m}^{-3}$ when $T_c - T \approx 5 \text{ K}$).

Thus, combining Eq. (4.14) and Eq. (4.28), the total free energy associated with the demagnetization effects, F_{dem} , becomes

$$F_{dem} = VM_s^2 \left[\frac{2\sqrt{2a} \tau}{3\xi_0^2 a_w} + \frac{C_1 a_w}{L_z} \right]. \quad (4.29)$$

F_{dem} is a minimum with respect to the domain width, a_w , when

$$a_w = \left[\frac{2\sqrt{2a} \tau L_z}{3\xi_0^2 C_1} \right]^{1/2} (-t)^{\frac{\nu}{2}} = a_{w0} (-t)^{\frac{\nu}{2}}, \quad (4.30)$$

where the reduced temperature dependence of a_w was written explicitly and is given by the exponent $\nu/2$ (ν is the critical exponent associated with the correlation length and is equal 1/2 in the mean field theory and around 0.7 from the renormalization group calculations - Table 3.2).

The minimized demagnetization free energy is given by

$$F_{dem} = 2VM_{s0}^2 \left[\frac{2\sqrt{2a} C_1}{3L_z \xi_0^2} \right]^{1/2} (-t)^{2\beta + \frac{\nu}{2}} = F_{dem}^0 (-t)^\Psi. \quad (4.31)$$

The reduced temperature dependence of the minimized demagnetization energy, F_{dem} , is given by $\Psi = 2\beta + \nu/2$.

The reduced temperature dependence of the domain width and of the demagnetization free energy is given by the exponents obtained within the mean field approximation. However there is agreement between the expressions obtained here for the reduced temperature dependence of the domain width and of the demagnetization free energy and the

exponents derived by Stauffer¹¹⁰ who analyzed a scaling form of the free energy of the domain wall. Stauffer obtained, for the domain width, the exponent $\nu(1-\eta)/2$, which becomes $\nu/2$ putting $\eta=0$ as the mean field result; the calculated exponent for the free energy also reduces to the mean field exponent obtained here for $\eta=0$.

At this point a number of important estimates can be made. One of them is the range of the validity of the model. It was assumed in the above calculations that $a_w \gg \lambda \approx \xi$. This is an important assumption because the sum of free energies of N non-interacting walls can give a reasonable approximation to the actual free energy of the domain walls only if the separation between the walls is sufficiently large. Otherwise, by not taking into account the interactions between the walls, the model developed here does not correctly address the entropy of the whole system.

From Eq. (4.30) $a_w \approx 6.7 \times 10^4 (-t)^{0.35} \text{ \AA}$ for $L_z \approx 0.22 \text{ mm}$ (this is the width of one of Gd samples investigated in this study) and for $\nu=0.7$. The domain width is of the order of the correlation length $(6.7 \times 10^4 (-t)^{0.35} \approx 2 (-t)^{-0.7})$ when $t \approx 5 \times 10^{-5}$ so the model breaks down at $T \approx T_c - 0.015 \text{ K}$.

From Eq. (4.31) the free energy is: $F_{\text{dem}} \approx 0.5 (-t)^{1.13} \text{ J/mol}$ putting for V the molar volume of Gd.

The contribution from the demagnetization processes to the total sample heat capacity can be estimated by

$$\Delta C_{dem} = -T \left[\frac{\partial^2 F_{dem}}{\partial T^2} \right] \approx \frac{-1}{T_c} F_{dem0}^0 \Psi(\Psi-1) (-t)^{\Psi-2} . \quad (4.32)$$

At $t=5 \times 10^{-5}$ ($T_c - T \approx 0.015$ K) this contribution is around $1.4 \text{ J mol}^{-1} \text{ K}^{-1}$ which is around 2% of the total heat capacity. The demagnetization contribution becomes negligibly small further away from T_c (it is around 0.3% at $t=5 \times 10^{-4}$; $T \approx T_c - 0.15$ K).

The results of the analysis presented here suggest that the contributions from demagnetization effects to the heat capacities presented in this thesis are negligible over almost the entire temperature range which can be experimentally accessed, even by a high-resolution heat capacity measurement. The analysis also indicates that for $t < 10^{-5}$ this contribution may become sufficiently large to need to be taken into account as one of the factors determining the shape of the heat capacity curve and hence the rounding which is observed very close to T_c .

The range of validity of this model is for reduced temperatures larger than 5×10^{-5} . When this model is used in the limit $t=0$ it predicts that $a_w=0$ at T_c and also that the heat capacity associated with the demagnetization processes diverges at T_c .

However when a_w becomes smaller than ξ then the domain wall assumes the role of the domain itself so the domain wall width should also be decreasing as a function of

temperature near T_c . It appears thus that very close to T_c a physically more appealing picture of the domain structure is a periodic structure with the period of the order of the correlation length (one may also say that very close to T_c there is no distinction between the domains and the domain walls).

Barker and Gehring¹¹¹ discussed the domain structure below T_c and showed that for reduced temperatures for which the assumption of non-interacting walls is no longer valid the domain structure could be approximated by a sinusoidal magnetization profile with a non-zero period at T_c . For the free energy of their structure they obtained an expression which differs from Eq. (4.14) by a numerical factor of around 1.7.

Thus the model presented here does not give a correct temperature dependence of the domain width and hence the demagnetization free energy in the proximity of T_c . This could be expected on general grounds since it is a mean field model and mean field theories do not give correct descriptions of the temperature dependence of thermodynamic parameters in the critical region. A correct treatment must take into account fluctuations and the associated entropy.

On the other hand, it may be expected that the calculated demagnetization heat capacity contribution to the total heat capacity gives a correct estimate of the magnitude of the demagnetization heat capacity over a wide

reduced temperature range below T_c .

In conclusion, the results of this section show that the demagnetization processes in Gd have a negligible effect on the critical heat capacity data in the temperature range which is typically accessed in heat capacity measurements and they can be neglected here in data analysis.

However, it should be also noted that if there is a significant amount of data available below $t=10^{-4}$ then the possibility that this data has the contribution from the demagnetization effects should be taken into account.

For example it may not be possible to fit the data points in this temperature range with expressions pertinent to the critical behaviour of Gd. This case will be discussed again in the experimental chapter (Chapter 7) of this thesis.

Chapter 5. CRITICAL BEHAVIOUR OF GADOLINIUM

5.1 Introduction

Gadolinium (Gd) is one of the rare earth metals and it exhibits a ferromagnetic phase transition at around 294 K.^{4,112,113} The crystalline structure of Gd is hexagonal close packed with a unit cell c/a ratio of 1.59 which is close to the ideal value of c/a=1.63.

Gadolinium may be expected to exhibit only weak single-ion anisotropy since its magnetism is produced almost wholly by spherically symmetric $^8S_{7/2}$ ions (the electron configuration of Gd is $4f^75d^16s^2$; the large magnetic moment of Gd is localized in the 4f shell and the effective Bohr magneton number in the paramagnetic region is around 8.¹¹⁴) There is also a small conduction electron contribution to the total magnetism which can be treated as a polarisation of spins of conduction electrons induced by the 4f moments.

Below T_c the easy direction of magnetization is temperature dependent. Magnetization measurements^{114,115}, neutron diffraction¹¹⁶ and crystalline anisotropy¹¹⁷ show that the angle between the c-axis and the easy axis increases from around 30° at 10 K to around 65° at 183 K and drops abruptly to zero at $T_0 \approx 232$ K. Quasielastic neutron scattering on a ^{160}Gd -enriched single crystal¹¹⁸ indicates

the presence of anisotropic short-range order above and below T_c .

5.2 Experimental measurements of critical exponents of Gd

Critical behaviour of gadolinium is not yet fully understood.^{113,119,120} On the one hand, the S-state nature of the Gd moments coupled by isotropic Ruderman-Kittel-Kasuya-Yosida interactions implies Heisenberg critical behaviour near T_c .¹¹³ On the other hand, the unique easy (c-axis) direction of magnetization implies uniaxial anisotropy which suggests Ising critical behaviour.¹¹³ Static critical exponent measurements span predictions of both the models¹¹³ (see Table 5.1 and Table 5.2).

The literature values of the critical exponent α listed in Table 5.1 were obtained from heat capacity measurements by AC calorimetry¹²¹, continuous warming calorimetry¹²², and from thermal expansion measurements^{123,122}. The values of α suggest Heisenberg behaviour by their sign, but are generally much larger than the theoretical value.

Under the constraint that $\alpha=\alpha'$ Lanchester *et al.*¹²² were able to obtain a good fit to their data only after allowing for a discontinuity at T_c (denoted as $B \neq B'$ in the Table 5.1). They suggested that in the observable temperature range Gd might have been in the process of crossing over to uniaxial dipolar behaviour.

Jayasuriya¹²⁴ remeasured the heat capacity of the Gd crystal used by Lanchester *et al.*¹²² and obtained a good fit to the data with the constraint $\alpha=\alpha'$ after including

Table 5.1. Selected literature experimental values of the critical exponents α for Gd.

Exp.	T _c /K	Range of t	Value	Ref.	Comments
α	291.05(2)	10 ⁻³ to 10 ⁻¹	-0.09(5)	[121]	significant
α'		10 ⁻³ to 10 ⁻¹	-0.32(5)		rounding
α	293.60	8x10 ⁻⁴ to 2x10 ⁻²	-0.30	[122]	with
α'			-0.30		constraint
α	293.54		-0.09		α=α' and B≠B'
α'			-0.42		α≠α' and B=B'
α	293.60	8x10 ⁻⁴ to 2x10 ⁻²	-0.32	[122]	α=α', B≠B'
α'			-0.32		derived
α	293.54		-0.12		from
α'			-0.39		thermal expansion α≠α, B=B'
α	293.46	3x10 ⁻⁵ to 1.3x10 ⁻³	-1.71	[123]	derived
α		1.3x10 ⁻³ to 6.6x10 ⁻²	-0.121		from thermal expansion

Table 5.1 continued ...

Exp.	T_c/K	Range of t	Value	Ref.	Comments
α α'	293.68(11)	1.6×10^{-4} to 2×10^{-2} $T < T_c$ 10^{-3} to 4×10^{-2} $T > T_c$	 -0.32(2) -0.32(2)	[124]	with constraint $\alpha = \alpha'$ and $B \neq B'$
α α'	293.70(13)	1.6×10^{-4} to 2×10^{-2} $T < T_c$ 10^{-3} to 4×10^{-2} $T > T_c$	 -0.03 -0.03	[124]	correction to scaling fit with constraint $\alpha = \alpha'$

Table 5.2 Selected literature experimental critical exponents for Gd.

Exp	T_c/K	Range of t	Value	Ref.	Comments
β γ δ	292.1(2)	$t > 2 \times 10^{-3}$	0.37(1) 1.25(10) 4.39(10)	[126]	scaling-equation analysis
β γ δ	293.3(1)	$t > 4 \times 10^{-3}$	0.381(15) 1.196(3) 3.615(15)	[127]	scaling equation analysis
β γ δ	293.3(1)	2×10^{-3} to 3.7×10^{-2}	0.390(5) 1.33(2) 4.8(1)	[107]	magnetiz. and suscep. measurement
β	291.85(5)	10^{-3} to 0.1	0.399(16)	[113]	PAC experiment
γ	291.1(1)	10^{-2} to 3.7×10^{-2}	1.24(3)	[128] [129]	AC susceptibility
γ	293.51(3)	$t > 10^{-3}$	1.22(2)	[130]	AC susceptibility
γ	292.1(5)	$t > 10^{-3}$	1.235(25)	[131]	AC susceptibility

the confluent singular term into the fit.

Dolejsi and Swenson¹²³ made thermal expansion measurements on a single crystal of Gd over a several decades of reduced temperature ($10^{-5} < |T_c| < 10^{-1}$) and could not find a single power law representation for their data even after restricting the fits to temperatures only above or below T_c . They¹²³ had to use four reduced temperature ranges to represent their data by power law fits. Above T_c the division point was selected at the reduced temperature $t = 1.3 \times 10^{-3}$. Above that temperature the critical exponent α was equal to -0.121 agreeing well with that predicted for three-dimensional Heisenberg model (-0.115 ± 0.009)¹²⁵. For $t < 1.3 \times 10^{-3}$ the value of α was -1.71 , a unrealistically large negative number suggesting that the data should be fit to another model very close to T_c .

Values of the critical exponent β cluster around 0.38 and also support the Heisenberg critical behaviour^{126,127,113}. The exponent for the magnetic susceptibility, γ , is typically found to be near the three-dimensional Ising value^{128 129 130,131}, while values of δ are generally too low for either prediction.^{126,127}

Inconsistency between the measurements leads to disagreement between theory and experiment, including the violation of scaling laws such as $\alpha + 2\beta + \gamma = 2$. There can be several causes for the inconsistency. Non-asymptotic data can lead to widely different values of critical exponents,

depending on the temperature range of the fit . The quality of a crystal also affects results: the presence of impurities or defects may lead to an entirely new critical behaviour. Finally, the critical behaviour of a real system may not be simple, but it may change depending on the distance from T_c (in the reduced temperature scale), exhibiting a pattern of overlapping crossovers. In such a case, analysis of data in terms of power laws will generally yield effective exponents even though corrections to asymptotic scaling are included.

5.3. Investigations of the effect of dipolar interactions on the critical behaviour of Gd

The suggestion that magnetic dipolar interactions may be important for understanding the critical behaviour of Gd was made in 1975 by Geldart and Richard.¹³² In 1987 Geldart et al.¹¹⁹ reported measurements of the electrical resistivity of a c-axis single crystal of high-purity gadolinium metal in the vicinity of the Curie temperature ($|t| < 10^{-3}$). Numerical analysis showed that the data could not be well described by a power law of the type expected for short-range interactions and tended to exhibit a change in effective slope at T_c . Good fits were obtained when the data were described in terms of logarithmic corrections to the regular term of the sort expected for a uniaxial dipolar system (Sec. 3.6). Geldart et al.¹¹⁹ suggested that the asymptotic critical behaviour of Gd is that of a uniaxial dipolar ferromagnet, described by Landau theory with logarithmic corrections. They pointed out that other experiments on Gd in the critical region were likely influenced by dipolar effects due to a crossover from Heisenberg to dipolar critical behaviour.

Anisotropy in the critical properties of Gd was seen in the work of Collins et al.¹³³ on perturbed $\gamma\gamma$ angular-correlation (PAC) experiments on a single crystal of Gd above T_c . Models of critical dynamics based on isotropic

spin fluctuations did not give good results for $t < 10^{-3}$. However, their experimental results for $t < 10^{-3}$ were well described by an anisotropic spin-fluctuation model.

Further evidence for the uniaxial anisotropy in Gd was provided by Geldart et al.¹²⁰, who measured the magnetic susceptibility along the c-axis and in the basal plane on a single crystal of Gd in the reduced temperature range $4 \times 10^{-4} < t < 1.3 \times 10^{-2}$. They observed that the basal plane (hard direction) susceptibility, χ_b , remained finite at T_c and extrapolated to zero at a temperature which was below T_c by 0.52 ± 0.05 K (such a difference is the signature of uniaxial anisotropy). Another estimate of the anisotropy scale was obtained by defining a reduced-temperature scale for the anisotropy: $\chi_b^{-1}(T_c) = \chi_c^{-1}(T_c + \Delta T_{\text{anis}})$, where χ_c is the c-axis susceptibility. This procedure gave $\Delta T_{\text{anis}} = 0.57 \pm 0.09$ K.

Recently a general method for the evaluation of lattice sums determining the effective parameters in the Hamiltonian of a dipolar magnetic system has been introduced.^{134,135} This method was used to examine the anisotropy of the Hamiltonian as a function of c/a for a variety of lattices and it was found that dipole-dipole interactions favour the c-axis as easy axis of magnetization for $c/a = 1.59$, i.e. the c/a ratio for Gd at T_c . It was concluded that the dipole-dipole interactions would themselves be sufficient, in the absence of any other interactions, to cause the observed uniaxial ordering at the Curie point. They found that

dipolar interactions in Gd raised the mean-field transition temperature above the corresponding isotropic short-range exchange value of T_{c0} for any direction of ordering, but the shift ΔT_{c0} was larger for ordering along the c-axis ($\Delta T_{c0}^c = 1.713$ K) than for ordering in the basal plane ($\Delta T_{c0}^b = 1.633$ K). Thus, the mean field temperature range with respect to T_c over which the anisotropic effects of dipolar interactions are important, is $\Delta T_{anis}^0 \approx 0.08$ K. Using appropriate crossover exponents to incorporate the effect of fluctuations beyond the mean field approximation, the temperature range for the uniaxial anisotropy was estimated to be $\Delta T_{anis} \approx 0.45$ K.

Fujiki et al.¹³⁴ and Fujiki¹³⁵ discussed the implication of dipolar interactions and their anisotropy close to T_c on the critical behaviour of Gd and proposed a sequence of overlapping crossovers to explain the observed critical behaviour of Gd. According to their theory, relatively far away from T_c ($t > 10^{-1}$) Gd is in the Gaussian regime, i.e. in the regime described by Landau theory with weak perturbations. When the reduced temperature is decreased the Gaussian behaviour is replaced first by the isotropic Heisenberg behaviour and below $t \approx 2.15 \times 10^{-2}$ by the isotropic dipolar regime. Fujiki^{134,135} and Geldart et al.¹²⁰ estimated that a reduced temperature $t \approx 1.52 \times 10^{-3}$ ($\Delta T = T - T_c \approx 0.45$ K) was a crossover temperature to the uniaxial anisotropic regime and the asymptotic critical regime was of uniaxial

(Ising) type with dipolar interactions playing an important role.

It should be noted that the above estimate of the scale of anisotropy is in good agreement with the experimental values of 0.52 ± 0.05 K and 0.57 ± 0.09 K obtained by Geldart et al.¹²⁰ from the magnetic susceptibility measurements and the experimental value of $t \approx 1.3 \times 10^{-3}$ ($\Delta T = T - T_c \approx 0.38$ K) suggested by Dolejsi and Swenson¹²³ as a crossover temperature to a new critical regime on the basis of their fit to thermal expansion data. It also should be emphasized that these crossover temperatures only set the scales of different crossover effects which may take a few decades to go to completion.

The effect of the dipolar interactions on the critical behaviour of Gd was also considered by Aliev et al.¹⁰⁷ in their analysis of experimental results of magnetization and susceptibility measurements on two single crystals of Gd. They analyzed their data in terms of power laws with correction to scaling and compared the numerically obtained values of the correction to scaling terms with theoretical estimates. Assuming that in the temperature range of the fits ($10^{-3} < t < 5 \times 10^{-2}$) the critical behaviour of Gd is essentially governed by the isotropic dipolar forces they obtained good agreement between the calculated and fitted values of the correction to scaling terms.

Recent muon spin relaxation time measurements (μ SR) on

a spherical single crystal of Gd showed¹³⁶ a strong effect of a crossover from a non-conserved dynamics (dipolar) regime to a conserved (exchange dominated) regime ca. 10 K above T_c and anisotropy in the muon relaxation rate along the c-axis and in the basal plane for $t < 0.01$.

In summary, there is considerable experimental and numerical evidence that the critical behaviour of Gd can be understood in terms of magnetic dipole-dipole interactions. Dipolar effects are present throughout the range of virtually all experimental measurements of critical exponents of gadolinium. In earlier experiments on Gd in the critical regime data analyses were based on fitting data to appropriate power laws and although a fit to the data was generally possible there were difficulties with interpreting critical exponents obtained. Those exponents should be seen as effective exponents which depend on the temperature range of the fit. For instance, the experiment by Chowdhury et al.¹¹³ yielded $\beta = 0.399$ for $|t| < 10^{-1}$ which is larger than the theoretical prediction of $\beta = 0.365$ for the Heisenberg model. However, if in that temperature range Gd is in the process of crossing over to the uniaxial dipolar behaviour in which magnetization varies⁶⁵, for $t \rightarrow 0$, as $M(t) \propto |t|^{1/2} |\ln|t||^{1/3}$ then it is reasonable to expect the effective value of β to lie between the Heisenberg value and the classical value, $\beta = 0.5$. The same observation can be made about other measurements of β (see Table 5.2).

Finally, it should be noted that logarithmic corrections characteristic of three-dimensional uniaxial dipolar magnets have not yet been conclusively observed experimentally in Gd. It is not trivial to detect multiplicative logarithmic corrections to the power laws even if the additional problems of crossover from Heisenberg behaviour are not present. For instance, the magnetic susceptibility in the uniaxial dipolar regime varies as $\chi \propto |t|^{-1} |\ln|t||^{1/3}$ and it is dominated by strong $|t|^{-1}$ dependence (measurements over a few decades of the reduced temperature may be needed to detect the slowly varying logarithmic term). However, heat capacity is found to have the leading singular dependence given by Eq. (3.38) and thus for heat capacity the logarithmic term is the leading singular term, and it is not masked by a power law. For that reason, high-resolution heat capacity measurements on Gd, in the reduced temperature range $|t| < 10^{-3}$, could provide important experimental evidence needed to determine the asymptotic critical behaviour of Gd.

5.4. Prior experimental measurements of the heat capacity of Gd

Gadolinium is also a good candidate for testing a high-resolution calorimeter because there is ample high-resolution and high-precision experimental data available on the heat capacity of gadolinium around its Curie point. The heat capacity of gadolinium was measured by adiabatic calorimetry by Griefel *et al.*¹³⁷ and A.V. Voronel *et al.*¹³⁸. Robinson *et al.*¹³⁹ investigated the heat capacity of gadolinium over the phase transition by differential scanning calorimetry. High-resolution heat capacity studies on gadolinium were performed by Lewis¹²¹, Simons *et al.*¹⁰¹, and Wantenaar *et al.*¹⁴⁰ by AC methods and by Lanchester *et al.*¹²² and Jayasuriya⁸⁴ by the continuous warming method.

Chapter 6. EXPERIMENTAL METHODS

6.1 The cryostat and the sample assembly

The immersion cryostat, shown schematically in Fig. 6.1, was made up of two compartments (V_1 and V_2 in Fig. 6.1), which could be evacuated separately. This design allowed either of the compartments to be filled with exchange gas of regulated pressure. The sample assembly was made of copper and consisted of three parts: an adiabatic shield (AS - in Fig. 6.1), a sample holder (SH), and a heat sink (HS).

The heat sink, constructed of a thick-walled copper cylinder, was silver-welded to the long thin-walled stainless-steel tube which also supported the inner vacuum can. The tube went outside the calorimeter and was connected to the vacuum pumps. All the electrical leads were carried out through the tube and sealed at two electrical feedthroughs mounted on the top of the tube. The adiabatic shield and the sample holder were connected to the heat sink with threaded joints and could easily be disassembled. The adiabatic shield did not have a separate heater but it was thermally well-coupled to the heat sink, and its function, together with the helium exchange gas, was to minimize temperature gradients around the sample.

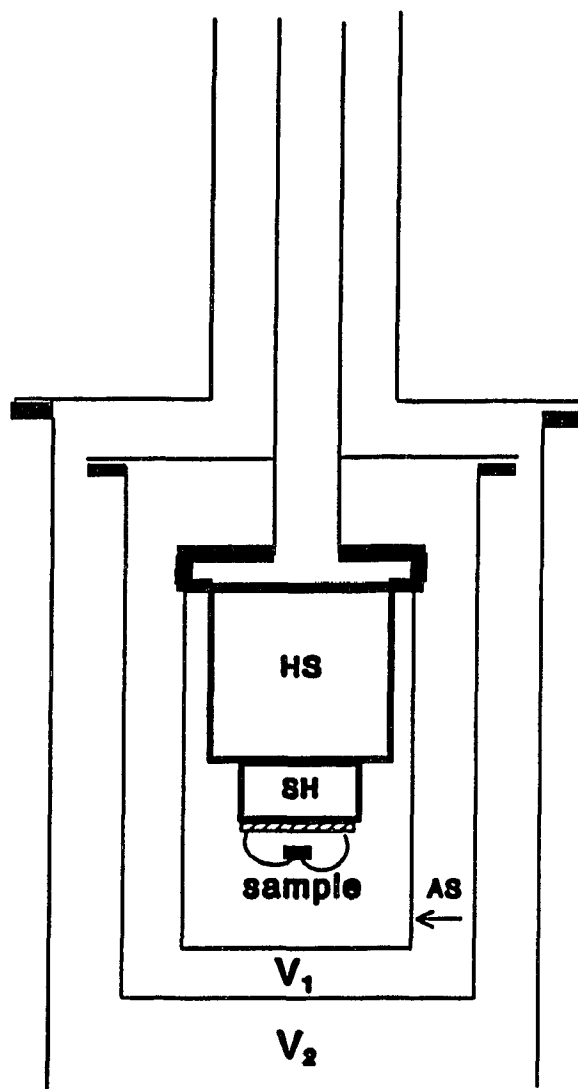


Fig. 6.1. Schematic of the cryostat and the sample assembly.

AS: adiabatic shield; HS: heat sink; SH: sample holder; S: sample; V_1 , V_2 : vacuum chamber.

A platinum resistance thermometer (Lake Shore Cryotronics, Pt-103, 100 Ω at $T = 273$ K) was inserted into a hole in the sample holder. The space between the hole wall and the thermometer was filled with Apiezon T vacuum grease, which was selected over Apiezon M and N because it has the highest operating temperature; it melts at around 400 K, compared to 310 K for Apiezon M and N.¹⁴¹ There also was an extra hole drilled in the sample holder to accommodate the reference junction of a thermocouple if it is used as a temperature sensor (instead of the thinistor used for a present work).

The sample was suspended from the sample holder with the sample heater and thinistor leads squeezed between two plastic rings screwed to the sample holder. Those leads were soldered to extension leads with thermal-free solder (Leeds and Northrup), all on a piece of a printed circuit board glued with 5-minute epoxy to the wall of the sample holder. All the extension leads were double-silk wound 38 SWG copper wire. The heat sink heater was made of approximately 2 m of double-silk wound 38 SWG manganin wire (25 Ω /m resistance) wound bifilarly around the heat sink and varnished into place with low-temperature varnish (GE 7031). Despite its relatively simple construction this cryostat allowed temperature stability at the heat sink to within ± 1 mK.

The design of the sample heater was given particular attention. Sometimes chopped light is used to heat the sample in AC calorimetry. However this method was not used here because it would not allow determination of the total power dissipated in the sample and because it is easier to stabilize the frequency and power of an electrical signal.

The resistance heater for the sample must satisfy a number of requirements. It should be electrically and mechanically stable on thermal cycling; it should be in good thermal contact with the sample; its heat capacity should be small compared with that of the sample.

Several prototype heaters were tested and found to be inadequate. A heater was made of 0.003 mm Mylar foil coated on one side with a 0.1 μm thick layer of manganese (purchased from Goodfellow) but that heater did not adhere well to the sample and there were problems with the attachment of leads to it. Schwartz¹⁴² made a sample heater by painting a piece of a Mylar foil with DAG 154 (graphite suspension diluted with acetone), and attached the leads by painting them into place. However, it was found here that such a heater was too thick (around 0.04 mm), i.e. it would make the internal relaxation time of the sample assembly too long.

The sample heater used in the present study was made by evaporating a layer of bismuth (Bi) on a sample surface painted for insulation with GE 7031 varnish diluted with a

50:50 toluene:ethanol solution. The contacts to the heater were made with two pieces of 20 μm diameter copper wire. The wires were glued across the sample close to its opposite edges with silver-loaded epoxy. The bismuth layer was evaporated on the sample after making the contacts and its thickness defined the resistance of the heater. Heaters of resistance of around 50 Ω were used; the resistance was determined by the heating power requirement and the design of the power supply. The total thickness of the heater was around 4 μm and its contribution to the total heat capacity was of the order of a few percent. Heaters made as described here were very reliable: they were in good thermal contact with the sample and did not significantly change their resistance over time or heat treatment.

6.2 Electronic instrumentation and data acquisition system

Unwanted fluctuations in the power and frequency of the heating signal could be mistaken for changes in heat capacity, reducing the sensitivity of the calorimeter. This problem was solved here by building a programmable microprocessor-controlled power supply (PS-1 in Fig.6.2 and Fig.6.3). This unit was designed to provide constant heating power to a heater whose resistance could vary as the temperature changes. The heating power requirement was very small; less than 0.5 mW.

An additional requirement was that this heating power could be applied as a low-frequency sine wave, with the frequency being both extremely stable and programmable. Because a lock-in amplifier was used to detect the temperature changes arising from the heating signal applied to the sample, and since the signal was very weak, the frequency stability of the heating signal was important. The Stanford-Research 530 lock-in amplifier used synthesizes a sine wave in its reference channel and uses a four-quadrant multiplier as its phase-sensitive detector; therefore it was decided that a sine wave heating signal would provide for better signal capture than a simple square-wave heating signal.

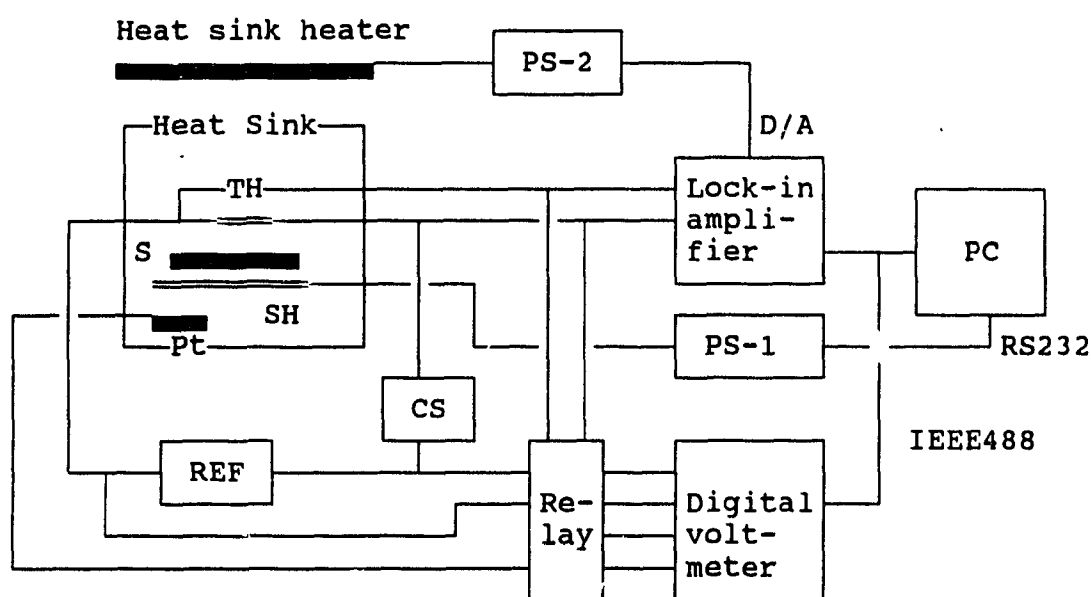


Fig. 6.2. Block diagram of the automated AC calorimeter.

PC: personal computer; RS232: serial interface;
 IEEE488: parallel interface; PS-1 and PS-2: power
 supplies; D/A: digital-to-analog outputs of the
 lock-in amplifier; CS: current source;
 REF: reference resistor; Pt: platinum resistance
 thermometer; SH: sample heater; S: sample; TH:
 thinistor.

Since a microprocessor was employed in the design, the sine wave was software-generated and the frequency was derived from a quartz crystal clock.

The basic algorithm used in this design was as follows. The operator would send the controller the following parameters, via an RS-232 serial data link from the host PC computer: (1) frequency (resolution to .01 Hz), (2) desired heater power, (3) approximate sample resistance (at that temperature). The controller then calculated the correct quartz clock divider ratio to produce a sine wave signal made up of 256 segments.

Using the power and resistance values given by the operator, an approximate heating voltage was derived. A sine wave of this voltage was generated using a dual 12 bit DAC. One half of this DAC was used to provide a DC voltage with an amplitude equal to the peak value of the sine wave needed. This voltage was then used to provide the reference voltage for the second half of the DAC to which the microprocessor was sending sine wave data at the selected frequency. The output of the second DAC was a unipolar signal with a sine waveform. By mixing in the signal from the first DAC, at a ratio of 0.5, a true sine wave signal centred at 0 V was derived.

[illegible]

This sine wave was buffered and applied to the sample in a feedback arrangement using two wires to apply heater power, and two wires to sense the actual voltage at the sample. This arrangement eliminated errors due to the resistance of connecting wires.

A 50 Ω precision resistor was placed in series with the sample to sense the current. The voltage across this resistor was amplified and sent to a SAMPLE/HOLD circuit. Since the current through the sample and 50 Ω resistor arose from the sine wave signal produced by the microprocessor, the microprocessor also could place the SAMPLE/HOLD circuit in the HOLD mode at the peak of the heater signal. The DC voltage provided by the SAMPLE/HOLD was fed to a synchronized voltage-to-frequency converter. The output pulse-train frequency was measured by the microprocessor, giving it a value for the heater current.

This circuit provided an accurate alternative to rectifying or phase-detecting the heater current AC signal since those methods require an output filter, which at the low excitation frequency used would result in a very slow response time.

The period of time during which the microprocessor counted the pulses from this converter, and also the clock that drove this converter, were both derived for high accuracy from the crystal-controlled microprocessor clock through digital divider circuits. Therefore the

microprocessor produced a sine wave heater excitation signal of known amplitude, and also measured the heater current accurately. Since power is the product of these two values, the microprocessor was programmed to stay in a loop measuring heater current, forming the voltage-current product, and "fine-tuning" the heater excitation voltage until the requested power was reached. The loop was performed ca. every 3 s.

At any time the host PC could interrogate the microprocessor, through the RS-232 link, to determine the heater voltage and current. Alternately, a new power level or excitation frequency could be specified. An additional relay control circuit was operated by the microprocessor in this unit (Relay in Fig. 6.2). The relay circuit was used for meter switching and was included with this circuit for convenience, as this controller had a serial link to the host PC, and was easily able to handle this additional task.

The amplitude and the phase of the temperature oscillation of the sample were measured by the SR 530 lock-in amplifier using a thinistor (thick film flake thermistor made by Victory Engineering Corporation, symbol 53K1A500, $250\text{ k}\Omega \pm 20\%$ zero power resistance at 25°C , dimensions $0.5 \times 0.5 \times 0.04\text{ mm}^3$) as a temperature sensor (TH in Fig.6.2).

The current to the thinistor was supplied by a very stable current source (CS in Fig.6.2 and Fig.6.4) also built for the purposes of this project. A Hewlett Packard 3456A

The diagram illustrates a control system for an isothermal block heater. It features a power transformer (229B24) with a 120 VAC primary and two 12V secondary windings. The primary is connected to a 1A fuse and a power switch. The secondaries are connected to a bridge rectifier (DF04) and a filter capacitor (470/25). The rectified output provides a +15V supply, which is regulated by a 1N4005 diode, a 100 ohm resistor, and a 1N4744 Zener diode. A -15V supply is also derived from the transformer. The control circuit includes an LM399 precision centimeter-to-centimeter converter, an OP-07CN8 operational amplifier, and a TIP122 power transistor. The LM399 is configured as a voltage-to-frequency converter, with its output driving the base of the TIP122 transistor. The transistor's emitter is grounded, and its collector is connected to the heater power supply line. A 6V ZENER diode and a 10K 10T potentiometer are used for heater power adjustment. The heater itself is represented by a 100 ohm 1W resistor. The entire system is powered by a +18V supply, which is also connected to a 1 MEGOHM 0014 resistor on an isothermal block.

digital voltmeter (Digital voltmeter in Fig.6.2) measured the resistance of the thinistor in the resistance ratio mode to give the absolute temperature of the sample.

The reference high-precision resistor (two connected in series; VHA518-7 100 k Ω resistors made by Vishay Resistive Systems Group, tolerance 0.001% , temperature coefficient ± 1.5 ppm/K around room temperature) was embedded in a temperature-regulated aluminium block (REF in Fig. 6.2).

The thinistor current was approximately 6.95 μ A, which was in the lower limit of the range recommended by the manufacturer. With the thinistor and standard resistor used, the compliance (output voltage range available) required was about 3.5 V.

The constant current source built provided at least 6 V compliance. The circuit centred around an oven-controlled reference IC (National Semiconductor LM399). This small IC, in an insulated can package, contained both a 6.95 V reference and a small temperature controlled heater, all on the same substrate. Soon after turning on, the LM399 oven stabilized its internal temperature above the ambient temperature. The temperature coefficient of the reference was typically 30 ppm/K.

A constant current was generated by passing 18 V through a 1 M Ω standard resistor (VHA518-10 made by Vishay, tolerance 0.001%, temperature coefficient 1.5 ppm/K), a pass element and then through the external thinistor-reference

resistor circuit to ground. The voltage drop across the 1 M Ω standard resistor, at 6.95 μ A, was 6.95 V. This was the same value as that of the LM399 voltage reference.

Therefore an operational amplifier was used to compare the above two voltages and its output was used to drive a 4N26N optocoupler's light emitting diode. The connection between the operational amplifier and optocoupler was such that if the output current was less than 6.95 μ A, the output of the operational amplifier would tend to go negative, causing the current through the infrared light emitting diode (LED) (in the optocoupler) which is referenced to +15 V, to increase. The increased LED current would cause the 4N26N phototransistor to pass more current, and this would increase the current output until stability was reached at 6.95 μ A.

More conventional circuits were tried earlier but were found to be prone to modulation by the low-frequency heater signal and/or noise. This could not be eliminated by RC filtering of the current source as this introduced amplitude and phase errors in the measurement of the temperature oscillation by the lock-in amplifier. Amplitude and phase errors in the signal measurement were minimized by isolating the highly sensitive operational amplifier input terminals from the thinistor/reference resistor.

The 1 M Ω resistor and the "Ratio" standard resistor were mounted in an isothermal block which was heated to a

relatively constant (± 1 K) above-ambient temperature, by a simple transistor pass regulator driving two $100\ \Omega$, 1 W resistors imbedded in the isothermal block (Fig.5). A solid-state temperature controller IC was used in an initial design, but was removed when it was found that its switching transients, which occurred around the setpoint temperature, were affecting the constant current source, even though the two circuits were individually powered from separate power supplies. Positive and negative 15 V supplies were provided by half-wave rectifiers and Zener diodes, from one secondary of the power transformer. A separate winding of the power transformer in conjunction with a bridge rectifier, was used to provide 16 V unregulated to both the isothermal block heater and the reference oven circuit.

The power supplied to the heat sink heater was controlled by the DAC outputs of the Stanford Research 530 lock-in amplifier. Because these are low current outputs, a buffer amplifier (741 operational amplifier with a 2N5195 emitter-follower buffer output) was used (Fig. 6.5). The configuration of the circuit was inverting: i.e. the 0 to 10.24 V output of the DAC's was converted to 0 to -10.24 V output to the heater. The gain of the buffer with respect to its DACX5 input was -1. The gain of the buffer with respect to its DACX6 input was -0.01, and the output signal was the algebraic sum of its inputs, weighted in the amounts indicated above.

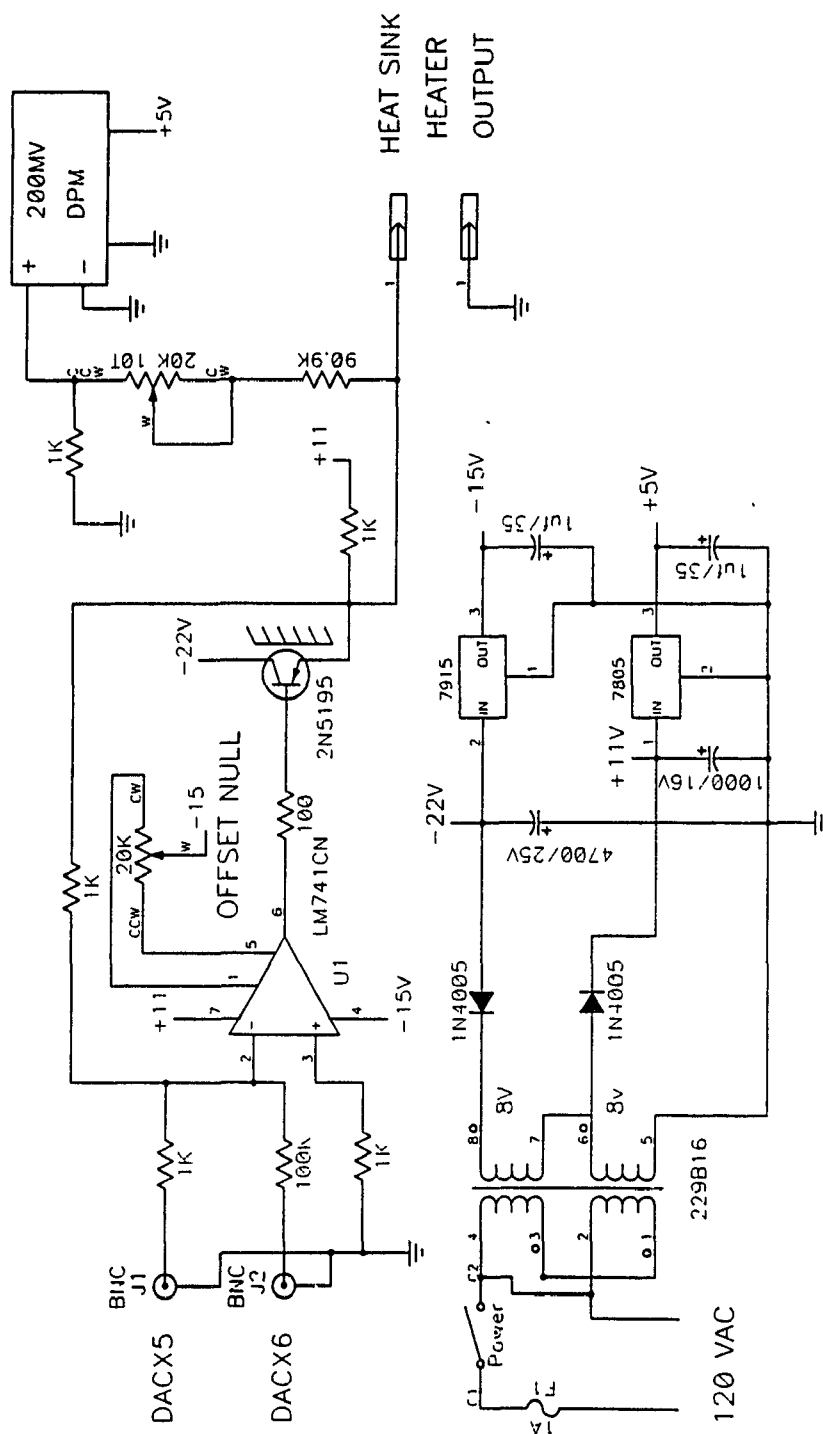


Fig. 6.5. Heat sink heater control circuit

This allowed for a coarse heat adjustment by setting DACX5, as well as a very fine adjustment by setting DACX6. Both the operational amplifier and the output buffer operated from a bipolar supply. The (negative) voltages used were not equal, but were chosen to match the output voltage requirement.

The heat sink temperature was measured with the platinum resistance thermometer (Pt in Fig.6.2) by the Hewlett Packard 3456A DVM in the 4-wire Ω mode with thermal emf compensation. The relay switched the 3456A DVM between the resistance of the Pt thermometer and the ratio measurement of the thinistor.

The DVM and the lock-in amplifier were interfaced with an IBM-compatible, 386 class computer by an IEEE-488 parallel data link. All the operations associated with the control of the electronics, temperature control and data acquisition were performed by the computer. The menu-driven software for the calorimeter was written in QuickBasic and because the speed of the measurements was not crucial it was run under the QuickBasic Interpreter. The software also incorporated a part written in a machine code for controlling the microprocessor of the power supply.

6.3 Thermometry

The temperature scale used in this experiment was based on the platinum resistance thermometer mounted inside the sample holder (Sec. 6.1). The measured resistance of the thermometer was converted to temperature using the Chebyshev polynomial calibration equations provided by the manufacturer. In the temperature range of the experiment the RMS error of the fit was around 5 mK.

The sample temperature and the AC temperature oscillation were measured with the thinistor mounted on the sample. The thinistor was calibrated against the Pt thermometer as follows. The thinistor resistance, R , was measured about every 0.5 K while the temperature, T , was increased linearly at a rate of a few hundreds of mK per hour with the inside of the calorimeter filled with He exchange gas. The simple polynomial,

$$T = A + B \ln R + C (\ln R)^2, \quad (6.1)$$

was fit to the calibration data by a least-squares procedure, giving a random scatter of ca. 30 mK over the temperature interval of the measurements. The use of Eq. (6.1) was preferred over other procedures¹⁴³ because of its simplicity. For the purpose of converting lock-in amplifier readings to temperature the inverse fit, i.e. $\ln R = f(T)$ also had to be found, and ΔT for small values of ΔR was

calculated by differentiation of Eq. (6.1).

The thinistor calibration was repeated periodically. When the thinistor was thermally cycled from 360 K down to liquid nitrogen temperature its calibration shifted towards lower temperature by about 200 mK. Over a few months, values tended to give higher temperatures for a given thinistor resistance when the thinistor was kept in vacuum or in helium atmosphere, which may indicate slow degradation of the thinistor, but results were within 150 mK. Most important, the sensitivity (resistance derivative of Eq. (6.1)) was constant for different calibrations in the temperature range from 220 to 330 K. The temperature coefficient of the resistance of the thinistor, $\alpha = \delta \ln R / \delta T$ decreased with temperature from a room-temperature value of around 4.6 % resistance change/K.

Thermistors are among the most sensitive thermometers; they are much more sensitive than thermocouples commonly used in AC calorimeters. The value of α obtained for the thinistor used here is typical for high-sensitivity bead (glass-encapsulated) thermistors. However, the thinistor is a superior temperature detector in an AC calorimetric experiment because it combines a high sensitivity with a very low thermal mass and it can be placed in very good thermal contact with the sample. A thermistor similar to the one used here also can be used successfully around the liquid-nitrogen temperature⁷ provided that it is not

thermally cycled to room temperature.

The temperature of the experiment was scanned linearly up or down by regulating the power to the heat sink. It was done by the computer which changed the voltage at the analog outputs of the lock-in amplifier (Sec. 6.2) so as to induce the preset temperature drift rate.

The design of this calorimeter allows its operation in the temperature range up to the melting point of the indium seals. The lower range of temperature is limited by the sensitivity of the platinum resistance thermometer, which loses sensitivity below about 20 K.

6.5 Performance of the calorimeter

The sensitivity of an AC calorimeter is limited by the accuracy of the measurement electronics, the stability of the thermal regulation, and by various thermodynamic noises, e.g., the Johnson noise in the thermometer, the $1/f$ noise, noise in the lock-in amplifier, and pick-up noise. (See Kenny and Richards¹⁸ for a discussion of the performance of an ideal AC calorimeter.) The major source of noise in the present experiment is $1/f$ noise. The noise density was measured using the noise-measurement capability of the lock-in amplifier, and it was found that it varied almost as $1/f$ in the frequency range from 1 Hz to 10 Hz. The noise contribution to the measured signal was around $0.5 \mu\text{V}$ (around 0.2 % of the total signal) for integration times typically used in the experiment (10 s) in good agreement with our calculated estimates of the $1/f$ noise in the thinistor, and with the observed scatter in the data. This set a lower limit on the resolvable change in ΔT_{AC} as around $5 \times 10^{-6} \text{ K}$.

Similar values for AC calorimeter sensitivity are given by Garland¹⁵ for a room-temperature experiment employing a microbead thermistor as a temperature oscillation detector. The sensitivity of the measurement could be improved significantly by further thinning the sample which would permit operation at higher frequency.

Chapter 7. Experimental results - Heat capacity of gadolinium

7.1 Sample preparation procedure

The heat capacities of four gadolinium samples (designated A, B, C and D) were measured in this study. Three of the samples (samples A, B and C) were cut from an electrotransport-purified single crystal of Gd grown at the Ames Laboratory, Energy and Mineral Resources Institute. This crystal has been characterized by previous electrical resistance¹¹⁹ [$R(293\text{ K})/R(4.2\text{ K}) \approx 150$] and magnetic susceptibility¹³⁰ studies.

Preliminary measurements were carried out on samples A and B. These samples and sample C were cut from the larger crystal with a diamond saw. After cutting, sample A was around 0.25 mm thick and it was subsequently ground to a thickness of 0.15 mm by rubbing against a silicon carbide 600 grit grinding paper (thickness chosen to ensure that the heating signal frequency would be of the order of few Hz), and polished with diamond paste (final polishing was done with 1 μm diamond paste). The final sample dimensions were $3.20 \times 5.28 \times 0.15\text{ mm}^3$ with the c-axis perpendicular to the sample surface.

Sample B was prepared in the same way and its final dimensions were $3.08 \times 5.18 \times 0.12\text{ mm}^3$. Afterwards sample B

was annealed at 850°C for 24 hours in a vacuum of 5×10^{-6} Torr in a tantalum foil wrap.

The following two steps of the sample preparation procedure were the same for all the samples measured. A heater was evaporated on one side of the sample (as described in Sec. 6.2). A thinistor was glued in the centre of the opposite side of the sample with thinned GE 7031 varnish. The thinistor extension leads, made of two pieces of platinum wire 17 μm in diameter, were soldered to the calorimeter extension wires on a piece of a printed board glued to the sample holder (Chapt. 6).

The total mass of the thinistor and Pt extension wires was around 0.4 mg. The sample assembly mass for sample A (gadolinium plus varnish plus silver loaded epoxy and plus thinistor with the extension wires) was: 0.0142 g; Gd mass: 0.0131. The sample assembly mass for sample B was: 0.0123 g; Gd mass: 0.0113 g.

7.2 Measurement in the AC mode, including heat treatments

7.2.a Measurements on samples A and B

The optimum range for the frequency of the heating signal was found by measuring the amplitude of the AC temperature oscillations, ΔT_{AC} , as a function of the inverse of the heating frequency, ω^{-1} . For heating frequencies in the range from 1 to 3.5 Hz, ΔT_{AC} was inversely proportional to ω and the phase shift between the heating signal and the AC oscillations was of the order of few degrees. The heating frequency selected was the frequency for which the phase shift was almost zero close to T_c ; this frequency also gave the maximum value of the product of the lock-in amplifier signal and the heating frequency. The heating frequency was 2.0 Hz for sample A and 1.9 Hz for sample B.

In a typical measurement series, a sample was heated with a signal of predetermined frequency and rms power of a few hundreds of μW ($P_{rms}=170 \mu W$ for most of the runs for the samples A and B). This heating signal induced temperature oscillations of the order of a few mK resulting in voltage oscillations over the thinistor of the amplitude of a few hundreds of μV . The voltage signal of this order was easily detected by the lock-in amplifier and was free of any visible noise. The SR-530 lock-in amplifier has a double-

section low-pass filter after its demodulator stage. The first section has a time constant from 1 ms to 100 s; it precedes the second section in the output amplifier. The second section can be excluded from the circuit or set to 0.1 s or 1 s. Each of the sections provide 6 dB/oct attenuation. The time constant used in the measurements were 10 s and 30 s on the first section, and 1 s on the second section.

The temperature of the heat sink was increased or decreased at a rate of a few mK per minute and the voltage oscillation amplitude and the heat sink temperature were recorded as functions of time. The sample temperature was determined by adding to the heat sink temperature the constant temperature difference between the sample and the heat sink, ΔT_{DC} , due to the sample heating. ΔT_{DC} was measured with the thinistor at the beginning and the end of each series and it depended on the heating power, the pressure of He exchange gas and the rate of heating. This temperature difference changed by at most 100 mK during a single run lasting more than 24 hours, and for the purpose of data analysis it was assumed to be a linear function of temperature. The average T_{DC} was usually used for calculations, which did not change the results in a noticeable way.

During measurement the inside of the calorimeter was filled with helium gas at 2×10^{-3} Torr. At this pressure the

thermal conductance of the leads contributed approximately 30% to the total heat conductance. The experimentally measured external time constant for this pressure, τ_2 , was around 3.5 s; the internal time constant, τ_1 , was estimated to be of the order of 10^{-3} sec. Measurements made at different pressures of helium (2×10^{-3} Torr to atmospheric pressure) and also when the inside chamber was evacuated (to 5×10^{-6} Torr) gave the same results. Increasing the temperature drift rate from 5 to 60 mK/min also did not affect the results. This indicates that the sample was in thermal equilibrium.

The results for samples A and B are shown in Figure 7.1. The data points were collected every 200 mK for sample A; for sample B they were collected every 100 mK away from the critical temperature and every 10 mK close to the critical temperature. The temperature was increased at a rate of around 6 mK per minute and ΔT_{AC} was in the range 2.5 to 3.5 mK.

The heat capacity curve for sample A exhibits a considerable smearing of the phase transition (the rounding is of the order of 2 K). Lewis¹²¹ and Simons²³ reported a similar large smearing for their measurements on unannealed samples. Lewis annealed his sample for 8 h at 1100 K under vacuum (the pressure was not stated). After annealing the rounding of the phase transition decreased to around 0.4 K. Simons obtained his sample from the source used by Lewis.

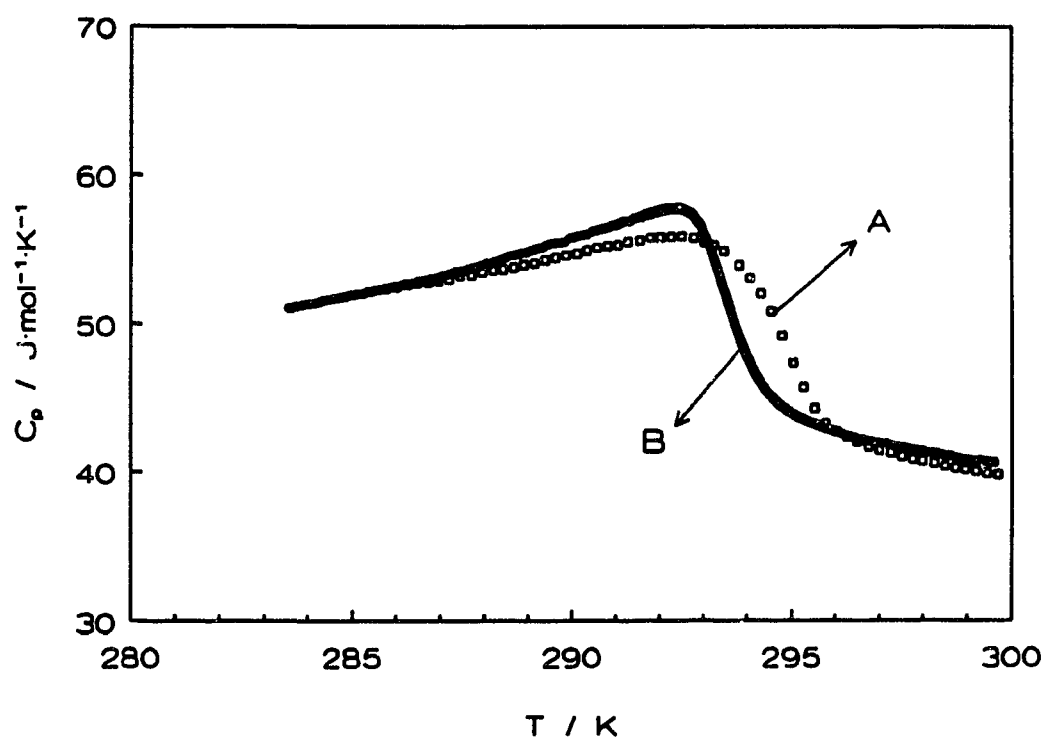


Fig. 7.1 The heat capacity of Gd near its ferromagnetic phase transition for sample A (curve A) and sample B (curve B).

The annealing procedure employed by Simons (the sample was annealed at 850°C for 24 hours in a vacuum of 5×10^{-6} Torr in a tantalum foil wrap) decreased the rounding in the heat capacity curve to a level stated to be around 0.1 K. The same annealing procedure was used here for sample B.

After annealing the sharpness of the phase transition for sample B improved significantly compared to sample A. Sharpening was accompanied with an increase in the Curie temperature. This suggests that at least part of the smearing in sample A was due to strains in the sample which could have been induced by cutting and grinding. The rounding in the heat capacity curve for sample B was around 0.5 K with a maximum heat capacity of around $58 \text{ J mol}^{-1} \text{ K}^{-1}$ which still compares rather poorly with the rounding reported by Simons after annealing (his sample displayed rounding of the order of 4 K before annealing) and with a very sharp transition reported by Lanchester et al.¹²² (the peak value of the heat capacity in their study was $66 \text{ J mol}^{-1} \text{ K}^{-1}$).

The residual resistance ratio, RRR, [$\text{RRR} = R(293 \text{ K})/R(4.2 \text{ K})$] of the crystal from which samples A, B and C were cut was measured in the basal plane using a four-wire method. The contacts to the crystal were made with four 20- μm -diam gold wires spot-welded to the crystal surface. The RRR for this crystal was around 150 and this value agreed with the value reported previously¹¹⁹. The

sample measured by Lanchester et al.¹²² had $RRR=163$. Lewis's sample had $RRR=19$; Simons did not give the resistance ratio for his sample but the RRR of his sample before annealing was probably near the value given by Lewis.

The RRR of sample A was measured after cutting ($RRR \approx 100$) and after grinding ($RRR \approx 60$) and also after annealing ($RRR \approx 30$). (Sample A was annealed after measuring its heat capacity and the annealing procedure was the same as for sample B.) The RRR of sample B after annealing was also around 30. The decreasing values of RRR indicate that grinding and polishing degraded the quality of samples A and B. Moreover, the annealing procedure, which was reported to have worked well for an apparently less pure sample in Simons's case, did not sufficiently improve the quality of samples A and B.

It was decided to carry out a systematic study of the effect of different annealing procedures on the sharpness of the phase transition in Gd using a sample for which the possible negative effects of cutting and grinding were minimized. The results are given in the next section.

7.2.b Measurements in the AC mode on sample C

Sample C was not subjected to extensive grinding after it had been cut from the larger crystal. It was polished and ground but only to the extent needed to smooth out the rough edges left after cutting (final dimensions $5.34 \times 3.02 \times 0.32 \text{ mm}^3$; sample assembly mass: 0.0330 g; Gd mass: 0.0320 g). The heating frequency for sample C was 1.5 Hz and the heating power was $P_{\text{rms}} = 300 \text{ } \mu\text{W}$.

The heat capacity of sample C before annealing and after three consecutive heat treatments is shown in Fig. 7.2. The data points were collected every 100 mK; the temperature drift rate was 12 mK/min.

Wantenaar *et al.*¹²⁹ measured AC susceptibility of Gd on a variety of unannealed and annealed polycrystalline samples. Some of their samples were annealed at 850°C for 24 hr in a low-pressure helium atmosphere and allowed to cool over 12 hr. This procedure was found to reduce the broadening of the transition. However, their best results were obtained for a sample annealed in a purified stream of argon. The annealing procedure of Wantenaar *et al.*¹²⁹ was employed in the heat treatments of sample C.

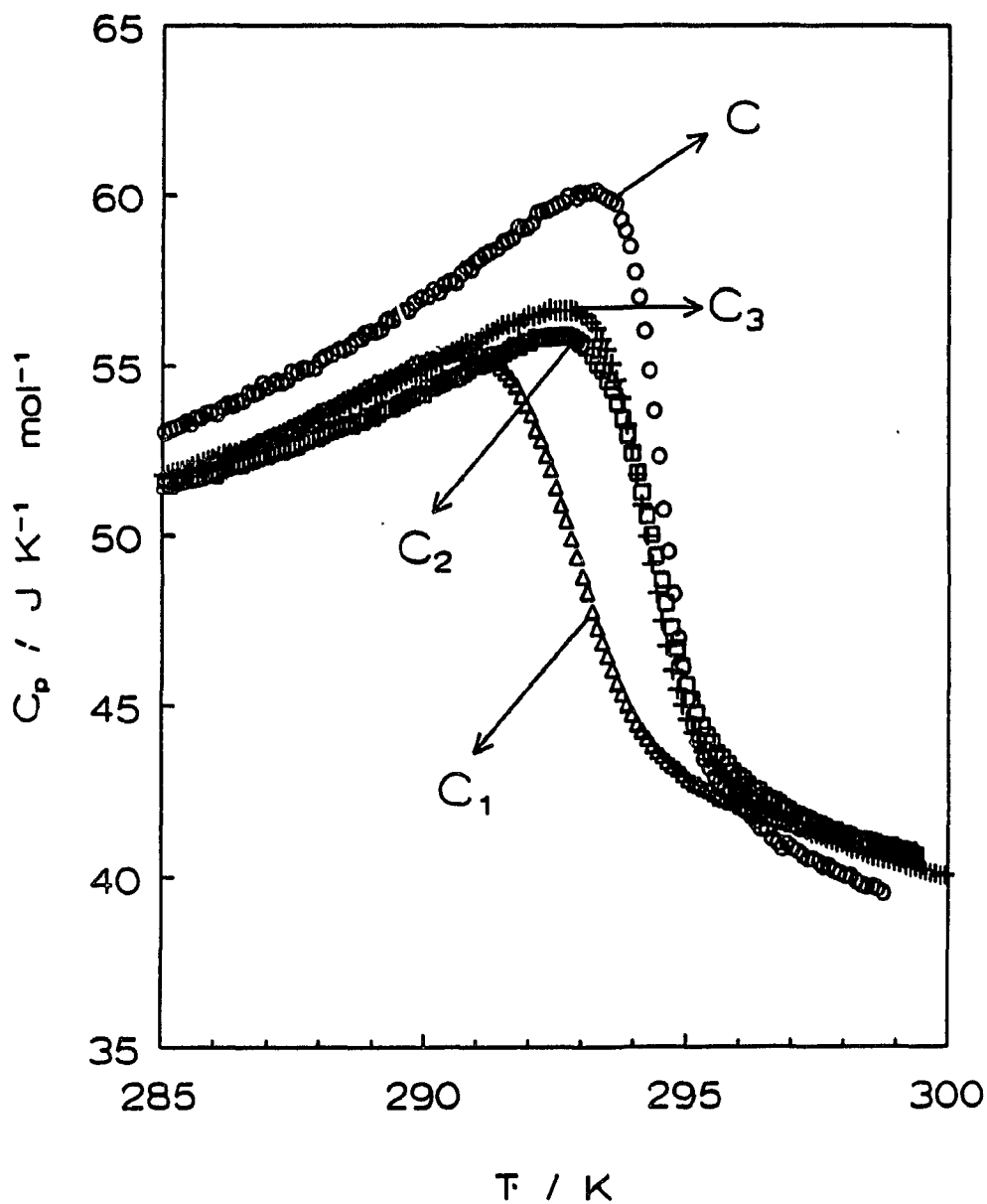


Fig 7.2. The heat capacity of Gd near its ferromagnetic phase transition for sample C; curve C - heat capacity of unannealed sample; curves C₁, C₂ and C₃ - heat capacity after consecutive heat treatments as described in the text.

During the first heat treatment, sample C was heated from room temperature to 850°C in a few minutes, annealed at 850°C for 1 hr and then cooled to room temperature over a few minutes. All these procedures took place in a continuous flow of high-purity helium (purity 99.999%). The Gd sample was wrapped in tantalum foil which acted as an oxygen trap.

This heat treatment resulted in a large smearing of the phase transition, considerable reduction of the peak value of the heat capacity, and in a decrease in the critical temperature as estimated by the peak temperature, by around 2.5 K, in comparison with the unannealed sample (Fig. 7.2, curve C1).

Because of the fast cooling, considerable strain was expected to be frozen-in, producing a large amount of disorder. Thus the results of the heat capacity measurement for this heat treatment suggest that strains may be one of the main reasons for observed smearing of the phase transition in Gd.

During the second heat treatment the sample was heated at 300 K/hr from room temperature to 850°C, held at 850°C for 2 hr and then cooled to room temperature over 24 hr, all in flowing high-purity He. The heat capacity curve after this second annealing is given by curve C2 in Fig. 7.2. This heat treatment almost restored the peak temperature observed for the unannealed sample but the peak value of the

heat capacity remained depressed.

In the third heat treatment the procedure from the second heat treatment was repeated but the sample was kept at 850°C for 8 hr. The heat capacity of the sample after the third annealing is given by curve C3 in Fig. 7.2. Curve C3 nearly overlaps with curve C2 and also with the heat capacity curve for sample A. However, curve C3 is steeper on the high-temperature side of the transition than curve C2 or the heat capacity curve for sample A.

The negligible improvement of the sharpness of the phase transition after the third heat treatment suggests that all the strains which were induced in the first heat treatment were removed, and the remaining smearing is probably caused by other factors; one of them could be sample contamination during one of the treatments.

It was realized that other variations of the annealing procedure were unlikely to further improve the sharpness of the phase transition. There may have been dissolved gases such as oxygen, nitrogen and hydrogen present in the initial crystal which could not be removed using the annealing procedures described here.¹⁴⁴ (One of the techniques used to purify rare earth metals with respect to oxygen and nitrogen is electrotransport purification in ultra-high vacuum.¹⁴⁴)

Gadolinium is known to absorb oxygen and hydrogen easily and it also oxidizes slowly when exposed to air.¹⁴⁴

The crystal from which samples A, B and C were cut had been exposed to air for long periods of time. This prolonged exposure to air may have a significant effect on the sample quality. For example Stetter et al.¹³¹ measured the magnetic susceptibility of Gd films and found that exposing a Gd film to air reduced the peak in the susceptibility by a factor of 4. Williams et al.¹⁴⁵ observed that exposure to air of a polycrystalline sample of Gd contributed to the broadening of the heat capacity curve at the critical temperature.

In view of concerns about the quality of samples A, B and C it was decided to obtain a high quality freshly grown sample.

7.2.c Measurements in AC mode on sample D

Sample D was grown at the Ames Laboratory, Energy and Mineral Resources Institute, by recrystallization (grain-growth method) from a high-purity stock material produced by a metallothermic method.¹⁴⁴ The sample D purity was 99.89 at% (99.99 mass%). (Chemical analysis for sample D is given in Appendix B.) The crystal from which sample D was made was grown to specified lateral dimensions and thickness of the order of 1 mm. This crystal was cut with a diamond saw into two pieces, each of thickness of the order of a fraction of a mm. The piece which had been glued to the backing during the cutting was electropolished and used for the measurements reported here as sample D (dimensions $7.4 \times 4.2 \times 0.22$ mm³; Gd mass: 0.0503 g). The sample residual resistance ratio was not measured in order to avoid any damage to the sample surface and also to avoid any effects due to thermal cycling of the sample. However, a Gd sample prepared in the same way and by the same laboratory was reported to have RR of the order of 200.¹²³

The measured heat capacity of sample D is shown in Figs. 7.3 and 7.4. The data points shown in Fig 7.3 and in Fig. 7.4 were collected every 50 mK and every 20 mK, respectively (temperature drift rate ca. 12 mK/min).

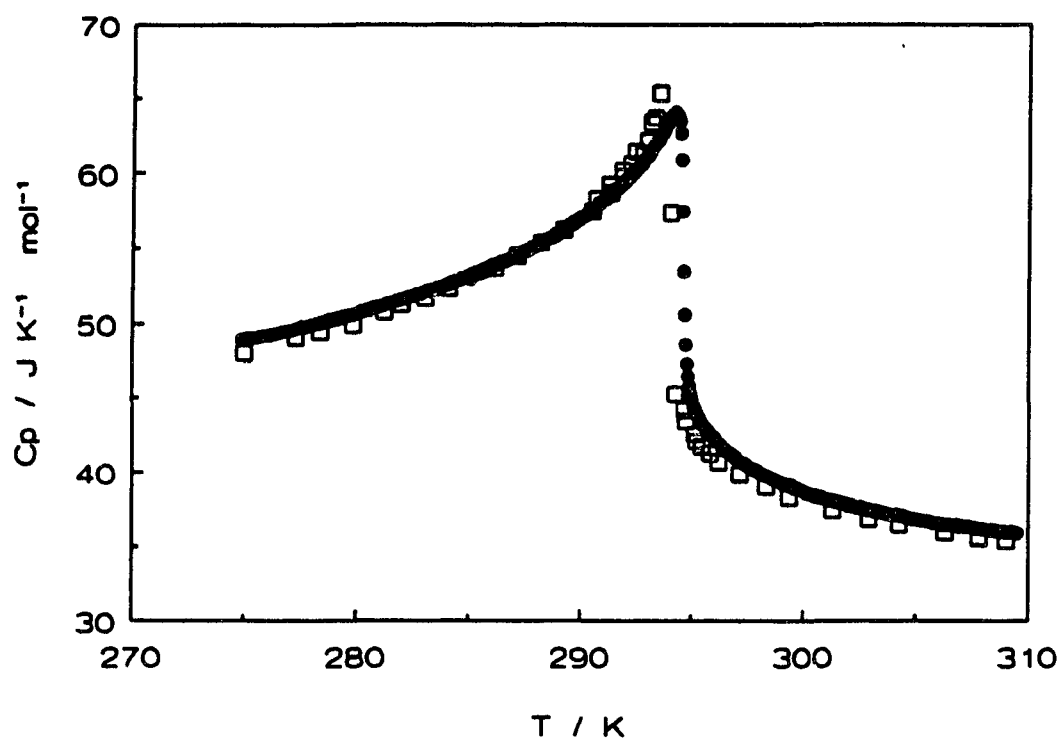


Fig. 7.3. The heat capacity of Gd near its ferromagnetic phase transition for sample D; squares denote the heat capacity data of Lanchester *et al.* (Ref. 122).

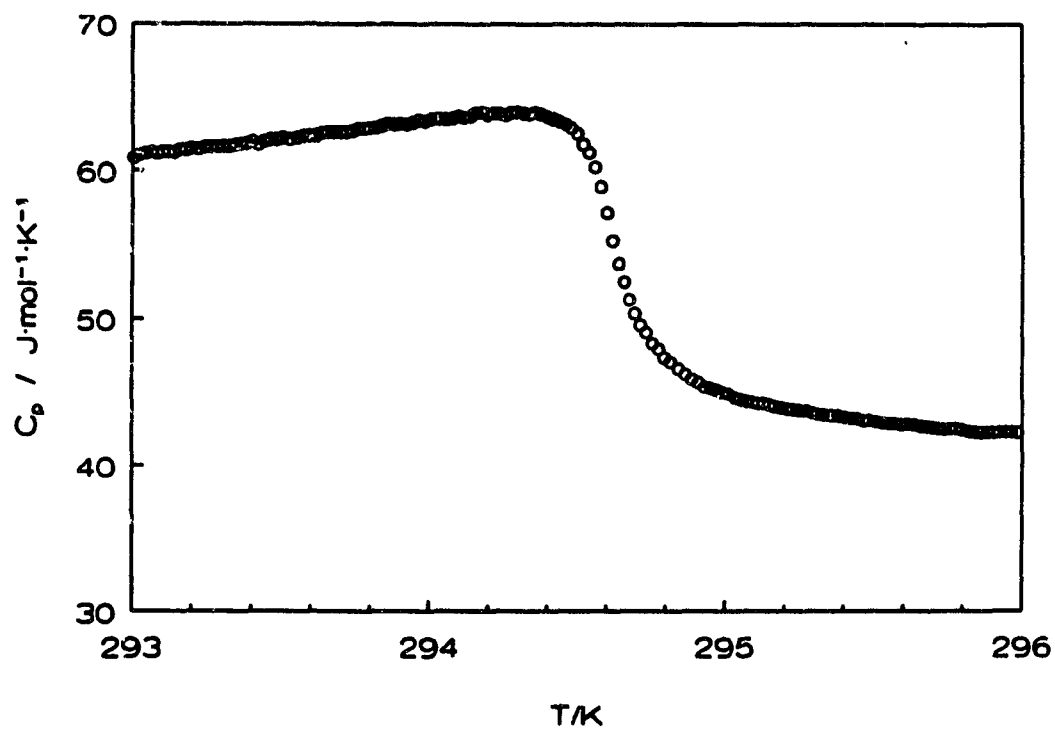


Fig. 7.4 The heat capacity of Gd in the proximity of the critical temperature (data for sample D).

In Fig. 7.5 the results for sample D are plotted together with the results for samples A, B and C. As it can be seen in Fig. 7.5 sample D exhibits the sharpest phase transition with the largest peak value of the heat capacity and the highest peak temperature of all the samples investigated in this work. The peak value of the heat capacity for sample D is around $64 \text{ J mol}^{-1} \text{ K}^{-1}$ in agreement with the peak value of around $65 \text{ J mol}^{-1} \text{ K}^{-1}$ reported by Lanchester et al.¹²² for a single crystal of Gd of comparable quality. The rounding of the phase transition is around 0.2 K as estimated from Fig. 7.4, which also compares well with the rounding reported in other high-resolution heat capacity measurements on Gd (Sec. 7.2.a).

In order to determine how the temperature drift rate affects the shape of the heat capacity curve near T_c a series of measurements was carried out with temperature drift rates in the range from 3 mK/min to 72 mK/min . The results were not affected by these drift rate changes (see Figs. 7.4 and 7.6). The data points in Fig. 7.6 were collected every 50 mK and the temperature was increased at a rate 72 mK/min . At this temperature drift rate it was more difficult to increase the temperature linearly as a function of time which probably explains a slightly larger scatter in the data. However the data from Figs. 7.4 and 7.6 are almost exactly superimposable, indicating that there is no long relaxation time effects (Sec. 3.8).

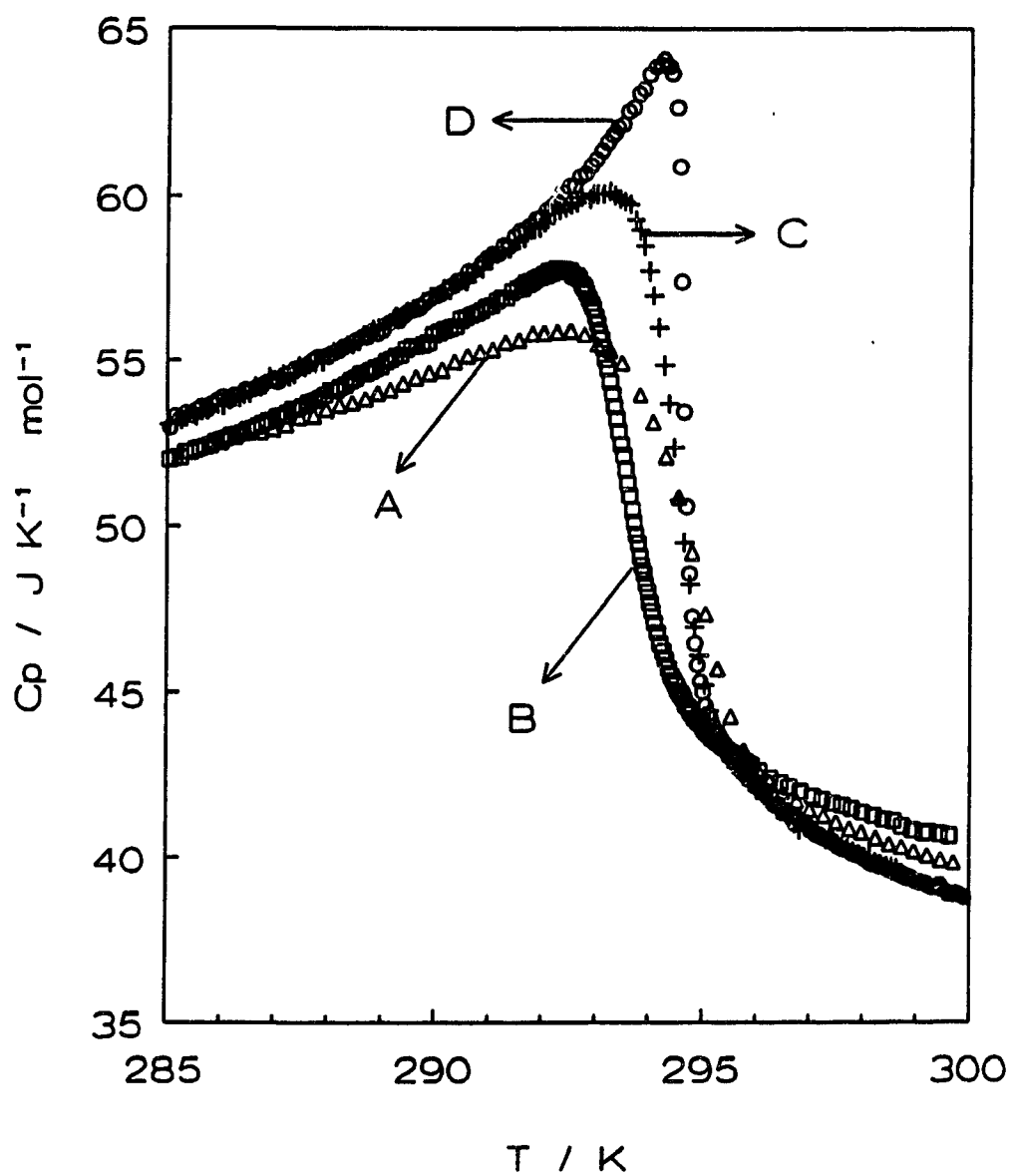


Fig. 7.5 The heat capacity of Gd near the critical temperature for samples A, B, C and D.

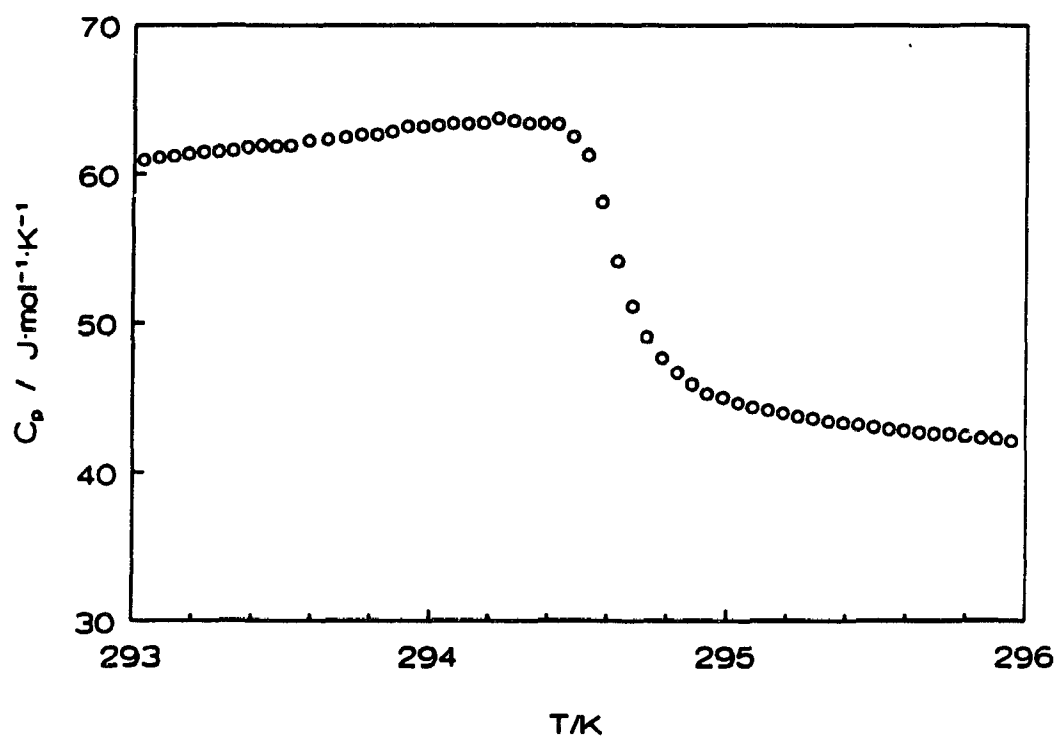


Fig. 7.6. The heat capacity of Gd sample D in the proximity of the critical temperature for a high temperature drift rate (72 mK/min).

The difference between the heat capacity at constant pressure and constant volume, ΔC_{p-v} , for a hexagonal crystal is quadratic in the diagonal components of the thermal expansion tensor (Sec. 4.1) and can be quite large if these components become divergent close to T_c . In Gd the magnitudes of α_a and α_c change by 100% in the temperature range from 280 K to the critical temperature¹²³. The elastic constant c_{33} has a small anomaly around T_c (small peak with height around 2% of the background value).^{146,147}

Using the literature values of the elastic constants of Gd^{147,146} and the power law representation of temperature dependence of α_a and α_c given by Dolejsi et al.¹²³, ΔC_{p-v} was calculated from Eq. (4.8) for Gd in the temperature range from 285 to 300 K; the results are shown in Fig. 7.7. The average values of the elastic constants were taken over the short temperature range of the calculations. The critical temperature was assumed to lie within the rounded portion of the heat capacity curve for sample D ($T_c=294.5$ K in Fig. 7.7). As it can be seen in Fig. 7.7 the difference between the heat capacity at constant pressure and at constant volume, ΔC_{p-v} , becomes important close to T_c , as this is the temperature range in which the thermal expansivities diverge rapidly. ΔC_{p-v} accounts for around 5% of the total heat capacity in the proximity of T_c for $T < T_c$.

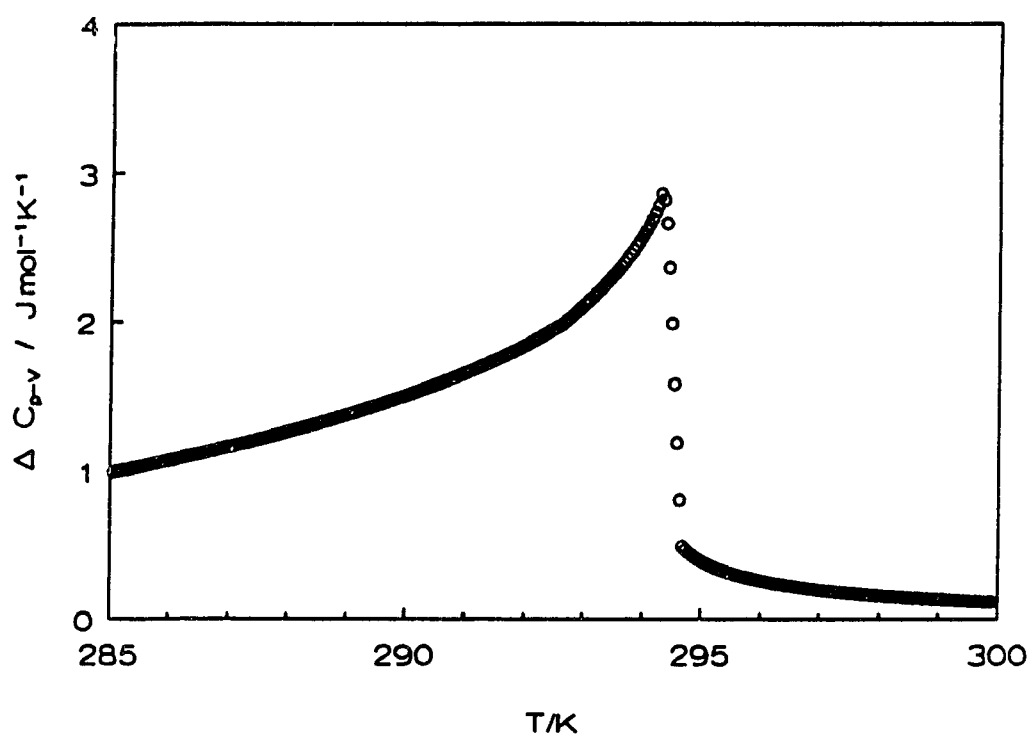


Fig. 7.7 The difference between the heat capacity of Gd at constant pressure and constant volume near the Curie temperature, calculated as described in the text.

Above T_c and a few K below T_c , $\Delta C_{p,v}$ is less than $1 \text{ J mol}^{-1} \text{ K}^{-1}$ and can be neglected. The heat capacity of Gd at constant volume (calculated from measured C_p and calculated $\Delta C_{p,v}$) near T_c for sample D is shown in Fig. 7.8.

The molar volume of Gd as a function of temperature near T_c also was calculated from the thermal expansion data.¹²³ It decreases by around 0.02% in the temperature range from 285 K to 300 K so that in the temperature range of the critical point analysis, i.e., within a few K of T_c , the calculated heat capacity at constant and *temperature-dependent* volume approximates well the heat capacity at constant and *fixed* volume required by the theory.

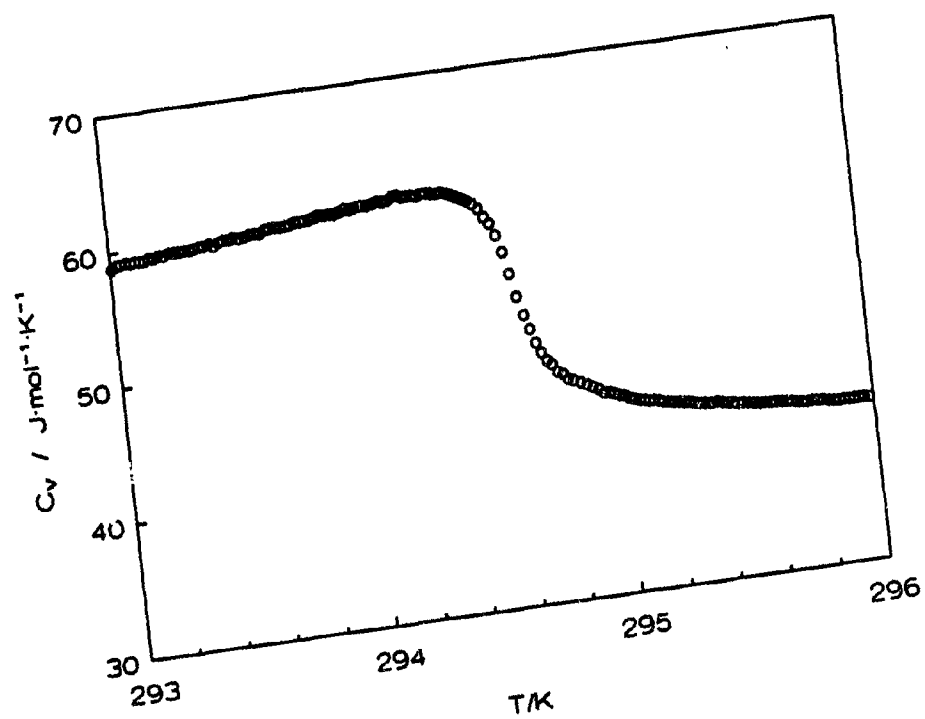


Fig. 7.8. Heat capacity of Gd at constant volume near the Curie temperature.

7.3 Measurement in the relaxation mode

The heat capacity data obtained by AC calorimetry were normalized to the absolute heat capacity data collected in the relaxation mode. In this mode the heat capacity of the sample was measured below the phase transition in the temperature range from 284 to 287 K and at 277 K, above the phase transition at 298, 299 K and at 307 K, and then again below the phase transition for sample B to check for thermal hysteresis effects.

The measurement procedure was as follows. The temperature of the heat sink was stabilized and the temperature difference between the sample and the heat sink, ΔT , was measured as a function of the sample heating power, P . The maximum temperature difference, $\Delta T_{\max}$, was around 300 mK. The thermal conductance was calculated from the plot of P as a function of ΔT . In the next step the sample temperature was raised to $\Delta T_{\max}$, then the heater was turned off, and the sample temperature was recorded as a function of time (at a rate of around 10 temperature readings per second). The last step was repeated several times. The thermal relaxation time was found by a least-squares fit to the temperature decay data with an exponential function (see Eq. (2.26)), and the sample heat capacity at $(T + \Delta T_{\max}/2)$

was calculated from Eq. (2.27). The precision of the measurement, as estimated from the standard deviations of the fits, was around 2%.

The heat capacity values used to calibrated the data obtained in the AC mode are listed in Table 7.1. The data in the table are corrected for the heat capacity of the addenda using the literature data for the heat capacity of silver-loaded epoxy¹⁴⁸ and copper¹⁴⁹. The correction terms contributed around 10% to the total heat capacity of the sample assembly for samples A and B and only a few percent for samples C and D. The data were not corrected for the heat capacities of the GE varnish, bismuth layer and the thinistor since their combined mass was less than 1% of the total sample assembly.

Table 7.1 The experimental heat capacities of Gd obtained by the relaxation method, in order of determination

T / K	C_p / (J K ⁻¹ mol ⁻¹)
Sample B	
284.1	51.45
285.1	51.59
286.1	51.86
297.1	39.95
298.1	39.27
299.1	39.13
285.2	52.29
286.1	52.00
286.2	52.49
Sample C	
285.0	52.14
298.0	40.70

continued ...

Table 7.1. continued ...

T / K	C_p / (J K ⁻¹ mol ⁻¹)
Sample C1	
285.0	51.10
298.0	41.71
Sample C2	
285.0	51.43
298.0	41.31
Sample C3	
285.0	51.69
298.0	41.09
Sample D	
277.0	50.51
307.0	35.68

7.4 Discussion

The only published data for Gd for which tabulated values are available are those of Griffel et al.¹³⁷. However these data are for a single crystal of Gd of lower quality than the samples used in this study. The heat capacity data of Lanchester et al.¹²² (the heat capacity values were taken from Fig. 1 of their paper^a) for a single crystal of Gd of quality comparable to the present samples are plotted in Fig. 7.3 for comparison with the present data. The scatter of the data points obtained in the present study, as estimated from the plot, is around 0.2%.

Based on the literature data, the resolution of these data is one of the highest reported to date for AC calorimetry and other calorimetric methods. This also is the first report of high-resolution data on heat capacity of Gd, measured by the AC method and calibrated with absolute heat capacity measurements made on the same sample. Lewis¹²¹ reported his results in relative units and Simons²³ calibrated his data using the data of Griffel et al.¹³⁷ near 0°C and shifting the temperature scales to account for the difference in the critical temperatures. Wantenaar et al.¹⁴⁰ made AC heat capacity measurements on relatively massive,

^a The data points were digitized from this figure, courtesy of Dr. Garland from Massachusetts Institute of Technology.

cylindrical samples of Gd (approximate mass 3 g) and they calibrated their data with the use of Eq.(2.3). However this procedure led to differences in heat capacity values for different samples as large as 20% far away from the phase transition (at temperatures of around 260 and 320 K). Wantenaar et al.¹⁴⁰ could not explain this scatter, which could be caused by a non-uniform heating of the samples.

There is good overall agreement between the data of this work and the data of Lanchester et al.¹²². However, the temperature of the peak value of the heat capacity for the present data is around 0.6 K higher than the corresponding temperature for their data. Since in the data of Lanchester et al.¹²² there is a temperature step of around 0.5 K between the peak value of the heat capacity and the next data point at increased temperature it is possible that a higher resolution in their measurements would shift the maximum value of heat capacity to higher temperature. Higher resolution could also show rounding in their heat capacity curve.

The differences between the present data and other data (see references in Sec. 5.4) are likely due to differences in sample quality. This view is supported by results of Robinson et al.¹³⁹ who investigated the influence of controlled amounts of carbon impurity on the shape of the heat capacity of Gd near the Curie point. Changing the amount of carbon added from 0 to 1% they found that the heat

capacity peak was decreased in magnitude and moved towards lower temperatures as the impurity concentration was increased. Wantenaar et al.¹⁴⁰ also obtained the highest critical temperature, as estimated from the susceptibility experiment, for the annealed sample of Gd in their studies of the magnetic susceptibility of Gd. The Gd sample that was annealed and then strained showed a slightly depressed critical temperature.

Williams et al.¹⁴⁵ investigated the effects of strains on the heat capacity of polycrystalline samples of Gd near the Curie temperature. They measured the heat capacity of a finely grained gadolinium sample (≈ 1 mm grains as observed by etching the surface), of a larger grained gadolinium sample obtained by zone melting recrystallization of the finely grained sample and of an annealed large-grained sample. The sharpest phase transition and the highest peak value of the heat capacity with the highest peak temperature was obtained for the large-grained and annealed sample. The transition was depressed for the large grained unannealed sample and significantly depressed and shifted to lower temperatures for the finely grained sample. Since all of the samples were of the same initial purity and zone melting does not result in significant purification of the sample (redistribution of impurities is the more usual result) Williams et al.¹⁴⁵ concluded that the broadening of the phase transition they observed is caused by different degrees of

strains in the samples.

The conclusion of Williams et al.¹⁴⁵ is confirmed by the results of the heat capacity measurements presented in this work. The heat capacity measurements made on single-crystal samples of Gd which were variously strained due to different preparation procedures showed that the annealing led to a significant reduction in the broadening of the phase transition. While the strains cannot account for all the observed smearing they were responsible for gross large-scale smearing and large shifts in the critical temperature.

In conclusion the main features of heat capacity curves in the vicinity of the Curie point in Gd as reported by different authors and as observed in the present study are their differences in Curie temperatures, the degree of rounding at T_c , the relative differences in heat capacities for the ferromagnetic to paramagnetic regions, and the peak value of the heat capacity. Those features depend on sample quality, i.e. on the degree of impurities in the sample, including gases dissolved in the sample such as oxygen, nitrogen and hydrogen, the distribution of dislocations or other static defects and on its annealed or non-annealed state.^{122,139,145}

Chapter 8. Analysis of the critical behaviour of the heat capacity of Gd

8.1. Introduction

The theoretical predictions about critical phenomena pertain to the asymptotic behaviour of C_v approaching T_c . Because experimental results are obtained at some non-zero values of the reduced temperature, it is not trivial to extract from them estimates of parameters which can be compared with the theory. Only fits based on a large number of data points collected close to the critical temperature can give reliable estimates of these parameters.

The analysis presented here focuses on the heat capacity measurement of sample D of Gd, as this sample exhibited the sharpest transition and gave the highest value of the peak heat capacity.

The measured heat capacity at constant pressure, C_p , and the calculated heat capacity at constant volume, C_v , for sample D were analyzed in terms of the fitting functions

$$C_{p,v} = \frac{A}{\alpha} |t|^{-\alpha+B+Et} , \quad (8.1a)$$

and

$$C_{p,v} = A |t|^{-\alpha(1+D|t|^x)+B+Et} , \quad (8.1b)$$

for $T > T_c$ and the same functions with primed coefficients for $T < T_c$. The term $(A/\alpha)|t|^{-\alpha}$ represents the leading contribution to the singularity of C_p or C_v . If one assumes that $x > 0$ ($x = x' = 0.5$ in the present analysis - see Sec. 3.8) then the term $D|t|^x$ vanishes at T_c and represents a singular contribution to the heat capacity which is of higher order than the leading singularity. It is known both from experiments⁸⁹ and theory^{150,151} that such a term generally must be considered in the data analysis (see also Sec. 3.8).

The data in the proximity of T_c also were fitted to the function

$$C_{H-0} = A \left| \ln \left| \frac{t}{t_0} \right| \right|^{\frac{1}{3}} + B, \quad (8.2)$$

for $T > T_c$ and the same function with primed coefficients for $T < T_c$. The values of the ratios $A/A' = 1/4$ and $t_0/t_0' = 2$ were constrained to those predicted by the theory.^{65,70}

It is difficult to interpret data extremely near T_c in terms of Eqs. (8.1) and (8.2) because of rounding in the heat capacity curve in that region. Certainly, the data affected by rounding should not be fit to Eq. (8.1) or Eq. (8.2) without some modifications which depend on possible causes of rounding. These data were excluded from the analysis in terms of the fitting functions given in this section. The factors which may contribute to the rounding were discussed in Secs. 3.8 and 4.2.b and will be summarized

later in this chapter.

Finally, fits to the heat capacity data were considered on the basis of Eq. (3.45) which describes a model system with random quenched impurities at its critical dimension in the proximity of the Curie temperature. However, the temperature range in which this random critical behaviour may be observed is not in the reduced temperature range accessible in the present experiment. In fact, the crossover from non-random to random behaviour is extremely slow and covers many decades in reduced temperature (Liebmann et al.⁸³ estimated that this crossover may take around ten decades in reduced temperature) so the random uniaxial critical behaviour may be unobservable in Gd. Moreover, the phase transition for the random uniaxial ferromagnet is sharp and second-order so Eq. (3.45) is not suitable to describe the heat capacity data which exhibit apparent smearing on a reduced temperature scale 10^{-4} .

Various methods have been employed to fit heat capacity data to non-linear functions like Eq. (8.1). For example, a popular method has been to subtract a regular lattice contribution to the total heat capacity and to do a linear fit to the "magnetic" part of the heat capacity (one may consider plotting the magnetic part as a function of $\ln|t|$). While it is quite a plausible approach it may lead to difficulties because it is not clear that subtraction of an estimated regular background eliminates all regular

contributions to the heat capacity; some may be associated with the transition. Secondly, the uncertainty in the subtracted regular term may have a large effect on the fitted values of the remaining parameters.

The method employed here allows simultaneous fitting of both linear and non-linear parts. The computer program used performs a non-linear least-squares fit to data. The program was initially developed by Malmström and Geldart¹⁵² and subsequently extended. It has been used previously to analyze resistivity¹¹⁹ and magnetic susceptibility data¹³⁰ on Gd and heat capacity data on Ni.¹⁵²

8.2 The fitting procedure

It was assumed initially that $D=D'=0$. In this case Eq. (8.1) reduces to a pure power law. The seven parameters (A , A' , $B=B'$, $T_c=T_c'$, α , α' , and $E=E'$) were least-square adjusted. (The condition $E=E'$ was imposed to assure that the regular contribution to the total heat capacity is indeed regular at T_c .) The data were analyzed in the temperature range $t_{\min} < |t| < t_{\max}$ where $t_{\min}$ and $t_{\max}$ are defined with respect to the initial choice for T_c .

In the first step of the analysis A , A' , $B=B'$, and $\alpha=\alpha'$, were fitted for some fixed value of T_c . The T_c selected was in the temperature range in which data affected by rounding were excluded. If the fitting routine converged, the next step was to fit the critical temperature. If the critical temperature could be fitted, the statistical parameters of the fit (the estimated standard deviation of the fit, the estimated 95% confidence intervals in the fitted parameters, the plot of residues [the difference between the measured C and the fit to the data] and the histogram of the residues) were printed out and analyzed. At the beginning almost all the data were kept in the fitted data set, and the plot of residues showed the presence of systematic structures near T_c in the region of the heat capacity curve affected by rounding. This indicated the poor quality of the fit and unreliable

representation of the data. Removing the data points affected by rounding resulted in a significant improvement of the fit quality.

Alternatively, the best fit could be located by least-squares fitting A , A' , $B=B'$, $E=E'$ for T_c and α stepped over a range of values; this best fit was then compared with the fit obtained by least-squares fitting of all the parameters in order to select the fit giving the smallest standard deviations and the best plot of residues. In practice these two procedures gave the same result, serving as a consistency check.

In the next step a range of fit analysis was performed for different values of $t_{\max}$ and $t_{\min}$. In this analysis the data were fitted for decreasing values of $t_{\max}$. This was done in order to find the temperature range in which α was not sensitive to further decrease in $t_{\max}$. In a similar way $t_{\min}$ was increased to see if this was going to bring about a further improvement in the fit quality. While the reason for varying $t_{\max}$ is to find the beginning of the asymptotic critical region, one generally insists that $t_{\min}$ be kept as close to T_c as possible. However, in the case of Gd the presence of crossovers justifies seeking also the temperature range in which a given fitting function best represents the data.

After finding the best $t_{\min}$ and $t_{\max}$ two predictions of the renormalization group theory were tested. Firstly, α

was permitted to be different from α' . In each case, the standard errors for α and α' overlapped and thus permitted $\alpha=\alpha'$, consistent with the scaling prediction. Secondly the constraint $B=B'$ which is predicted by the RG theory⁹⁰ was tested. It was found that $B=B'$ within experimental error, i.e. the transition is continuous.

The data for all the samples also were analyzed by fitting to Eq. (8.1) with D and D' least-squares adjusted. The constraints $\alpha=\alpha'$, $E=E'$, $B=B'$ were retained and $x=x'$ was fixed at 0.5, consistent with the theoretical predictions and other experiments.¹⁵³

Finally, the data for sample D very close to T_c were fitted to Eq. (8.2). The parameters in Eq. (8.2) were fitted for different fixed values of T_c . The constraint on each parameter were systematically relaxed to test whether this was going to improve the fit. This fitting was performed for the combined data from the both sides of the transition, and also for the high-temperature side of the transition separately.

8.3 Results for the fitted parameters

The parameters obtained by fitting the heat capacity data for sample D to Eq. (8.1) are given in Table 8.1.

The critical point analysis for sample D started by finding the best pure power law fit and the correction to scaling fit to the C_p data. It was found that generally a reasonable power law fit was possible over a rather wide temperature range (the range overlapped with the temperature range of the correction to scaling fit given in Table 8.1). However a subsequent range-of-fit analysis showed that the quality of the fit could be improved considerably by decreasing $t_{\max}$. It was also found that the fit could be further improved by dropping a number of points close to T_c , i.e. by increasing $t_{\min}$, although these points did not appear affected by rounding. Thus, the best power law fit was obtained over a rather restricted reduced temperature range which however lay in the critical region. Both T_c and α were least-squares fitted in this analysis.

Inclusion of the confluent correction to scaling term in the fit brought about a decrease in the standard deviation of the fit and also permitted a good fit in a wider temperature range (over one decade in the reduced temperature).

Table 8.1 Results of fitting for the data for sample D.

The estimated errors are 95% confidence intervals obtained from the fits assuming independent and random errors in the heat capacity measured.

	PL - C_p^a	CRSC - C_p^b	PL - C_v^c	CRSCI- C_v^d	CRSCII- C_v^e
T_c	294.25 ± 0.05	294.5 ± 0.05	294.2 ± 0.1	294.5 ± 0.1	294.5 ± 0.1
α	-0.208 ± 0.014	-0.026 ± 0.002	-0.187 ± 0.023	-0.020 ± 0.002	-0.020 ± 0.002
A'	1.57 ± 0.34	-43.74 ± 7.76	2.07 ± 0.28	30.2 ± 20.5	-37.39 ± 9.95
A	16.1 ± 2.1	-67.05 ± 7.72	11.7 ± 4.8	48.8 ± 20.1	-56.40 ± 9.89
A/A'	10.3 ± 2.6	1.52 ± 0.32	5.65 ± 2.44	1.62 ± 1.28	1.51 ± 0.48
D'	-	1.15 ± 0.36	-	1.17 ± 0.49	1.00 ± 0.36
D	-	0.58 ± 0.15	-	1.36 ± 0.68	0.98 ± 0.27
D/D'	-	0.51 ± 0.21	-	1.17 ± 0.77	0.98 ± 0.46
E	508 ± 54	63 ± 30	295 ± 50	148 ± 85	105 ± 35
B	65.8 ± 0.7	102 ± 6	64.3 ± 2.7	89 ± 17	95 ± 9
σ_{FIT}	0.0604 ± 0.0091	0.0545 ± 0.0060	0.0641 ± 0.0089	0.0580 ± 0.0081	0.0574 ± 0.0067

^a PL - C_p : power law fit to C_p data.

Range of the fit: $t=5.9 \times 10^{-3}$ to 0.5×10^{-3} , $T < T_c$

$t=3 \times 10^{-3}$ to 6.9×10^{-3} , $T > T_c$.

75 data points in the fit.

Table 8.1 continued ...

^b **CRSC** - C_p : fit with the correction to scaling term to C_p data. Range of the fit: $t=15.3 \times 10^{-3}$ to 2.6×10^{-3} , $T < T_c$

$t=2.0 \times 10^{-3}$ to 11.9×10^{-3} , $T > T_c$.

130 data points in the fit.

^c **PL** - C_v : power law fit to C_v data.

Range of the fit: $t=9 \times 10^{-3}$ to 0.7×10^{-3} , $T < T_c$

$t=3 \times 10^{-3}$ to 8×10^{-3} , $T > T_c$.

79 data points in the fit.

^d **CRSCI** - C_v : correction to scaling fit to C_v data over the temperature range of the power law fit.

^e **CRSCII** - C_v : fit with the correction to scaling term to C_v data. Range of the fit: $t=12 \times 10^{-3}$ to 1.7×10^{-3} , $T < T_c$

$t=1.7 \times 10^{-3}$ to 13×10^{-3} , $T > T_c$.

116 data points in the fit.

The exponent α was least-squares fitted but the critical temperature could not be least-squares fitted and was determined by fitting α for a range of T_c values.

It was reported in Sec. (7.2) that the difference between C_p and C_v for Gd is significant on the low-temperature side of the transition close to T_c . Therefore the C_v data for sample D were fitted separately to Eq. (8.1); the results are given in Table 8.1.

Finally the C_v data for sample D in the proximity of T_c ($t < 10^{-4}$) were fitted to Eq. (8.2). Both sides of the transition were used in the fit and the constraints $A/A' = 1/4$ and $t_0/t_0' = 2$ were initially imposed. When a good fit could not be obtained these constraints were either relaxed or the ratios changed to other values. However a satisfactory fit was not obtained.

Taking into account the fact that the low-temperature side of the transition could be affected by an unknown temperature dependence of the demagnetization term which may be important close and below T_c , it was decided to fit the high-temperature side of the transition separately to Eq. (8.1) and Eq. (8.2).

A good logarithmic fit was obtained over the 10^{-4} decade in the reduced temperature ($3.2 \times 10^{-4} < t < 1.7 \times 10^{-3}$) for $T_c = 294.6$ K (the estimated standard deviation of the fit $\sigma_{FIT} = 0.0855$). The fit was based on twenty data points and the other parameters of the fit were: $B = -11.5 \pm 1.6$, $A = 29.8$

± 0.8 and $t_0=1$ was kept constant. (Other values of t_0 were tested and σ_{FIT} was minimized for $t_0=1$).

The power law fit in the same range gave the least-squares adjusted $\alpha=0.98 \pm 0.07$, which is not physically realistic. This is considered in more detail in Sec. 8.4.

Fitting the high temperature data to the power law over wider temperature ranges resulted in good fits but they were extremely dependent on the range of temperature. On excluding data points which were around 10^{-2} on the reduced temperature scale the exponent α changed its value from $\alpha=-0.288$ in the reduced temperature range $2 \times 10^{-3} < t < 1.8 \times 10^{-2}$ to $\alpha=0.774$ in the range $1.3 \times 10^{-3} < t < 8.8 \times 10^{-3}$ ($T_c=294.5$ K for these fits). The fitting routine failed to least-squares adjust the exponent α when the correction to scaling term was included into the fit. When different fixed values of the exponent α were tried in this fit the fitting routine also failed to converge. In some cases the values of the fitted parameters oscillated around some average values under iteration of the fitting routine.

In order to obtain a good power law fit to the heat capacity data for the remaining samples a large number of points affected by rounding had to be excluded in each case from the fit. This resulted in removing almost all data points below $t=5 \times 10^{-3}$ from the analysis. The number of data points left in the fits was around 100 for samples A, C, C1, C2, C3 and around 300 for sample B. The power law

parameters for samples A, B, C, C1, C2, C3, are given in Table 8.2.

When a correction to scaling term was included into the fit a satisfactory fit could not be obtained. The fitting procedure always failed to converge on α and/or T_c . It was possible to least-squares adjust linear parameters for fixed values of α and T_c but the errors in D and D' were of the order or larger than D and D' themselves. In most cases the fitted values of either A or A' were almost zero with the very large value of the corresponding parameter D or D'.

Table 8.2. Power law parameters of the fits to the data for samples A, B, C, C1, C2, C3.

σ_{FIT} is in the range from 0.03 to 0.06.

Sam- ple	T_c (K)	Range of fit t_{max} to t_{min} , $T < T_c$ t_{min} to t_{max} , $T > T_c$	α	B	A/A'
A	294.3 ± 0.3	3.2×10^{-2} to 10^{-2} 5.1×10^{-3} to 1.5×10^{-2}	-0.068 ± 0.041	79 ± 18	1.66 ± 0.53
B	293.86 ± 0.02	2.5×10^{-2} to 5.8×10^{-3} 1.4×10^{-3} to 6.6×10^{-3}	-0.156 ± 0.007	62 ± 1	6.97 ± 1.44
C	293.8 ± 0.1	3.2×10^{-2} to 7.7×10^{-3} 5×10^{-3} to 1.7×10^{-2}	-0.100 ± 0.016	83 ± 6	1.79 ± 0.22
C1	293.06 ± 0.05	3.4×10^{-2} to 1.1×10^{-2} 3×10^{-3} to 1.6×10^{-2}	-0.098 ± 0.015	73 ± 4	1.97 ± 0.27
C2	294.47 ± 0.06	2.8×10^{-2} to 9.7×10^{-3} 2.7×10^{-3} to 1.7×10^{-2}	-0.065 ± 0.020	84 ± 11	1.57 ± 0.25
C3	293.7 ± 0.1	2.8×10^{-2} to 7×10^{-3} 5×10^{-3} to 2×10^{-2}	-0.144 ± 0.016	67 ± 2	2.54 ± 0.36

8.4. Discussion

The best representation of both C_p and C_v data was obtained in terms of the correction to scaling fit. This fit gave the smallest standard deviation and represented the data over the widest temperature range (Fig. 8.1). The pure power law fit to C_p and C_v data gave a standard deviation similar to that for the fits with the correction to scaling term but it represented the data over narrower temperature range and it also gave unphysically large values of the ratio A/A' and of the regular term E .

The values of the fitted parameters for the fits with the correction to scaling term are in good agreement with the corresponding results obtained by Jayasuriya¹²⁴ also from a fit with a correction to scaling term. He obtained $\alpha = -0.03 \pm 0.02$ and the universal ratios $A/A' = 1.42 \pm 0.75$ and $D/D' = 0.71 \pm 0.56$, and also $B = 108 \pm 12$. Jayasuriya¹²⁴ and Lanchester et al.¹²² reported that a good pure power law fit to their data also was obtained when a discontinuity in the heat capacity at T_c was allowed ($B \neq B'$). The assumption that B can be different from B' corresponds to introducing one more free parameter into the fit. It appears that if such extra free parameters are needed to fit the data one should rather introduce the confluent singular correction term predicted by the renormalization group theory.

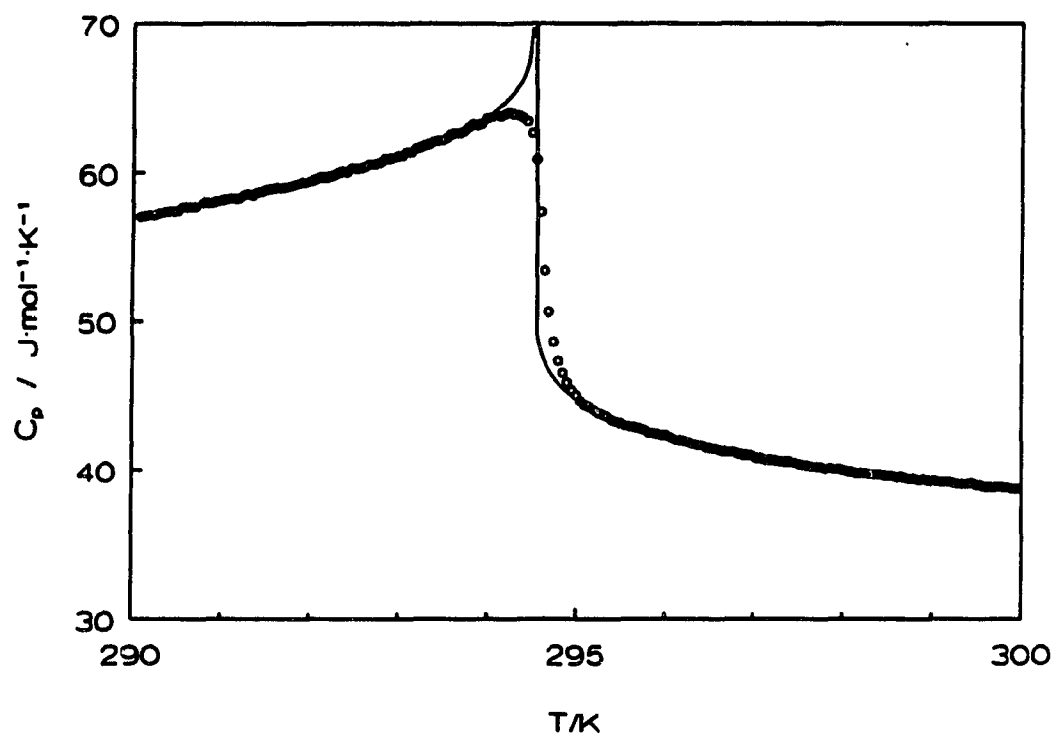


Fig. 8.1 Fit of Eq. (8.1) with the correction to scaling term (solid line) to the C_p data (open circles) for sample D.

The correction to scaling fit to the C_v data for sample D gave values of the parameters of the fit that were different from those for the same fit to the C_p data. The ratio A/A' did not change within the statistical error but the magnitude of the exponent α became smaller and the ratio D/D' increased. This suggests that the reduction of the experimental data collected at constant pressure to the heat capacity data at constant volume is an important consideration for Gd, and it may also be relevant in other materials.

The RG calculations^{53,64} give $(A/A')_H = 1.52 \pm 0.02$ in 3d for the Heisenberg universality class in the second-order ϵ -expansion. The ratio $(A/A')_{dp}$ for a system with both isotropic short range and dipolar interactions is known only to the zeroth order in ϵ : the ratio is $1.2 + O(\epsilon)$. $A/A'=1$ to the zeroth order for the Heisenberg (short-range) 3d system suggests that $(A/A')_{dp} > (A/A')_H$ although the difference is not expected to be large.⁶⁴

The ratio $D/D'=1.4$ for the Heisenberg system in 3d, as given by the field theoretical methods.⁵³

The ratios $A/A'=1.51 \pm 0.48$ and $D/D'=0.98 \pm 0.46$ obtained for the C_v data here are in reasonable agreement with the ratios for the Heisenberg system; if, in the temperature range of the fit, Gd is in the process of crossing over to dipolar isotropic behaviour from the Heisenberg behaviour (as suggested by other evidence -

Sec. 5.3) then these ratios are certainly plausible. However this agreement may be only accidental because the α value does not match and there exists a coupling between A values and α values.

The critical exponent $\alpha = -0.020 \pm 0.002$ as determined from the correction to scaling fit to the C_v data does not correspond within the statistical error to any of the model values of exponents calculated for various universality classes (see Table 3.2). Instead, in light of the theoretical and experimental evidence about the presence of a series of crossovers in the critical behaviour of Gd (Sec. 5.3) this exponent should be regarded as an effective exponent.

This view can be supported by noting that the scaling laws for effective exponents are correct to the zeroth order in the ϵ expansion¹⁵⁴ so that, for example, $\alpha_{\text{eff}} \approx 2 - 2\beta_{\text{eff}} - \gamma_{\text{eff}}$. This relation and the experimentally determined values of $\gamma \approx 1.22 \pm 0.02$ and $\beta \approx 0.399 \pm 0.016$ from Table 5.2 give $\alpha_{\text{eff}} \approx -0.02 \pm 0.03$, in good agreement with the experimental value obtained here. This value for α_{eff} is also consistent with experimental results for the temperature dependence of the susceptibility of Gd in the hard direction, χ_b , reported by Geldart et al.¹²⁰ χ_b^{-1} is expected to vary with t as $A+Bt^y$, $y=1-\alpha_{\text{eff}}$ and their fit to $\chi_b^{-1}(T)$ data yielded $y=1.01 \pm 0.03$.

It was concluded in Sec 4.2 that the sample demagnetization field may have an effect on the measured

heat capacity below and very close to T_c . In order to take that possibility into account the data on the high-temperature side of the transition were fitted separately to Eq. (8.1) and Eq. (8.2). As reported in the preceding section no conclusive fit of the high-temperature data to the power law or to the power law with the correction to scaling term could be obtained. The power law fit depended strongly on the temperature range of the fit; the fit with the correction to scaling term even failed to converge on the values of the linear parameters for a range of fixed values of α and T_c .

However it was possible to fit the high-temperature data to Eq. (8.2). A good fit was obtained in the temperature range from $t_{\min}=3.2 \times 10^{-4}$ to $t_{\max}=1.7 \times 10^{-3}$ ($T > T_c$). The range-of-fit analysis for the temperature intervals starting between $t_{\min}$ and $t_{\max}$ and extending above $t_{\max}$ showed that Eq. (8.2) gave a good representation of the data only very close to T_c . A power law fit performed in the temperature range of the logarithmic fit converged on $\alpha \approx 1$ thus indicating that the power law is not a good representation of the data in this temperature region.

Geldart et al.¹²⁰ estimated that the crossover reduced temperature to the asymptotic uniaxial critical regime in Gd is 1.52×10^{-3} ($T - T_c \approx 0.45$ K) which is in excellent agreement with the $t_{\max}$ found for the logarithmic fit in the present work. These results give evidence that the critical

behaviour of Gd very close to T_c is that of the uniaxial system with dipolar interactions. Since it was not possible to describe the data very near T_c on both sides of the transition, the crucial theoretical amplitude ratio $A/A'=1/4$ could not be tested.

Certainly one of the reasons for the failure of the logarithmic fit to both sides of the phase transition is the rounding in the heat capacity curve over much of the temperature range where uniaxial dipolar behaviour is expected. ΔT_{anis} is very small relative to T_c for Gd and this limits the reduced temperature range for an analysis with the logarithmic formula. In contrast, for LiTbF_4 where $T_c \approx 2$ K, essentially all data in the critical region are in the uniaxial regime. Therefore, after removing the data in the smeared region, there is still sufficient data in the asymptotic critical range for full analysis.⁷

It is known from experiments on Gd^{129,139,145} and other magnetic systems^{14,72} that sample imperfections (impurities and dislocations) can lead to a large broadening of the phase transition and a decrease in the critical temperature. Sample D was a very pure sample and it compared very well with the other Gd samples measured. It is difficult to say, however, how important are the dislocations (and hence strains) still present in the sample. The results of this work (Sec. 7.4) showed how sensitive the phase transition in Gd is to the presence of strains. It is possible that in

spite of its high purity and the care in preparation the rounding observed for sample D is caused by dislocations still present in the sample. Dislocations as a factor disturbing the ideal crystalline lattice and limiting the growth of correlation length may be an underestimated cause of the rounding in the heat capacity curve observed in so many experiments.

Another factor limiting the sharpness of the phase transition in Gd and changing the shape of the heat capacity curve below T_c may be the demagnetization effects and formation of magnetic domains. As noticed by Kadanoff³⁴ the domain walls may serve to break up the long-range correlations so essential to critical behaviour. He suggested that if idealized theories (like the Heisenberg or Ising models) are to be compared with experiment it might be essential that the domains be larger than the theoretical coherence length. This may be true for long needle-shaped samples. However, magnetic domains will be formed for rectangular slab or flattened ellipsoid sample geometries. Dislocations and other static defects can serve as the domain nucleation centers and pinning sites. The domain formation and the presence of an essentially random distribution of domain nucleation centers and pinning sites may lead to smearing.

The shape of the heat capacity curve near T_c also may be affected by the earth's magnetic field. However, the

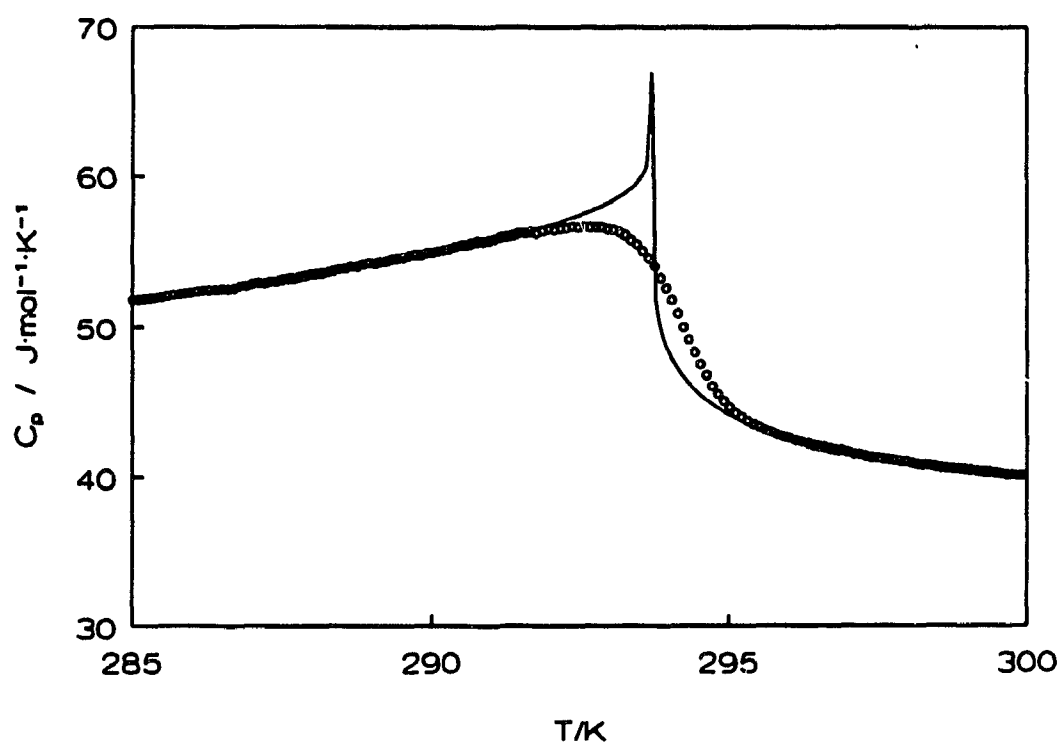


Fig. 8.2 Power law fit (solid line) to the C_p data (open circles) for sample C3.

reduced temperature scale for such effects is likely well below the reduced temperatures accessed in the present experiment. For instance it may be estimated that in the earth's magnetic field the Griffiths' singularity (see Sec. 4.2.a) will occur for $t \approx 10^{-9}$.

Table 8.2 presents results of the best power law fits for samples A, B and C. Figure 8.2 shows the plot of the power law fit for sample C3 (sample C after the third heat treatment). The data in Table 8.2 show that the fits are based on half of a decade or less in reduced temperature on each side of the transition. The temperature ranges of the fits are also very asymmetric; they cover part of the 10^{-3} decade in the reduced temperature scale on the high-temperature side and part of the 10^{-2} decade on the low-temperature side of the transition. Because of the strong sample dependence of the fits, their asymmetry and the large gaps around T_c , these fits for samples A, B and C do not give meaningful information about critical behaviour of Gd. The results of power law analysis for samples A, B, C are similar to the results of the power law fits for sample D, i.e. satisfactory fits were possible only over restricted temperature ranges. This appears to indicate that because of the complex critical behaviour of Gd the correction to scaling term is necessary to obtain a correct representation of the critical behaviour of Gd in the temperature range from $t \approx 10^{-2}$ to $t \approx 10^{-3}$.

Chapter 9. SUMMARY

Despite its relatively simple mechanical and electronic construction the calorimeter described in this thesis compares well with other high-resolution AC calorimeters^{15,18,19,155}. This calorimeter makes it possible to highly resolve a useful temperature signal without the expensive addition of a good quality AC bridge. This was achieved by using a very stable current source and a miniature and very sensitive temperature detector. The simple temperature control system was based on two D/A outputs of the lock-in amplifier which better utilized the capabilities of this instrument and made computer control of the temperature drift rate relatively easy. The microprocessor-controlled sample heater appears to be the first attempt to provide a constant and known oscillatory heat input to a sample in an AC experiment by accounting for the temperature dependence of the heater resistance. This heater made it possible not only to highly resolve the heat capacity of the sample but also to measure its absolute heat capacity. This is especially important in light of the fact that heat capacity changes near a phase transition depend very much on a sample quality and many other ill-defined factors, so that reference to the literature for data calibration often seems unwarranted.

The calorimeter was used to measure the heat capacities of several single crystals of Gd in the vicinity of the Curie point in Gd. These measurements showed that the calorimeter permits the measurement of very small samples (<20 mg) with temperature resolution of a few mK and sensitivity of around 0.2 %.

The systematic investigation of the heat capacity of Gd near T_c for a number of single crystals of Gd subjected to different heat treatments and preparation procedures showed that the presence of strains and associated dislocations in Gd leads to a broadening of the phase transition. It was suggested that since dislocations are always present in real crystals this may be an important reason for rounding of the phase transition observed even in crystals of very high purity.

It was also shown that the formation of magnetic domains may affect the measured heat capacity very close to T_c and may also contribute to the observed rounding of the heat capacity near the peak temperature. The effect may be particularly pronounced in the presence of a random distribution of domain nucleation and pinning sites.

It also was found that the difference between the heat capacity at constant pressure and at constant volume for Gd is significant near T_c and should be taken into account in data analyses.

Analyses of the critical behaviour of Gd were carried

out in terms of power laws, power laws with the correction to scaling term, and the logarithmic expression characteristic of the critical behaviour of uniaxial systems with dipolar interactions in 3d, i.e. at their critical dimension. The results of these analyses showed that the best representation of the data in the reduced temperature range from $t=10^{-2}$ to $t=10^{-3}$ was obtained in terms of the power law with the correction to scaling term.

The differences between the fitted parameters for C_p and C_v data indicated that reduction of the experimental data collected at constant pressure to the heat capacity at constant volume was an important step in the analysis; this has not been done in other analyses of the critical heat capacity of Gd.

The critical exponent, α , obtained from a correction to scaling fit to the C_v data was interpreted as an effective exponent; it was shown using the literature data for the critical exponents β and γ that the exponent α obtained from this experiment satisfied scaling relations for the effective exponents. The values of the ratios A/A' and D/D' of the critical amplitudes and correction to the critical amplitudes respectively were found to be consistent with crossover from the Heisenberg critical regime to the isotropic dipolar regime in the temperature range of the fit

Finally, since the data close to T_c on the low-

temperature side of the transition may be affected by formation of domains which are not yet accounted for by the renormalization group theory, the data on the high-temperature side of the transition were analyzed separately. A good fit to these data was obtained with the logarithmic law in the reduced temperature determined by a range-of-fit analysis. A meaningful fit to the data in the same temperature range could not be obtained on the basis of a simple power law. The range of fit determined for the logarithmic behaviour is in agreement with estimates of the temperature scale of the uniaxial anisotropy obtained from other experiments and numerical calculations.

Appendix A Experimental heat capacities of gadolinium
from measurements in the AC mode.

Table A1

The experimental heat capacities of gadolinium samples
 A and B.

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
Sample A			
285.767	52.419	293.463	54.918
285.997	52.509	293.815	53.961
286.251	52.650	294.061	53.132
286.485	52.795	294.303	52.080
286.728	52.820	294.540	50.849
286.964	52.919	294.786	49.220
287.207	53.044	295.038	47.379
287.453	53.267	295.269	45.723
287.713	53.305	295.518	44.277
287.948	53.507	295.772	43.265
288.193	53.633	296.023	42.694
288.428	53.707	296.264	42.315
288.671	53.823	296.502	41.990
288.905	53.999	296.764	41.709
289.145	54.113	297.009	41.450
289.384	54.306	297.269	41.270
289.618	54.475	297.507	41.067
289.865	54.622	297.755	40.870
290.109	54.722	297.984	40.763
290.340	54.960	298.249	40.599
290.575	55.144	298.500	40.405
290.811	55.249	298.733	40.301
291.045	55.327	298.965	40.184
291.282	55.553	299.211	40.070
291.548	55.629	299.455	39.913
291.796	55.827	299.701	39.834
292.019	55.841		
292.259	55.876		
292.508	55.910		
292.766	55.809		
293.003	55.491		
293.241	55.307		

continued ...

Table A1 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
Sample B			
283.565	51.073	287.422	53.524
283.666	51.119	287.511	53.597
283.759	51.201	287.617	53.709
283.858	51.258	287.725	53.779
283.953	51.329	287.827	53.852
284.048	51.369	287.922	53.950
284.149	51.399	288.030	54.086
284.250	51.482	288.135	54.098
284.346	51.598	288.203	54.193
284.477	51.668	288.299	54.259
284.576	51.721	288.394	54.377
284.668	51.765	288.485	54.464
284.764	51.813	288.585	54.591
284.856	51.875	288.682	54.672
284.945	51.949	288.773	54.701
285.049	51.989	288.865	54.773
285.145	52.041	288.964	54.819
285.249	52.046	289.061	54.955
285.335	52.203	289.157	55.032
285.429	52.194	289.250	55.129
285.520	52.284	289.345	55.167
285.607	52.336	289.444	55.348
285.703	52.366	289.540	55.432
285.793	52.421	289.635	55.437
285.892	52.522	289.747	55.482
285.991	52.576	289.848	55.557
286.087	52.621	289.950	55.786
286.181	52.724	290.053	55.855
286.276	52.726	290.153	55.941
286.374	52.790	290.256	56.002
286.472	52.888	290.356	56.057
286.568	52.930	290.453	56.255
286.661	52.977	290.550	56.323
286.753	53.063	290.647	56.402
286.846	53.128	290.737	56.457
286.936	53.160	290.832	56.536
287.034	53.278	290.925	56.641
287.126	53.307	291.020	56.692
287.225	53.404		
287.323	53.514		

continued ...

Table A1 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
291.117	56.839	292.381	57.792
291.210	56.937	292.402	57.812
291.304	56.936	292.427	57.741
291.402	57.114	292.449	57.804
291.500	57.197	292.472	57.751
291.584	57.260	292.495	57.756
291.595	57.215	292.504	57.740
291.605	57.222	292.524	57.738
291.615	57.281	292.539	57.641
291.636	57.312	292.556	57.648
291.655	57.323	292.576	57.591
291.676	57.390	292.596	57.554
291.697	57.361	292.617	57.610
291.718	57.354	292.637	57.496
291.738	57.359	292.663	57.506
291.757	57.425	292.691	57.447
291.781	57.358	292.714	57.332
291.801	57.433	292.736	57.279
291.822	57.503	292.757	57.236
291.843	57.512	292.778	57.182
291.865	57.513	292.800	57.087
291.888	57.554	292.822	56.970
291.911	57.552	292.843	56.910
291.929	57.570	292.866	56.844
291.948	57.524	292.887	56.742
291.969	57.583	292.908	56.694
291.991	57.591	292.930	56.610
292.014	57.648	292.950	56.451
292.036	57.584	292.968	56.346
292.058	57.628	292.988	56.223
292.080	57.728	293.006	56.125
292.102	57.734	293.022	56.000
292.121	57.766	293.043	55.839
292.140	57.744	293.065	55.807
292.159	57.744	293.082	55.646
292.179	57.704	293.101	55.473
292.200	57.709	293.120	55.363
292.221	57.807	293.140	55.225
292.242	57.751	293.159	55.040
292.262	57.803	293.183	54.872
292.284	57.739	293.203	54.766
292.324	57.785		
292.348	57.774		

continued ...

Table A1 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
293.224	54.529	294.099	47.115
293.246	54.371	294.124	46.964
293.267	54.157	294.152	46.809
293.288	54.004	294.180	46.630
293.309	53.792	294.205	46.490
293.332	53.606	294.227	46.399
293.354	53.399	294.253	46.250
293.373	53.228	294.281	46.105
293.393	53.053	294.310	46.002
293.411	52.846	294.336	45.878
293.430	52.675	294.362	45.730
293.449	52.443	294.384	45.623
293.466	52.336	294.408	45.515
293.495	52.126	294.432	45.462
293.518	51.887	294.453	45.366
293.539	51.688	294.474	45.282
293.558	51.452	294.496	45.221
293.577	51.283	294.518	45.153
293.600	51.069	294.538	45.081
293.619	50.907	294.558	45.009
293.640	50.763	294.575	44.962
293.667	50.473	294.593	44.874
293.687	50.284	294.612	44.889
293.708	50.117	294.629	44.817
293.725	49.901	294.651	44.768
293.742	49.767	294.671	44.687
293.760	49.597	294.686	44.625
293.781	49.500	294.707	44.582
293.805	49.270	294.725	44.576
293.823	49.109	294.742	44.491
293.841	48.946	294.759	44.443
293.855	48.836	294.776	44.397
293.877	48.669	294.798	44.345
293.895	48.596	294.821	44.318
293.912	48.478	294.846	44.227
293.928	48.294	294.874	44.184
293.946	48.189	294.899	44.131
293.966	48.036	294.924	44.075
293.986	47.862	294.939	44.062
294.008	47.720	294.965	43.987
294.030	47.656	294.989	43.954
294.052	47.470		
294.076	47.328		

continued ...

Table A1 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
295.019	43.889	296.066	42.647
295.041	43.837	296.273	42.415
295.065	43.844	296.462	42.258
295.085	43.786	296.629	42.133
295.108	43.752	296.829	41.996
295.132	43.701	297.066	41.858
295.156	43.681	297.250	41.770
295.178	43.619	297.436	41.656
295.203	43.610	297.618	41.568
295.222	43.597	297.793	41.477
295.245	43.563	297.998	41.360
295.269	43.522	298.197	41.262
295.286	43.497	298.390	41.146
295.300	43.466	298.582	41.086
295.332	43.398	298.739	40.946
295.357	43.399	298.936	40.829
295.382	43.389	299.141	40.756
295.407	43.330	299.237	40.760
295.435	43.309	299.330	40.759
295.463	43.268	299.439	40.704
295.487	43.249	299.527	40.642
295.511	43.201	299.618	40.647
295.534	43.226		
295.559	43.166		
295.583	43.119		
295.606	43.087		
295.630	43.092		
295.651	43.047		
295.671	43.040		
295.693	42.995		
295.706	43.015		
295.722	42.944		
295.741	42.958		
295.773	42.916		
295.787	42.933		
295.807	42.884		
295.824	42.864		
295.839	42.855		
295.852	42.837		
295.875	42.789		
295.888	42.811		
295.909	42.793		
295.923	42.764		

Table A2

The experimental heat capacities of gadolinium samples C, C1, C2 and C3.

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
Sample C			
284.168	52.760	287.553	54.799
284.253	52.781	287.656	54.940
284.286	52.779	287.742	54.917
284.331	52.805	287.890	54.949
224.395	52.737	287.988	55.151
284.480	52.811	288.081	55.262
284.562	52.840	288.220	55.358
284.655	52.847	288.335	55.482
284.749	52.963	288.438	55.484
284.844	52.932	288.549	55.587
284.941	52.997	288.646	55.771
285.040	53.056	288.749	55.807
285.154	53.141	288.811	55.947
285.259	53.198	288.917	56.002
285.358	53.268	289.015	55.998
285.456	53.372	289.114	56.064
285.537	53.306	289.211	56.293
285.636	53.470	289.257	56.361
285.746	53.503	289.353	56.349
285.832	53.607	289.459	56.520
285.932	53.646	289.557	56.596
286.035	53.605	289.658	56.626
286.146	53.784	289.759	56.833
286.244	53.888	289.902	56.982
286.331	53.855	290.047	57.038
286.415	53.954	290.139	57.217
286.515	53.985	290.249	57.149
286.619	54.211	290.352	57.375
286.716	54.191	290.456	57.463
286.805	54.255	290.556	57.439
286.891	54.481	290.663	57.690
286.987	54.393	290.756	57.856
287.095	54.484	290.851	57.817
287.151	54.577	290.937	58.049
287.257	54.508	291.020	58.150
287.354	54.591		
287.443	54.827		
		continued ...	

Table A2 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
291.110	58.260	295.329	43.439
291.203	58.336	295.434	43.163
291.349	58.432	295.532	42.936
291.456	58.621	295.624	42.747
291.539	58.665	295.715	42.569
291.642	58.759	295.805	42.421
291.746	59.058	295.913	42.232
291.826	59.022	296.014	42.054
291.929	59.054	296.114	41.930
292.026	59.186	296.218	41.778
292.115	59.479	296.317	41.634
292.206	59.529	296.419	41.431
292.303	59.572	296.520	41.401
292.411	59.661	296.625	41.134
292.510	59.757	296.733	41.012
292.618	59.805	296.822	40.851
292.698	59.968	296.916	40.989
292.862	59.925	297.019	40.851
292.915	60.076	297.124	40.762
293.002	60.062	297.217	40.648
293.111	60.075	297.320	40.538
293.230	60.144	297.412	40.545
293.317	60.027	297.526	40.433
293.422	59.923	297.618	40.310
293.517	59.840	297.721	40.324
293.619	59.755	297.822	40.202
293.724	59.287	297.927	40.119
293.808	58.973	298.042	40.032
293.897	58.502	298.133	40.046
293.993	57.742	298.242	39.878
294.074	57.000	298.337	39.790
294.172	56.020	298.440	39.727
294.277	54.865	298.552	39.726
294.366	53.695	298.643	39.665
294.461	52.353	298.747	39.538
294.553	50.774		
294.646	49.521		
294.747	48.271		
294.839	46.987		
294.926	46.130		
295.031	45.209		
295.123	44.461		
295.219	43.966		

continued ...

Table A2 continued ...

T / K	C _p / J mol ⁻¹ K ⁻¹	T / K	C _p / J mol ⁻¹ K ⁻¹
Sample C1			
282.435	50.224	286.345	52.431
282.544	50.251	286.435	52.492
282.633	50.246	286.531	52.584
282.732	50.273	286.633	52.664
282.819	50.337	286.732	52.739
282.916	50.384	286.830	52.820
283.008	50.425	286.930	52.883
283.111	50.416	287.027	52.951
283.207	50.492	287.119	53.020
283.303	50.539	287.211	53.058
283.397	50.600	287.306	53.109
283.487	50.653	287.402	53.238
283.578	50.709	287.495	53.283
283.686	50.750	287.587	53.356
283.786	50.825	287.680	53.432
283.881	50.850	287.770	53.509
283.985	50.947	287.863	53.553
284.084	51.018	287.961	53.692
284.183	51.113	288.059	53.727
284.281	51.117	288.155	53.806
284.381	51.166	288.248	53.846
284.480	51.276	288.337	53.948
284.580	51.343	288.434	54.047
284.680	51.370	288.528	54.101
284.776	51.460	288.627	54.191
284.876	51.498	288.727	54.267
284.977	51.533	288.823	54.383
285.084	51.645	288.920	54.424
285.184	51.668	289.017	54.548
285.285	51.765	289.115	54.551
285.383	51.782	289.211	54.623
285.479	51.911	289.310	54.691
285.573	51.974	289.421	54.743
285.681	51.971	289.525	54.871
285.780	52.101	289.633	54.952
285.876	52.132	289.729	55.063
285.975	52.207	289.827	55.110
286.068	52.239	289.926	55.107
286.159	52.298		
286.250	52.432		

continued ...

Table A2 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
290.024	55.208	294.243	44.050
290.123	55.238	294.340	43.844
290.231	55.358	294.433	43.663
290.335	55.315	294.535	43.534
290.433	55.357	294.634	43.372
290.531	55.420	294.732	43.242
290.629	55.379	294.831	43.130
290.727	55.412	294.930	42.998
290.823	55.394	295.028	42.849
290.918	55.347	295.132	42.735
291.018	55.351	295.230	42.694
291.115	55.314	295.327	42.583
291.216	55.170	295.423	42.542
291.316	55.118	295.519	42.445
291.414	54.967	295.617	42.332
291.516	54.816	295.721	42.263
291.613	54.639	295.823	42.214
291.711	54.432	295.915	42.190
291.811	54.127	296.009	42.064
291.911	53.872	296.101	42.037
292.005	53.569	296.199	41.985
292.105	53.142	296.299	41.926
292.198	52.840	296.396	41.841
292.295	52.387	296.493	41.784
292.387	51.978	296.596	41.733
292.493	51.450	296.695	41.686
292.594	50.942	296.794	41.622
292.688	50.452	296.893	41.644
292.788	49.916	296.991	41.537
292.890	49.374	297.089	41.520
292.994	48.789	297.187	41.444
293.094	48.328	297.279	41.441
293.191	47.777	297.368	41.414
293.282	47.283	297.466	41.387
293.376	46.869	297.563	41.342
293.471	46.474	297.662	41.287
293.566	46.063	297.760	41.219
293.662	45.668	297.857	41.267
293.760	45.371	297.958	41.176
293.858	45.039	298.055	41.156
293.954	44.755	298.151	41.134
294.048	44.482		
294.145	44.263		

continued ...

Table A2 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
298.247	41.090		
298.343	41.081		
298.439	41.055		
298.590	41.013		
298.687	40.926		
298.785	40.934		
298.883	40.940		
298.982	40.852		
299.084	40.861		
299.184	40.851		
299.278	40.829		
299.369	40.819		

Sample C2

284.307	51.383	286.784	52.737
284.398	51.436	286.887	52.742
284.500	51.469	286.986	52.879
284.603	51.513	287.086	52.944
284.702	51.591	287.194	52.913
284.801	51.622	287.285	53.039
284.904	51.705	287.385	53.055
285.007	51.800	287.485	53.162
285.104	51.822	287.584	53.223
285.194	51.866	287.678	53.239
285.288	51.927	287.771	53.334
285.384	51.932	287.867	53.398
285.478	51.978	287.961	53.504
285.572	52.065	288.055	53.529
285.681	52.152	288.150	53.575
285.778	52.177	288.257	53.655
285.870	52.250	288.354	53.746
285.966	52.282	288.448	53.855
286.075	52.351	288.548	53.896
286.174	52.443	288.644	54.034
286.271	52.456	288.743	54.010
286.379	52.480	288.843	54.161
286.484	52.540	288.938	54.241
286.587	52.531		
286.687	52.589		

continued ...

Table A2 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
289.034	54.200	293.252	56.087
289.134	54.323	293.348	55.767
289.233	54.365	293.451	55.481
289.323	54.497	293.548	55.066
289.420	54.532	293.647	54.576
289.519	54.609	293.745	54.053
289.616	54.722	293.847	53.273
289.717	54.786	293.940	52.606
289.814	54.756	294.036	51.814
289.911	54.922	294.138	50.929
290.009	54.936	294.237	49.991
290.110	55.016	294.329	49.143
290.208	55.101	294.426	48.306
290.303	55.172	294.523	47.485
290.398	55.305	294.625	46.743
290.490	55.411	294.724	46.020
290.586	55.440	294.821	45.473
290.679	55.558	294.919	45.002
290.772	55.669	295.015	44.583
290.866	55.658	295.115	44.202
290.962	55.709	295.214	43.952
291.060	55.835	295.316	43.662
291.157	55.940	295.411	43.441
291.258	56.000	295.507	43.267
291.356	56.072	295.606	43.076
291.450	56.200	295.707	42.924
291.561	56.217	295.804	42.748
291.660	56.276	295.905	42.622
291.758	56.213	296.011	42.547
291.859	56.378	296.113	42.384
291.958	56.482	296.221	42.289
292.062	56.445	296.322	42.190
292.164	56.503	296.413	42.056
292.269	56.561	296.507	42.002
292.366	56.654	296.605	41.958
292.468	56.605	296.701	41.840
292.566	56.614	296.799	41.762
292.664	56.610	296.898	41.702
292.766	56.615	296.998	41.607
292.864	56.604	297.099	41.491
292.960	56.484	297.200	41.472
293.058	56.431		
293.159	56.267		

continued ...

Table A2 continued ...

T / K	C _p / J mol ⁻¹ K ⁻¹	T / K	C _p / J mol ⁻¹ K ⁻¹
297.293	41.370		
297.390	41.276		
297.488	41.262		
297.585	41.198		
297.681	41.129		
297.779	41.099		
297.878	41.012		
297.974	41.006		
298.070	40.911		
298.165	40.824		
298.264	40.789		
298.363	40.744		
298.457	40.676		
298.556	40.603		
298.658	40.577		
298.760	40.535		
298.864	40.521		
298.964	40.467		
299.061	40.420		
299.178	40.352		
299.277	40.295		
299.375	40.290		
299.474	40.233		
299.565	40.186		
299.754	40.111		
299.848	40.047		
299.939	40.052		
300.046	40.034		
300.143	39.963		
300.240	39.978		
300.336	39.898		
300.428	39.851		
300.524	39.808		
300.618	39.801		
300.712	39.754		
Sample C3			
284.307	51.383	284.702	51.591
284.398	51.436	284.801	51.622
284.500	51.469		
284.603	51.513		
		continued ...	

Table A2 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
284.904	51.705	289.134	54.322
285.007	51.800	289.233	54.365
285.104	51.822	289.323	54.497
285.194	51.866	289.420	54.532
285.288	51.927	289.519	54.609
285.384	51.932	289.616	54.722
285.478	51.978	289.717	54.786
285.572	52.065	289.814	54.756
285.681	52.152	289.911	54.922
285.778	52.177	290.009	54.936
285.870	52.250	290.110	55.016
285.966	52.282	290.208	55.101
286.075	52.351	290.303	55.172
286.174	52.443	290.398	55.305
286.271	52.456	290.490	55.411
286.379	52.480	290.586	55.440
286.484	52.540	290.679	55.558
286.587	52.531	290.772	55.669
286.687	52.589	290.866	55.658
286.784	52.737	290.962	55.709
286.887	52.742	291.060	55.835
286.986	52.879	291.157	55.940
287.086	52.944	291.258	56.000
287.194	52.913	291.356	56.072
287.285	53.039	291.450	56.200
287.385	53.055	291.561	56.217
287.485	53.162	291.660	56.276
287.584	53.223	291.758	56.213
287.678	53.239	291.859	56.378
287.771	53.334	291.958	56.482
287.867	53.398	292.062	56.445
287.961	53.504	292.164	56.503
288.055	53.529	292.269	56.561
288.150	53.575	292.366	56.654
288.257	53.655	292.468	56.605
288.354	53.746	292.566	56.614
288.448	53.855	292.664	56.610
288.548	53.896	292.766	56.615
288.644	54.034	292.864	56.604
288.743	54.010	292.960	56.484
288.843	54.161	293.058	56.431
288.938	54.241		
289.034	54.200		

continued ...

Table A2 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
293.159	56.267	297.390	41.276
293.252	56.087	297.488	41.262
293.348	55.767	297.585	41.198
293.451	55.481	297.681	41.129
293.548	55.066	297.779	41.099
293.647	54.576	297.878	41.012
293.745	54.053	297.974	41.006
293.847	53.273	298.070	40.911
293.940	52.606	298.165	40.824
294.036	51.814	298.264	40.789
294.138	50.929	298.363	40.744
294.237	49.991	298.457	40.676
294.329	49.143	298.556	40.603
294.426	48.306	298.658	40.577
294.523	47.485	298.760	40.535
294.625	46.743	298.864	40.521
294.724	46.020	298.964	40.467
294.821	45.473	299.061	40.420
294.919	45.002	299.178	40.352
295.015	44.583	299.277	40.295
295.115	44.202	299.375	40.290
295.214	43.952	299.474	40.233
295.316	43.662	299.565	40.186
295.411	43.441	299.658	40.121
295.507	43.267	299.754	40.111
295.606	43.076	299.848	40.047
295.707	42.924	299.939	40.052
295.804	42.748	300.046	40.034
295.905	42.622	300.143	39.963
296.011	42.547	300.240	39.978
296.113	42.384	300.336	39.898
296.221	42.289	300.428	39.851
296.322	42.190	300.524	39.808
296.413	42.056	300.618	39.801
296.507	42.002	300.712	39.754
296.605	41.958		
296.701	41.840		
296.799	41.762		
296.898	41.702		
296.998	41.607		
297.099	41.491		
297.200	41.472		
297.293	41.370		

Table A3

The experimental heat capacities of gadolinium sample D.

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
274.872	48.922	276.738	49.488
274.917	48.918	276.790	49.495
274.957	48.978	276.841	49.461
275.006	48.977	276.890	49.462
275.048	49.016	276.937	49.558
275.090	48.946	276.986	49.530
275.132	49.039	277.036	49.574
275.178	48.997	277.085	49.532
275.228	48.974	277.130	49.586
275.270	49.007	277.178	49.603
275.316	49.023	277.227	49.675
275.361	49.027	277.276	49.637
275.408	49.076	277.325	49.669
275.451	49.037	277.373	49.684
275.502	49.043	277.421	49.648
275.552	49.057	277.469	49.679
275.601	49.101	277.519	49.686
275.650	49.075	277.566	49.805
275.701	49.130	277.613	49.739
275.750	49.154	277.660	49.755
275.798	49.183	277.708	49.761
275.848	49.201	277.758	49.808
275.894	49.172	277.806	49.819
275.941	49.237	277.857	49.823
275.988	49.185	277.907	49.862
276.034	49.169	277.955	49.890
276.083	49.205	278.003	49.872
276.132	49.227	278.053	49.948
276.180	49.269	278.102	49.927
276.234	49.304	278.152	50.001
276.284	49.281	278.203	49.944
276.334	49.365	278.254	49.981
276.384	49.329	278.304	49.995
276.436	49.381	278.353	50.012
276.487	49.373	278.406	49.999
276.536	49.409	278.458	50.080
276.585	49.406	278.509	49.981
276.636	49.473		
276.689	49.440		

continued ...

Table A3 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
278.560	50.080	280.740	51.014
278.612	50.157	280.792	51.097
278.663	50.135	280.843	51.109
278.714	50.153	280.892	51.073
278.764	50.269	280.945	51.065
278.815	50.183	280.996	51.156
278.865	50.200	281.047	51.184
278.918	50.286	281.098	51.148
278.969	50.252	281.147	51.251
279.019	50.296	281.195	51.198
279.066	50.328	281.246	51.350
279.111	50.401	281.297	51.292
279.163	50.315	281.348	51.319
279.215	50.404	281.398	51.377
279.266	50.425	281.447	51.350
279.327	50.433	281.497	51.349
279.380	50.410	281.545	51.388
279.428	50.435	281.593	51.375
279.476	50.499	281.641	51.416
279.523	50.507	281.691	51.474
279.574	50.517	281.742	51.432
279.628	50.457	281.792	51.544
279.681	50.577	281.841	51.480
279.731	50.620	281.892	51.547
279.781	50.566	281.942	51.516
279.832	50.596	281.992	51.639
279.883	50.630	282.043	51.625
279.944	50.700	282.093	51.641
279.991	50.667	282.145	51.666
280.043	50.689	282.197	51.707
280.100	50.723	282.248	51.776
280.146	50.747	282.299	51.779
280.193	50.822	282.350	51.740
280.239	50.778	282.401	51.793
280.288	50.822	282.450	51.879
280.336	50.851	282.501	51.851
280.386	50.881	282.552	51.933
280.437	50.841	282.602	51.927
280.487	50.953	282.652	51.971
280.537	50.873	282.703	51.896
280.588	50.907	282.754	51.978
280.639	50.967		
280.690	51.052		

continued ...

Table A3 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
282.804	52.119	284.949	53.137
282.852	51.965	284.998	53.106
282.903	52.096	285.050	52.961
282.954	52.117	285.100	53.239
283.003	52.146	285.153	53.305
283.054	52.139	285.201	53.240
283.104	52.192	285.248	53.232
283.153	52.239	285.297	53.382
283.202	52.261	285.348	53.399
283.252	52.171	285.397	53.365
283.303	52.289	285.444	53.327
283.350	52.280	285.491	53.444
283.398	52.339	285.539	53.478
283.478	52.216	285.586	53.540
283.525	52.296	285.635	53.601
283.574	52.391	285.684	53.592
283.625	52.308	285.734	53.493
283.675	52.313	285.780	53.561
283.726	52.416	285.827	53.686
283.775	52.449	285.875	53.734
283.825	52.483	285.927	53.783
283.873	52.462	285.978	53.721
283.921	52.709	286.027	53.895
283.967	52.605	286.079	53.841
284.015	52.571	286.132	53.837
284.064	52.560	286.183	53.846
284.112	52.752	286.234	53.944
284.161	52.742	286.286	53.979
284.207	52.622	286.337	53.965
284.255	52.677	286.387	54.057
284.305	52.720	286.436	54.111
284.356	52.823	286.485	54.051
284.406	52.822	286.543	54.102
284.456	52.863	286.598	54.100
284.504	52.891	286.649	54.196
284.555	52.865	286.699	54.203
284.603	52.995	286.749	54.220
284.652	53.031	286.799	54.287
284.699	52.952	286.848	54.346
284.747	53.012	286.895	54.393
284.798	52.975	286.948	54.403
284.849	53.069		
284.899	53.117		

continued ...

Table A3 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
287.002	54.426	289.204	56.226
287.059	54.370	289.255	56.161
287.110	54.546	289.303	56.234
287.161	54.540	289.350	56.367
287.214	54.588	289.397	56.377
287.264	54.604	289.443	56.503
287.314	54.718	289.491	56.532
287.364	54.736	289.540	56.582
287.415	54.754	289.588	56.557
287.466	54.801	289.638	56.707
287.524	54.853	289.688	56.618
287.580	54.837	289.735	56.746
287.630	54.857	289.791	56.779
287.680	54.979	289.834	56.899
287.730	55.001	289.889	56.906
287.779	55.094	289.933	56.897
287.829	55.119	289.983	57.013
287.881	55.106	290.031	57.088
287.931	55.143	290.081	57.056
287.979	55.162	290.129	57.119
288.026	55.210	290.177	57.180
288.075	55.232	290.229	57.152
288.125	55.287	290.280	57.289
288.177	55.310	290.333	57.372
288.227	55.476	290.384	57.437
288.280	55.450	290.442	57.434
288.339	55.519	290.494	57.490
288.391	55.494	290.542	57.710
288.442	55.559	290.592	57.732
288.494	55.621	290.642	57.721
288.547	55.622	290.693	57.749
288.598	55.718	290.792	58.024
288.648	55.709	290.838	57.990
288.697	55.711	290.889	58.005
288.748	55.801	290.941	58.138
288.800	55.890	290.992	58.197
288.849	55.960	291.043	58.269
288.898	55.834	291.092	58.325
288.957	55.941	291.145	58.266
289.007	55.936	291.198	58.350
289.057	56.131	291.246	58.522
289.107	56.156		
289.155	56.182		

continued ...

Table A3 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
291.292	58.610	293.467	62.164
291.347	58.491	293.518	62.313
291.395	58.711	293.568	62.558
291.448	58.782	293.619	62.678
291.498	58.900	293.672	62.675
291.548	58.945	293.722	62.809
291.600	59.022	293.773	63.073
291.651	58.999	293.822	63.266
291.703	59.040	293.870	63.209
291.754	59.123	293.921	63.312
291.804	59.209	293.980	63.658
291.854	59.298	294.038	63.746
291.902	59.391	294.091	63.884
291.952	59.366	294.142	63.784
292.002	59.458	294.190	63.964
292.049	59.566	294.239	64.085
292.096	59.679	294.292	63.916
292.146	59.703	294.342	63.857
292.194	59.727	294.390	63.679
292.248	59.851	294.438	63.438
292.307	60.030	294.489	62.664
292.359	60.111	294.540	60.891
292.411	60.066	294.587	57.420
292.461	60.307	294.636	53.447
292.514	60.259	294.686	50.593
292.563	60.314	294.741	48.591
292.612	60.420	294.794	47.298
292.661	60.582	294.845	46.487
292.717	60.556	294.895	45.837
292.771	60.692	294.948	45.322
292.822	60.936	294.997	45.012
292.871	60.933	295.046	44.616
292.920	61.007	295.096	44.354
292.969	61.111	295.147	44.218
293.021	61.146	295.200	43.996
293.072	61.389	295.252	43.827
293.123	61.372	295.303	43.716
293.171	61.617	295.353	43.585
293.219	61.703	295.408	43.339
293.267	61.829	295.461	43.224
293.317	61.921	295.511	43.117
293.367	62.079		
293.417	62.150		

continued ...

Table A3 continued ...

T / K	C _p / J mol ⁻¹ K ⁻¹	T / K	C _p / J mol ⁻¹ K ⁻¹
295.561	42.964	297.753	40.202
295.611	42.900	297.804	40.103
295.664	42.866	297.853	40.141
295.716	42.774	297.902	40.057
295.767	42.666	297.953	40.093
295.818	42.470	298.004	40.000
295.866	42.457	298.055	39.919
295.913	42.390	298.107	39.883
295.961	42.295	298.158	39.796
296.011	42.304	298.207	39.819
296.063	42.148	298.258	39.809
296.114	41.990	298.306	39.726
296.162	41.979	298.355	39.726
296.211	41.930	298.405	39.719
296.263	41.842	298.455	39.658
296.313	41.734	298.502	39.603
296.363	41.666	298.550	39.599
296.412	41.636	298.599	39.517
296.464	41.506	298.646	39.563
296.514	41.452	298.694	39.477
296.565	41.425	298.744	39.411
296.623	41.329	298.795	39.439
296.675	41.236	298.847	39.340
296.724	41.224	298.895	39.385
296.775	41.209	298.944	39.328
296.826	41.107	298.990	39.264
296.878	41.032	299.039	39.259
296.930	41.015	299.089	39.206
296.980	40.967	299.141	39.216
297.033	40.814	299.194	39.199
297.082	40.798	299.242	39.126
297.140	40.683	299.290	39.082
297.194	40.692	299.342	39.074
297.244	40.621	299.393	39.081
297.293	40.582	299.444	39.152
297.342	40.543	299.495	38.996
297.388	40.569	299.545	38.962
297.446	40.484	299.595	38.870
297.497	40.389	299.645	38.896
297.547	40.327	299.694	38.852
297.594	40.305	299.745	38.902
297.645	40.228		
297.702	40.221		

continued ...

Table A3 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
299.793	38.854	301.959	37.793
299.843	38.833	302.009	37.779
299.893	38.763	302.059	37.691
299.942	38.764	302.109	37.697
300.002	38.718	302.157	37.694
300.053	38.618	302.205	37.755
300.103	38.617	302.259	37.665
300.154	38.601	302.309	37.653
300.206	38.576	302.361	37.650
300.257	38.544	302.411	37.580
300.309	38.478	302.458	37.619
300.362	38.495	302.504	37.608
300.410	38.480	302.553	37.676
300.463	38.469	302.601	37.558
300.512	38.379	302.648	37.540
300.563	38.414	302.698	37.516
300.613	38.345	302.747	37.501
300.663	38.347	302.793	37.517
300.713	38.266	302.836	37.472
300.761	38.369	302.891	37.409
300.810	38.230	302.942	37.468
300.861	38.242	302.991	37.400
300.910	38.245	303.040	37.438
300.959	38.175	303.086	37.384
301.009	38.177	303.133	37.320
301.059	38.147	303.182	37.378
301.110	38.072	303.232	37.390
301.160	38.118	303.283	37.400
301.209	38.153	303.330	37.276
301.258	38.084	303.379	37.297
301.306	38.089	303.426	37.280
301.358	38.007	303.476	37.292
301.407	38.076	303.525	37.260
301.456	37.987	303.584	37.270
301.513	37.958	303.635	37.246
301.564	38.011	303.685	37.159
301.615	37.895	303.735	37.173
301.666	37.922	303.786	37.177
301.716	37.876	303.836	37.111
301.767	37.898	303.883	37.150
301.816	37.872	303.930	37.101
301.865	37.868		
301.908	37.834		

continued ...

Table A3 continued ...

T / K	C_p / J mol ⁻¹ K ⁻¹	T / K	C_p / J mol ⁻¹ K ⁻¹
303.977	37.121	306.145	36.437
304.026	37.061	306.192	36.501
304.075	37.092	306.242	36.481
304.125	37.079	306.293	36.505
304.174	37.149	306.343	36.435
304.223	37.065	306.395	36.435
304.275	37.002	306.445	36.445
304.326	37.058	306.492	36.468
304.375	37.005	306.543	36.485
304.424	37.059	306.592	36.374
304.470	36.978	306.642	36.355
304.523	36.998	306.694	36.386
304.572	36.905	306.744	36.317
304.621	36.891	306.794	36.403
304.671	36.906	306.844	36.460
304.721	36.883	306.894	36.383
304.769	36.911	306.944	36.300
304.817	36.815	306.997	36.360
304.868	36.809	307.047	36.343
304.918	36.828	307.099	36.376
304.963	36.847	307.149	36.293
305.022	36.824	307.197	36.279
305.072	36.814	307.246	36.318
305.125	36.745	307.294	36.284
305.173	36.774	307.343	36.344
305.228	36.715	307.389	36.321
305.280	36.780	307.433	36.263
305.330	36.717	307.480	36.275
305.381	36.735	307.531	36.266
305.432	36.684	307.579	36.254
305.483	36.696	307.626	36.253
305.534	36.693	307.676	36.170
305.586	36.711	307.728	36.191
305.637	36.653	307.778	36.162
305.689	36.657	307.829	36.207
305.741	36.562	307.881	36.121
305.789	36.593	307.931	36.177
305.849	36.557	307.989	36.151
305.900	36.563	308.040	36.065
305.948	36.553	308.092	36.058
305.996	36.580	308.143	36.136
306.046	36.568		
306.095	36.520		

continued ...

Table A3 continued ...

T / K	C _p / J mol ⁻¹ K ⁻¹
308.193	36.124
308.242	36.081
308.293	36.129
308.342	36.079
308.392	35.983
308.440	36.106
308.486	36.109
308.537	35.986
308.588	36.021
308.638	36.017
308.687	36.040
308.736	35.943
308.788	35.929
308.839	35.926
308.891	36.039
308.943	35.946
309.003	35.984
309.059	35.892
309.116	35.920
309.167	35.940
309.222	35.979
309.274	36.008
309.325	35.893
309.377	35.929
309.426	35.849
309.476	35.850
309.527	35.889

Appendix B Chemical analysis for sample D'.**Table B1 Spark surface mass spectrometric analysis in atomic ppm**

Li < 0.1	Be < 0.01	B < 0.09	Na < 0.2	Mg < 0.2
Al < 2	Si < 1	P < 0.1	S < 0.3	Cl < 2
K < 1	Ca < 1	Ti < 0.6	V < 2	Cr < 4
Mn < 0.06	Co < 0.1	Ni < 5	Cu < 6	Zn < 0.18
Ga < 0.2	As < 1	Se < 0.4	Br < 0.5	Rb < 0.06
Sr < 0.2	Zr < 0.6	Nb < 1	Mo < 1	Ru < 0.6
Rh < 0.1	Pd < 0.3	Ag < 0.05	Cd < 0.1	In < 0.06
Sn < 0.07	Te < 0.1	I < 0.06	Cs < 0.006	Ba < 0.1
Hf < 2	Ta < 12	Re < 0.8	Os < 1	Ir < 0.5
Pt < 0.7	Au < 0.1	Hg < 0.1	Tl < 0.09	Pb < 0.3
Bi < 0.07	Th < 0.9	U < 0.4		
Rare earth impurities				
Sc < 0.05	Y < 0.63	La < 0.5	Ce < 1	Pr < 0.5
Nd < 2	Sm < 2	Eu < 0.2	Tb < 3	Dy < 1
Ho < 0.4	Er < 1	Tm < 0.4	Yb < 4	Lu < 2

Table B2 Vacuum fusion results in atomic ppm

O ≈ 344	N ≈ 45	H ≈ 622	C ≈ 131	F < 25
Fe < 18.5	W < 0.86			

* The analyses were provided by the sample producer.

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