Specific heat and resistivity of gadolinium near the Curie point in external magnetic fields*†

D. S. Simons and M. B. Salamon
Department of Physics and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801
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A modification of the ac calorimetric technique has been used to test the proportionality of the specific heat and temperature derivative of the basal-plane resistivity of gadolinium through the Curie point. Because of a large temperature-dependent background to the resistivity derivative, a direct comparison of the critical contributions to the two quantities was impossible. It was found, however, that the background was insensitive to applied magnetic fields so that a direct comparison of the deviation of the specific heat at a finite field from its zero-field value with the similar deviation of the resistivity derivative demonstrated the proportionality of the two quantities. In applied fields below 585 Oe, a "kink point" was observed in the specific heat below T_C which moved to lower temperatures with increasing fields. Such an effect has been predicted to occur at fields and temperatures for which the internal magnetic field vanishes. The specific heat in several fields above 585 Oe was compared with the predictions of scaling laws and with the linear approximation to the parametric equation of state. Reasonable agreement between the data and the specific-heat scaling function predicted by the linear model could only be obtained by using an unrealistic value of the critical exponent describing the zero-field specific heat.

I. INTRODUCTION

It is generally agreed that the magnetic contributions to the temperature derivative of the electrical resistivity and the specific heat of a ferromagnet should be proportional near the Curie point, since the temperature dependence of both quantities is dominated by the short-range part of the spin-correlation function.[1,2] This prediction, commonly referred to as the Fisher-Langer theory,[1] has been quantitatively verified in nickel[3] and iron,[4] quasi-itinerant ferromagnets, and in β-brass,[5] an order-disorder alloy system. However, a well-localized ferromagnet, on which the theory was originally based, has not yet been examined in detail. For this reason the rare-earth ferromagnet gadolinium was chosen for this investigation.

The specific heat[6-8] and electrical resistivity[9,10] of gadolinium have been previously studied through the Curie transition (~18 °C). Because of its hexagonal crystal structure, the resistivity of gadolinium as well as other transport properties is anisotropic, requiring that measurements be made on single crystals if meaningful results are to be obtained. Two measurements are necessary to completely characterize the resistivity in this system, one along the hexagonal axis (c axis) and one in the basal plane.

The c-axis resistivity of gadolinium has been investigated in detail by Zumsteg.[10] He attributes a peak in the c-axis resistivity at T_C to the effect of an anomalous lattice contraction in the c direction. When this effect is taken into account, the resistivity that remains is qualitatively of the form that one would expect from the Fisher-Langer theory of spin-disorder scattering.[1] Zumsteg also concludes that his measurement of the a-axis resistivity is qualitatively of the Fisher-Langer form, with no observable thermal expansion contribution. It was therefore decided to focus the effort of the present experiment on the basal-plane resistivity of gadolinium, seeking a quantitative verification of the Fisher-Langer theory.

II. ac CALORIMETRY

Specific-heat measurements through a phase transition are conveniently made using ac calorimetry.[11] In this method a sample is heated by mechanically chopped light to induce a periodic temperature variation. The operating frequency ω is chosen such that the sample-bath thermal-relaxation time $\tau_1 \gg \omega^{-1}$, while the sample's internal thermal-relaxation time $\tau_2 \ll \omega^{-1}$. When these conditions are satisfied, the amplitude of the temperature oscillations is inversely proportional to the specific heat of the sample.

A useful feature of ac calorimetry is that it lends itself to the simultaneous measurement of other physical properties. Since we intend to compare the temperature derivative of the resistivity with the specific heat, we have extended the ac calorimetric method to resistance measurements.[5] Current and voltage leads are attached to the specific-heat sample and a constant direct current I is passed through it. Voltage oscillations are induced across the sample by its temperature oscillations. These quantities are related by the Taylor series

$$\Delta V(t) = I\sum_{n=1}^{\infty} \frac{1}{n!} \frac{d^{(n)}R}{dT^{(n)}}[\Delta T(t)]^n \quad . \tag{1}$$

If the temperature oscillations are given by $\Delta T(t) = T_{ac}\sin(\omega t)$, then the amplitude of the fundamental frequency component of the voltage oscillations is

$$V_{ac} = I\left(\frac{dR}{dT}\ T_{ac} + \frac{1}{8}\frac{d^3R}{dT^3}\ T_{ac}^3 + \frac{1}{192}\frac{d^5R}{dT^5}\ T_{ac}^5 + \cdots\right) , \tag{2}$$

with only odd powers of $\sin(\omega t)$ giving contributions at the fundamental frequency. A similar equation is used in magnetic resonance where field modulation is used to deduce the field derivative of the resonance line.[12] The temperature derivative of the resistivity α_R, independent of sample dimensions, can be calculated from the expression

$$\alpha_R \equiv \frac{1}{\rho_0}\left(\frac{d\rho}{dT}\right) = \frac{1}{R_0}\left(\frac{dR}{dT}\right) \approx \frac{1}{V_0}\left(\frac{V_{ac}}{T_{ac}}\right) \quad , \tag{3}$$

where $V_0 = IR_0$ and R_0 and ρ_0 are the room-temperature resistance and resistivity, respectively, provided that

$$\frac{1}{\rho_0}\left|\frac{d^{(n)}\rho}{dT^{(n)}}\right| \ll \frac{1}{V_0}\left|\frac{V_{ac}}{T_{ac}^n}\right| , \quad n = 3,\ 5,\ 7,\ \ldots \quad . \tag{4}$$

It is therefore advantageous to have small values of T_{ac} where the resistivity derivative is changing rapidly with temperature, as occurs near phase transitions. Fortunately, this adjustment is accomplished automatically, since the increasing specific heat near a phase transition will reduce T_{ac}. The temperature resolution of the resistivity derivative will ultimately be limited by the size of T_{ac}, which is typically 10–20 mK.

III. EXPERIMENT

The single-crystal samples of gadolinium on which the measurements were made were taken from the source used by Lewis to measure the specific heat near the Curie point.[8] From mass-spectrographic analysis the samples were estimated to have 0.1-at.% rare-earth impurities and 0.5-at.% other impurities. Rectangular pieces were prepared by spark cutting and then thinned by mechanical polishing. Sample A, on which the data presented here were taken, had rectangular dimensions 6.9×1.7 mm^2 and thickness 0.15 mm, with the longer side of the rectangle parallel to the a axis and the shorter side parallel to the c axis. The orientation of the axes was determined by Laue x-ray photography and is estimated to be accurate to about 3°.

Preliminary specific-heat measurements through the Curie point on both polycrystalline and single-crystal samples showed severe rounding of the transition over a range of about 4 °C. Since it has been demonstrated in the case of nickel that lattice strains are an important cause of rounding,[13] the gadolinium samples were subjected to an annealing process. Optimum results were obtained when a sample was annealed between two tantalum sheets at a temperature of 850 °C for 24 h in a vacuum of 5×10^{-6} Torr. The Ta sheets were required to minimize oxidation of the surface of the sample. At temperatures above 850 °C the sample tended to adhere to the sheets. With the above annealing procedure the rounding of the Curie transition was reduced to about 0.1 °C.

After annealing a sample, tantalum current and voltage leads were spot welded to it such that the direction of current flow was parallel to the longer dimension of the rectangle. The amplitude of the temperature oscillations was measured with a chromel-alumel thermocouple made by spot welding together the ends of 25-μm-diam chromel and alumel wires and then attaching the junction to the back face of the sample with diluted GE 7031 varnish.

The sample was mounted in the holder shown in Fig. 1, with each lead connected to a copper segment by a screw and washer. The top face of the sample was blackened with Aquadag. A small factory-calibrated platinum resistance thermometer (Rosemount Model 118F) was thermally potted within the copper cylinder beneath the sample. The window cap provided a vacuum seal by crushing a copper washer between two stainless-steel knife edges. Thermal conductance between the

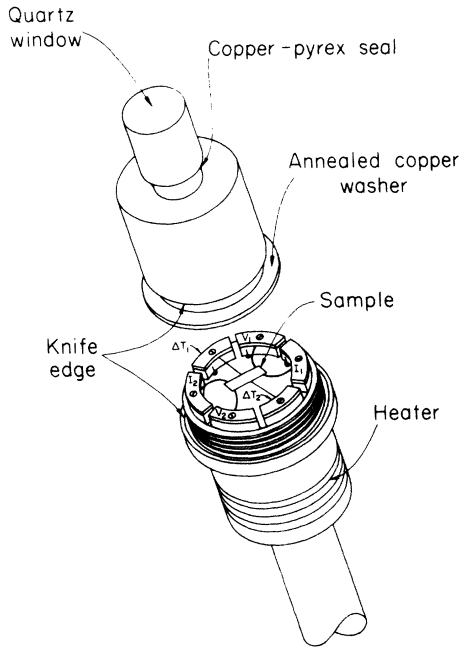

FIG. 1. Detail of sample holder for gadolinium.

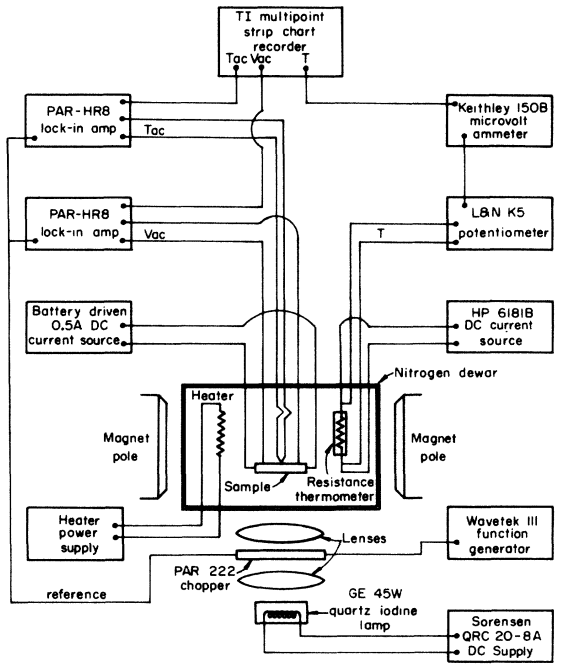

FIG. 2. Experimental schematic.

sample and holder was provided by 0.5 atm of helium gas. The sample holder could be heated or cooled by adjusting exchange gas pressure or current to a heater wound as shown in Fig. 1. A typical heating rate was 0.5 °C/min. Near T_C, the rate was reduced to 0.25 °C/min. Even at these rates, which would be high for conventional calorimetry, the thin samples remained in internal thermal equilibrium and the measurements were averaged over several hundred periods of temperature oscillations in the time required to pass through the rounded portion of the peak at T_C.

The electronics used in this experiment are indicated in Fig. 2. The liquid-nitrogen Dewar which housed the sample holder was located in the fringe field of an electromagnet. The sample was mounted so that the direction of the external magnetic field was parallel to the plane of the sample in order to minimize demagnetizing effects. The field at the sample was measured by positioning a gaussmeter probe at the sample site.

The temperature of the sample holder was measured with the resistance thermometer. The dc temperature of the sample was about 5 °C above that of the sample holder owing to heating from the current and the light. This temperature difference, which varied monotonically by less than 1 °C over the range of sample temperatures, was determined at the beginning and end of a run by measuring the dc component of the ΔT thermocouple signal with a microvoltmeter. The linearly interpolated temperature rise was added to the sample-holder temperature to calculate the temperature of the sample with an estimated absolute accuracy of 0.1 °C.

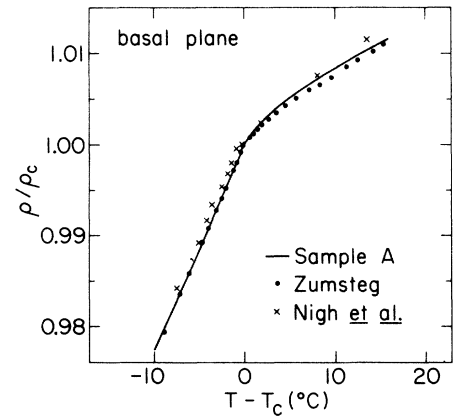

FIG. 3. Comparison of basal-plane resistivity measurement of sample *A* with data of Zumsteg (Ref. 10) and Nigh *et al.* (Ref. 9).

To determine the correct operating frequency, τ_1 and τ_2 were estimated for the gadolinium samples to be about 1 sec and 10^{-3} sec, respectively, at room temperature. A frequency of 11 Hz was chosen and was found to be in the center of the frequency range in which $T_{ac} \propto \omega^{-1}$, which is a necessary condition of the ac calorimetric method.

IV. RESULTS

Initially, a dc resistance measurement was made on sample *A* to compare it with the previous results of Nigh, Legvold, and Spedding[9] and Zumsteg.[10] This comparison is shown in Fig. 3, where the resistivity is scaled to its value at T_C.

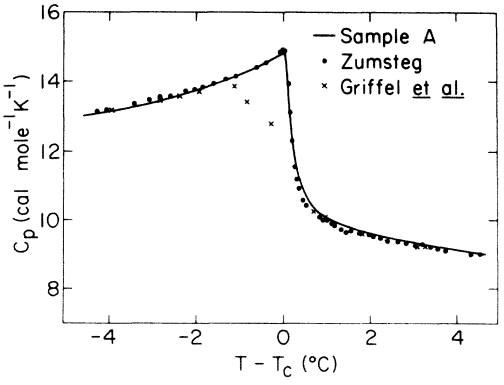

FIG. 4. Comparison of specific-heat measurement of sample *A* with data of Zumsteg (Ref. 10) and Griffel *et al.* (Ref. 6).

The resistivity of sample A appears identical to the previous basal-plane measurements, within experimental error.

The specific heat of sample A is compared with the measurements of Griffel, Skochdopole, and Spedding[6] and Zumsteg[10] in Fig. 4. The sample-A data were normalized to those of Griffel *et al.* near 0 °C after an appropriate shift of temperature scales was made to account for the difference in transition temperatures. For Zumsteg's data, which were expressed in arbitrary units and contained an unknown addendum contribution, a constant was subtracted and a normalization factor applied to fit his data at the two ends of the sample-A curve. The specific-heat data of Lewis,[8] which also contained an unknown addendum contribution, could not be made to coincide with the other curves by following the same normalization procedure. This same problem was encountered when Robinson and Milstein[14] compared their specific-heat measurements on Gd with those of Lewis, casting doubt on the reliability of Lewis's data. Figure 4 indicates that the rounding of the specific-heat anomaly of sample A is comparable to that of Zumsteg's sample (~0.1 °C) and significantly better than the rounding displayed by Lewis's best sample (~0.4 °C).

Figure 5 shows the a-axis resistivity derivative α_R over a wide temperature range, measured with the ac technique. Peaks are observed at both the Curie temperature of 18 °C and at a lower temperature of −47 °C, where a change of easy magnetization axis occurs. A detailed study of the resistivity derivative and specific heat at this lower "tilting" transition has been reported separately.[15] We concentrate here on these same properties at the Curie transition. The Curie peak of α_R in Fig. 5 is similar in shape to the specific heat, as reported by Zumsteg.[10] However, the strong temperature dependence of the background prevents a direct comparison between α_R and C_p as was done for β-brass[5] and iron.[4] Rather than attempt to subtract this background

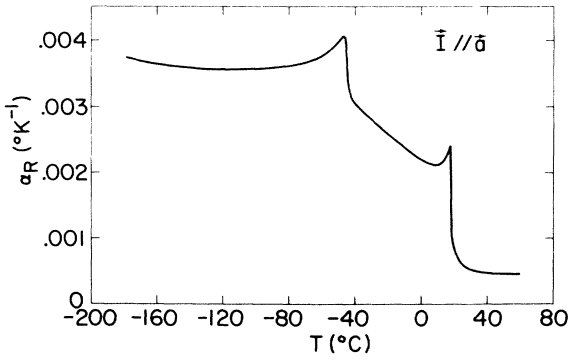

FIG. 5. Resistivity derivative of gadolinium along the a axis over a wide temperature range.

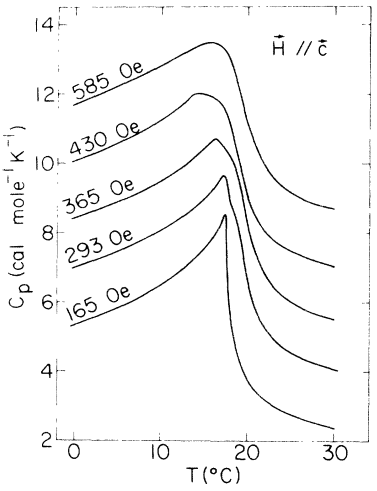

FIG. 6. Specific heat of gadolinium near the Curie point in a low range of applied fields. Vertical scale applies to upper curve, with other curves shifted downward. Kinks are due to exclusion of the external field by the demagnetizing field, as described in the text.

from the curve empirically, measurements were made in applied magnetic fields in an attempt to gain additional information on the nature of the background in Fig. 5. Even if such an approach proved unsuccessful, the measurements would still give useful information on the field dependence of α_R and C_p.

Specific-heat measurements in small applied fields exhibited unusual behavior, as shown in Fig. 6. In fields between 165 and 585 Oe applied along the hexagonal axis, the specific heat had a distinct "kink point" below the zero-field transition temperature, which moved to lower temperatures as the field was increased. Similar behavior was observed in basal plane fields.

Such an effect has been predicted to occur because of demagnetizing effects within the sample.[16,17] For a material in which the external field is parallel to the direction of uniform magnetization, the internal field can be written

$$H_i = H_e - DM\,, \tag{5}$$

where D is the shape-dependent demagnetizing factor. Griffiths[17] has argued that singular behavior should occur in the specific heat at constant external field C_e at the temperature T_1 defined by $M_s(T_1) = H_e/D$, where M_s is the temperature-dependent spontaneous magnetization. Below T_1, the magnetization assumes a constant value $M = H_e/D$ which makes the internal field zero. Hence, in this temperature range C_e is identical to the specific heat in zero field C_0. Above T_1 two limiting types of behavior can occur. In low fields C_e will resemble the specific heat at

constant magnetization C_M. In the high-field limit C_e will look like the specific heat at constant internal field C_H. The detailed behavior depends on the form chosen for the equation of state, but in either limit C_e will fall below C_0 for $T \gtrsim T_1$. The singular behavior at T_1 will be most easily observed in fields corresponding to a crossover between the two cases. Griffiths defines a characteristic internal field H_h such that the internal field is half of the external field at $T = T_C$. Then the low- and high-field limits correspond to $H_e \ll 2H_h$ and $H_e \gg 2H_h$, respectively. H_h can be calculated for sample A using the formula of Griffiths

$$H_h = H_I(1/E)^{1/(\delta-1)}(DM_0/H_I)^{\delta/(\delta-1)}, \quad (6)$$

where $H_I = k_B T_C/M_0$ and the experimental parameters $E = 1.6$ and $\delta = 4.0$, which characterize the critical isotherm, are taken from Heller.[18] The demagnetizing factor $D = 0.67$ is calculated by approximating the sample as a flattened ellipsoid.[19] We find that $2H_h = 320$ Oe, a value consistent with the curves in Fig. 6. This is believed to be the first experimental evidence of the "kink point" in the specific heat.

The specific heat and resistivity derivative of sample A in fields greater than 585 Oe are shown in Figs. 7 and 8, respectively. No "kink points" are observed, and it is assumed that these measurements are in the high-field limit where field penetration is nearly complete in the vicinity of T_C.

Figure 8 shows that the high-field behavior of α_R does not represent the background contribution to α_R in the absence of an external field, since the high-field curves lie above the zero-field curve for $T > T_C$. Instead, the difference between α_R at a finite field and α_R at zero field as a function

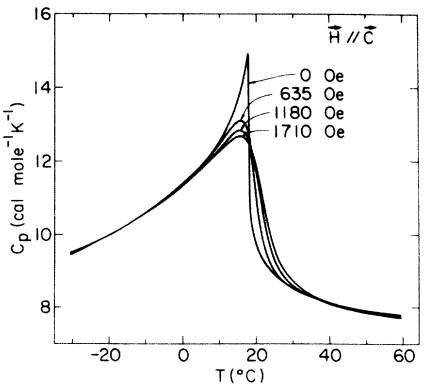

FIG. 7. Specific heat of gadolinium through the Curie point in several fields. Normalization of finite-field curves has been chosen to give best agreement to the zero-field curve far from the Curie point.

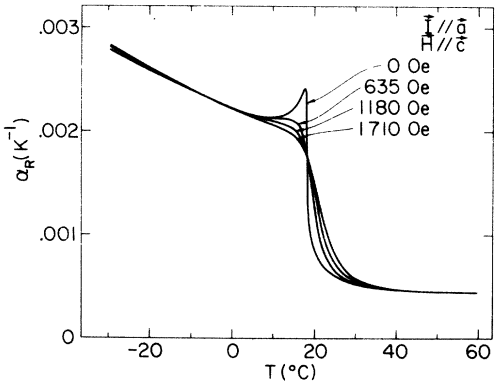

FIG. 8. Temperature derivative of the a-axis resistivity for the same fields as in Fig. 7.

of temperature appears similar to the corresponding difference in the specific heat. This is not an unusual occurrence in ferromagnets. Potter had previously noted the similarity between the change in resistance in applied fields (magnetoresistance) and the change in magnetic energy (magnetocaloric effect) as a function of temperature through the Curie point in nickel and iron.[20] We make the same observation here about the temperature derivatives of these quantities in gadolinium.

The visual similarity between $C_p(H, T) - C_p(0, T)$ and $\alpha_R(H, T) - \alpha_R(0, T)$ suggested a quantitative comparison of the two differences. Such a comparison is shown in Fig. 9 for three fields, with tem-

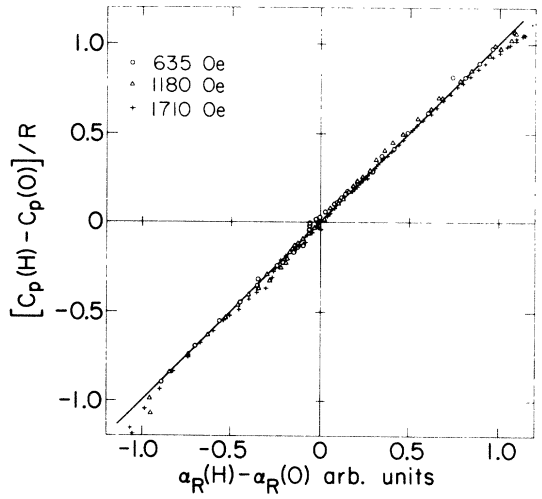

FIG. 9. Deviation of the specific heat in finite magnetic fields from that in zero field vs the similar deviation of the resistivity derivative. Temperature is an implicit variable, with temperatures far from T_C near the origin, negative deviations mainly below T_C, and positive deviations mainly above T_C.

perature as an implicit variable. Most of the data points far from T_C have been eliminated to avoid crowding near the origin. The plot shows that there is a direct proportionality between the specific-heat deviations and the resistivity-derivative deviations for each field through the Curie point, with the same proportionality constant in each case.

The arguments which led to Fisher and Langer's conclusion that the magnetic resistivity derivative and specific heat are proportional[1] should also be valid in the presence of a magnetic field. These arguments are based on considerations of momentum conservation and phase-space density, so there is nothing in them unique to the region where $H=0$. Therefore both α_R and C_p will continue to be determined by the short-range part of the spin-correlation function, although the correlation function will of course be altered by the field. Taking differences between finite-field and zero-field values of the quantities is merely a convenient way of cancelling the nonmagnetic but temperature-dependent background effects. We therefore take the proportionality shown in Fig. 9 to be a verification, albeit indirect, that the Fisher-Langer prediction holds for the a-axis resistivity of gadolinium.

The behavior of the specific heat of gadolinium in applied fields (Fig. 7) is similar to that of nickel.[13] Since the nickel data were well described by the linear-model approximation of the parametric equation of state,[21] that same model was applied to the gadolinium data.

The parametric equations are constructed in such a way that they will inherently satisfy the scaling-law relations.[22] In particular, they predict that the magnetic specific heat at constant internal field H will scale like

$$(C_h - C_0)\, h^{\alpha/\beta\delta} = g(t/h^{1/\beta\delta}) , \qquad (7)$$

where h is the reduced field M_0H/k_BT_C, t is the reduced temperature $(T-T_C)/T_C$, α, β, and δ are the critical exponents of the specific heat, the magnetization, and the critical isotherm, respectively, and $g(x)$ is a scaling function which can be obtained in explicit form from the parametric equations.[21] The specific-heat data of Fig. 7 are plotted in Fig. 10 according to Eq. (7). Also shown in Fig. 10 is the function g calculated from the parametric equations. The constants $a=1.03$ and $k=0.98$ which are required for the calculation of g were determined by Ho[21] from the magnetization measurements of gadolinium by Graham.[23] The critical exponents $\alpha=0.1$ and $\beta=0.4$ were chosen to give reasonable agreement between the experimental data and the theoretical curve, with $\delta=3.75$ determined from the scaling relation $2-\alpha=\beta(\delta+1)$.

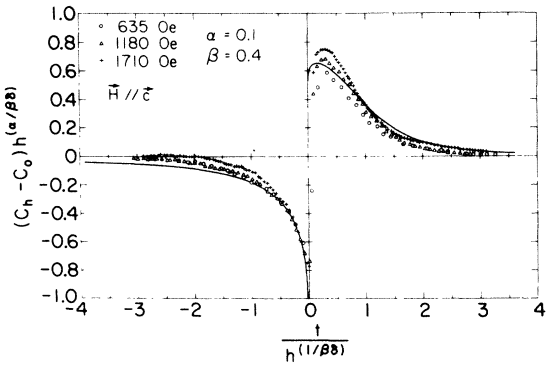

FIG. 10. Scaled plot of the specific heat of gadolinium in three applied fields. Solid line is calculated from the linearized parametric equation of state. Parameters α and β have been chosen for best agreement between experiment and theory.

The value of the magnetization exponent β is close to a recent experimental determination of 0.38,[24] but the value of the specific-heat exponent α does not agree well with the findings of Lewis that $\alpha=-0.1$ $(T>T_c)$ and $\alpha'=-0.3$ $(T<T_c)$.[8] Because of the breakdown of scaling indicated by Lewis's result that $\alpha\neq\alpha'$, we have examined our zero-field specific-heat data in a way which tests the scaling hypothesis.[25] We find our data consistent with the assignment $\alpha=\alpha'=-0.20\pm0.02$. However, when this value of the specific-heat exponent is used to compare the data with the prediction of the parametric equations, the positive peak in the data curves of Fig. 10 becomes more than eight times larger than the peak in the theoretical curve. The experimental curves for different fields do coincide better when $\alpha=-0.20$, indicating that a single scaling function can be applied to the data, but the amplitude of the function does not agree with the prediction of the linear model. Similar difficulties were encountered in attempting to fit the data to the Heisenberg specific-heat scaling function of Krasnow and Stanley.[26] At present we can find no explanation for the poor agreement between these theories and the data when the experimentally determined critical exponents are used.

V. CONCLUSION

This magnetic field study was undertaken to circumvent the temperature dependence of the background in the basal-plane resistivity derivative shown in Fig. 5. We have reached no conclusions on the origin of this background, but find it similar to the behavior of the basal-plane resistivity derivative of dysprosium near its Néel point.[27] This suggests a common feature of the basal-plane re-

sistivity of the heavy rare earths which remains to be investigated.

The primary result of this study, illustrated in Fig. 9, is that a direct proportionality exists between the critical contributions to the specific heat and basal-plane resistivity derivative of gadolinium. The generality of the Fisher-Langer model has thus been strengthened by showing this proportionality to hold over a wide temperature range for yet another system, the ferromagnet with highly localized magnetic moments.

ACKNOWLEDGMENT

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