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Evidence for a Second Magnetic Phase Transition in Gadolinium*

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The heat capacity and temperature derivative of the electrical resistivity of Gd have been measured simultaneously in the vicinity of 226 K, where the easy axis of magnetization tilts away from the crystallographic *c* axis. In addition to the known anomaly in the *a*-axis resistivity, a small step change in the specific heat was observed. Application of magnetic fields above 1000 Oe along the *c* axis or 120 Oe along the *a* axis suppressed both the resistive and specific-heat anomalies. This behavior is discussed in terms of a molecular-field model which treats the anisotropy energy as a term in the magnetic free energy. The tilting of the easy axis is driven by the temperature dependence of the magnetization, which causes the lowest-order anisotropy constant K_1 to change sign. The magnitudes of the step in the specific heat and the critical field in the *c*-axis direction calculated in this model are in good agreement with experiment.

Gadolinium has long been considered a simple ferromagnet below its Curie temperature of 291 K, although its easy magnetization axis is known to vary with temperature. The magnetization is aligned with the hexagonal *c* axis just below T_C, but tilts away from it to form a cone below a temperature of 220–240 K.[1–3] In this same temperature range, anomalies have been found in many magnetic, thermal, and electrical properties of gadolinium, including the magnetization,[4,5] magnetostriction,[6,7] thermal expansion,[7] elastic constants,[8,9] electrical resistance,[10] and magnetoresistance.[11] We report here a simultaneous measurement of the specific heat and temperature derivative of the electrical resistance of gadolinium between 213 and 243 K and attempt to clarify the nature of the anomalous behavior by means of a simple molecular-field model.

An ac calorimetry technique which has been previously described[12] was used to make the measurements. The sample of gadolinium was a single crystal cut from the same source used by Lewis to measure the specific heat near the Curie point,[13] and was estimated to have 0.1% rare-earth impurities and 0.5% other impurities. It was cut to dimensions $7.0\times1.5\times0.1$ mm^3, with the 7.0-mm side parallel to the *a* axis and the 1.5-mm side parallel to the *c* axis. The sample was annealed between two tantalum sheets in a vacuum of 5×10^{-6} Torr for 24 h at 850 °C. Tantalum current and voltage leads were spot welded such that the current was directed along the *a* axis. Measurements were made in magnetic fields applied along the *a* or *c* axis. Since the field was always in the plane of the sample, demagnetizing effects were negligible.

In Fig. 1(a) we have plotted the results of specific-heat measurements made with fields applied along the *c* axis. In zero field, a step change in the specific heat is observed at 226 K with a value

$$\Delta C_p = 0.09 \pm 0.01 \text{ cal/mole K}. \quad (1)$$

Increasing the field decreases the size of the specific-heat anomaly, and it apparently disappears between 0.7 and 1.0 kOe.

The temperature derivative of resistance shown in Fig. 1(b) provides a more sensitive measure of the presence of a transition. Behavior which strongly suggests spin-disorder scattering[14,15] is observed in zero field. Application of the magnetic field shifts the peak to lower temperatures, distorts its shape, and finally suppresses it com-

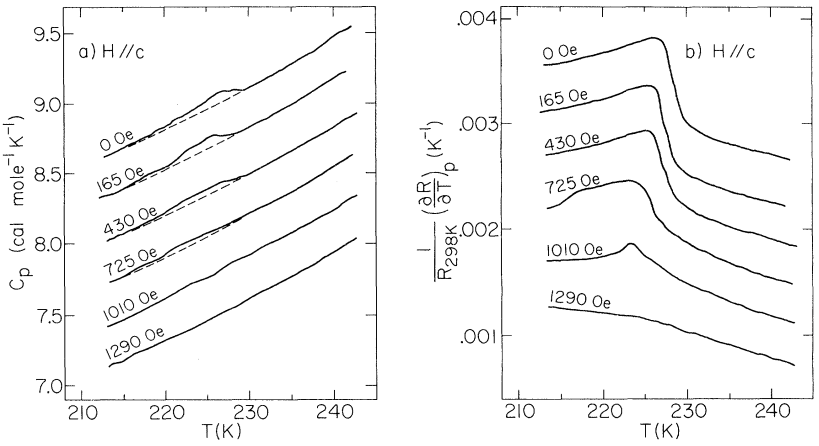

FIG. 1. (a) Specific heat and (b) temperature derivative of basal plane resistance of gadolinium in magnetic fields parallel to c axis. Vertical scales apply to 0-Oe curves. The other curves are shifted downward for clarity. Dashed line is extension of background.

pletely between 1.0 and 1.3 kOe.

With fields along the a axis, the transition is suppressed at much smaller fields, as seen in Fig. 2. We again note a shift of the peak in dR/dT to lower temperatures as the field is increased.

Measurements with the current flowing along the c axis show no resistive anomaly, as may be seen in Fig. 3. This, together with the a-axis-resistivity behavior, suggests that additional ordering occurs only in the basal plane below 226 K. One possibility, a helicoidal structure, has been proposed to explain magnetization anomalies in polycrystalline gadolinium[4]; however, a neutron-diffraction study on a sample of unknown thermal history failed to reveal any evidence of a spiral structure.[2] Since the anomalies we have reported here were unobservable in unannealed slices of the crystal, we must await further neutron-diffraction measurements on a well-annealed sample before discarding the possibility of a spiral structure below 226 K.

A simple model for the anisotropy qualitatively reproduces the major features of this transition. For an axially symmetric crystal we may express the anisotropy energy as

$$E_A = \kappa_2\, Y_2^0(\theta) + \kappa_4\, Y_4^0(\theta)\ , \tag{2}$$

where Y_2^0 and Y_4^0 are spherical harmonics and θ is the angle between the magnetic moment and the c axis of the crystal. The coefficients κ_2 and κ_4 are temperature dependent and, at low temperatures, may be related to the magnetization by

$$\kappa_l(T) = \kappa_l(0)\, m(T)^{l(l+1)/2}\ , \tag{3}$$

where $m(T)$ is the reduced magnetization.[16] This theorem holds for localized spins and should be a reasonable approximation for gadolinium. The anisotropy energy (2) can also be expressed in the more familiar form

$$E_A = K_1 \sin^2\theta + K_2\ \sin^4\theta\ , \tag{4}$$

if we make the identification

$$K_1 = -3a_2 m^3 - 40 a_4 m^{10}$$

and

$$K_2 = 35 a_4 m^{10}\ . \tag{5}$$

The constants a_2 and a_4 are products of the zero-

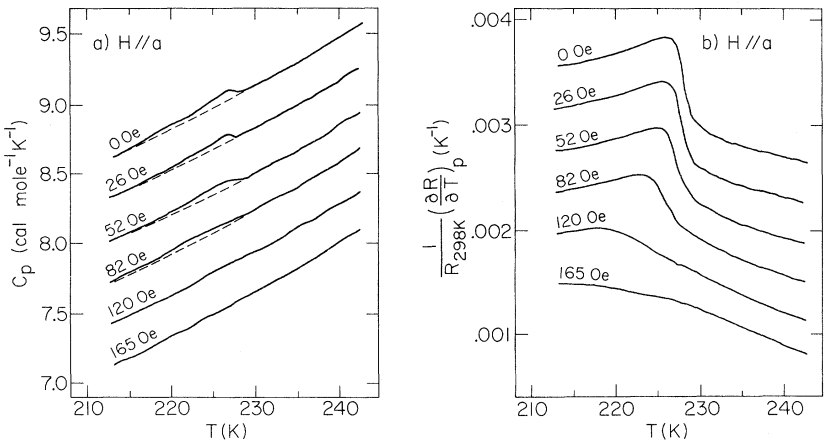

FIG. 2. (a) Specific heat and (b) temperature derivative of basal plane resistance in fields parallel to a axis. Curves shifted as in Fig. 1. Note lower range of fields.

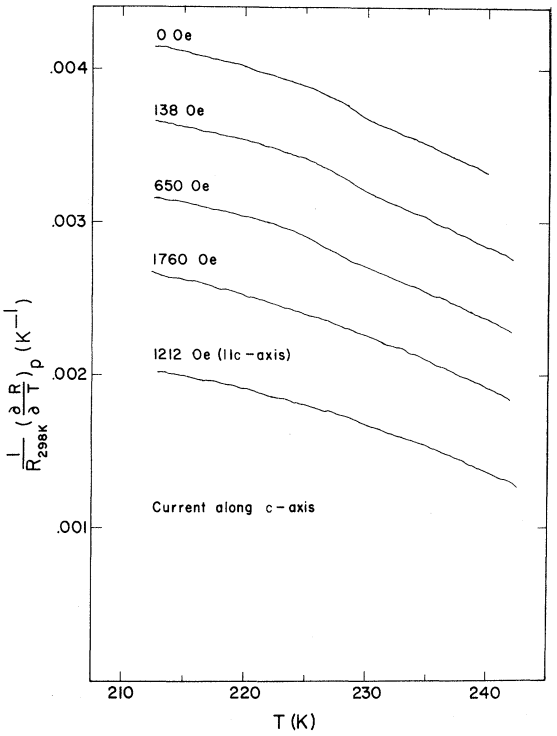

FIG. 3. Temperature derivative of c-axis resistivity in fields parallel to the a axis (c axis for lowest curve). Curves shifted as in Fig. 1. The slight dip at zero field is due to the slight misalignment of the current and the c axis.

temperature anisotropy constants in (3) and the normalization factors in the spherical harmonics. For gadolinium K_2 is positive at all temperatures, while K_1 becomes negative below 220–240 K.[1,3] From (5) we conclude that a_4 is positive and a_2 negative, and that K_1 changes sign at

$$m_t^7 = -3a_2/40a_4 . \tag{6}$$

Examination of (4), which has the same form as the free energy of a magnetic system in the Landau model if $\sin\theta$ is taken as the order parameter,[17] shows that for K_1 positive the minimum energy occurs at $\sin\theta = 0$, while for negative values of K_1 the minima occur at

$$\sin^2\theta = -K_1/2K_2 . \tag{7}$$

Let us now make the assumption that

$$m = (1 - T/T_C)^{\beta} , \tag{8}$$

and indicate the temperature at which the magnetization tilts away from the c axis by T_t. Immediately below T_t we may write (7) as

$$\sin^2\theta = \left(\frac{4}{7}\right)\left[1 - \left(\frac{m_t}{m}\right)^7\right] \simeq \frac{4\beta(T_t - T)}{(T_C - T_t)} . \tag{9}$$

As the temperature is decreased below T_t the angle θ increases rapidly, reaching a value of $\sin^{-1}[(\frac{4}{7})^{1/2}] \simeq 49°$ at 0 K. This behavior is qualitatively similar to the experimental values of $\theta(T)$[1-3] especially in the prediction of an infinite slope at T_t.

Equation (4) predicts a decrease in the anisotropy energy below T_t and will, therefore, contribute to the specific heat. Just below T_t we may write

$$E_A = -20\left(\frac{10}{3}\right)^{3/7} K_1^{\max} \frac{\beta^2(T_t - T)^2}{(T_C - T_t)^2} , \tag{10}$$

where $K_1^{\max} = 2.5 \pm 0.5 \times 10^5$ erg/cm^3 is the maximum (positive) value of K_1.[1] Using $\beta = 0.370$,[18] the "tilting" transition yields a step change in the specific heat given by

$$\Delta C_p = -T_t\left(\frac{\partial^2 E_A}{\partial T^2}\right)_{T_t} = 0.06 \pm 0.01 \text{ cal/mole K}, \tag{11}$$

in reasonable agreement with (1).

According to the above theory (see Fig. 4) there will be no phase transition if a magnetic field is applied in the basal plane, since any finite field will tilt the moment from the c axis. If a field is applied along the c axis, the transition will be shifted

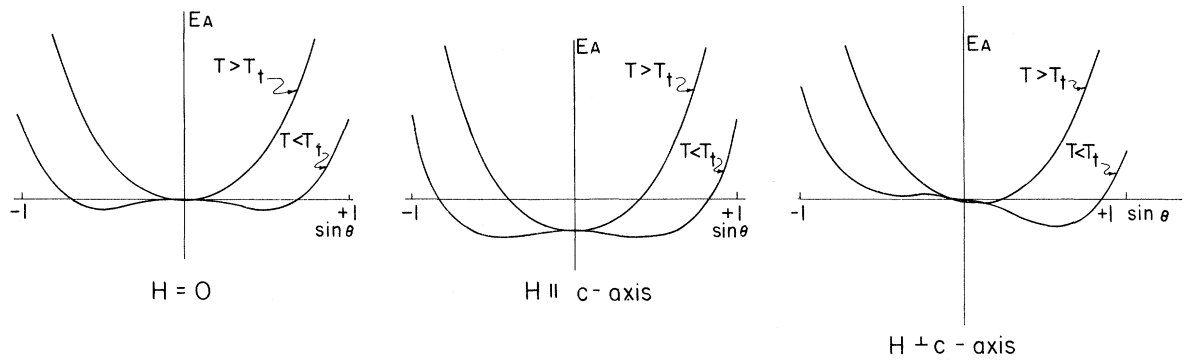

FIG. 4. Anisotropy energy as a function of $\sin\theta$ for temperatures above and below the zero-field tilting temperature T_t. When the field is applied along the c axis, the minima are reduced and the transition is suppressed at a critical field. Any field in the basal plane, however, removes the degeneracy of the minima and suppresses the transition.

to lower temperatures and will be completely suppressed by a field

$$H_{cr} \cong \frac{8K_1^{max}}{N_a M(0)} \cong 1 \text{ kOe},$$

where we take $M(0) = 7.55\mu_B$/atom.[5] Again this is in agreement with our measurements, although we do see a small critical field along the a axis which the theory does not explain.

It is clear from our measurements as well as others that the molecular-field model presented here is too simple to explain the detailed nature of this transition. Recently, Sherrington[19] has calculated the properties of an anisotropic ferromagnet at zero temperature in a more general way. In that model, as well, the change in sign of the lowest-order anisotropy constant leads to a second-order transition due, in that case, to the presence of a soft mode. We hope that the qualitative agreement between our experimental results and a molecular-field model will encourage a general treatment of the anisotropic ferromagnet at finite temperatures.

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Feynman-Graph Expansion for the Equation of State near the Critical Point*

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The scaling equation of state for a generalized classical Heisenberg ferromagnet near the critical point is derived by an expansion in $\epsilon = 4 - d$, where d is the dimension of space. It is shown that, though infrared divergences are induced by the Goldstone modes, the equation of state is divergence free. The results are compared with previous numerical calculations. It is also shown that, for non-Ising-like systems the "linear model" cannot be exact, even at first order in ϵ (although the numerical deviations from linearity are small).

I. INTRODUCTION

The understanding of the physics of the critical region has been improved by the use of the ϵ expansion technique.[1,2] This method provides systematic corrections to mean-field theory by a perturbation expansion about four dimensions. Critical exponents have been calculated[2] and the known terms in the expansion in powers of $\epsilon = 4 - d$, where d is the dimension of space, give sensible results in three dimensions. In a previous work[3] the scaling equation of state was calculated up to order ϵ^2 for an Ising-like system. Here we present the details of a similar calculation, to the same order, for a generalized classical Heisenberg system.