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Bicritical and Tetracritical Behavior of $GdAlO_3$

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(Received 4 February 1977)

We have experimentally investigated the phase diagram of antiferromagnetic $GdAlO_3$ near its spin-flop multicritical point (T_M, H_M) in the three-dimensional space spanned by the uniform fields $H_\parallel$ and $H_\perp$ and the temperature T. In the $H_\parallel$-T plane, (T_M, H_M) appears as a bicritical point, but as a tetracritical point in the $H_\perp$-T plane. The approach of all six boundaries to (T_M, H_M) is described by a single exponent $\psi = 1.17 \pm 0.02$. This implies crossover exponents $\varphi = 1.17 \pm 0.02$ and $\varphi_v = \pm 0.03$ in excellent agreement with renormalization group theory.

The work on bicritical and tetracritical points by Fisher and Nelson[1] and Aharony and Bruce[2] has opened an area of intensive theoretical investigations of such points.[3] Experimental studies have, however, been confined to bicritical points.[4,5] The reason is that systems with the appropriate quadratic[6] or quartic[2,3] anisotropies required to yield a tetracritical point with three ordered phases of different symmetry are not very abundant. Recently, Mukamel[7] has proposed some planar antiferromagnets with possible tetracritical points at zero field. In some of these systems, a tetracritical behavior is expected only for distinct field directions, whereas for all other directions, it appears as a bicritical point. Thus, the type of critical behavior depends on the direction of the applied field.

The situation is similar in antiferromagnets with a spin-flop multicritical point at finite fields.[3] The present work verifies such tetracritical behavior and is the first experimental observation bearing on φ_v, the crossover exponent associated with cubic anisotropy. In addition, the bicritical lines have been obtained for considerably improved alignment.[4] Figure 1 shows the phase diagram of a uniaxial antiferromagnet in the space of uniform fields $H_\parallel$ and $H_\perp$ and the temperature T.[3,4] $H_\parallel$ is applied along the easy axis of magnetization, $H_\perp$ perpendicular to it. The shelf of first-order spin-flop (SF) transitions touches the surface of second-order transitions to the paramagnetic (PM) state in a multicritical point (T_M, H_m). In the $H_\parallel$-T plane, we find the well-known bicritical behavior,[1,2] where the first-order SF transition line meets the antiferromagnetic (AF)-PM and flop (FL)-PM λ lines. In the $H_\perp$-T plane [or, more precisely, in the plane tangent to the SF transition shelf at (T_M, H_M)], this point is tetracritical and the four critical lines meet tangentially: the two spin-flop critical lines T_c^{SF} bounding the SF transition shelf and the two PM transition lines T_c^{PM}. It should be noted that this is a special type of tetracritical point with four Ising-like critical lines. For other tetracritical points, the SF transition shelf of Fig. 1 can be parallel to $H_\parallel$. Bicritical behavior is then found in the $H_\perp$-T plane.

For $GdA10_3$ with orthorhombic anisotropy,[8] Fig. 1 only applies if $H_\perp$ is applied along the axis of

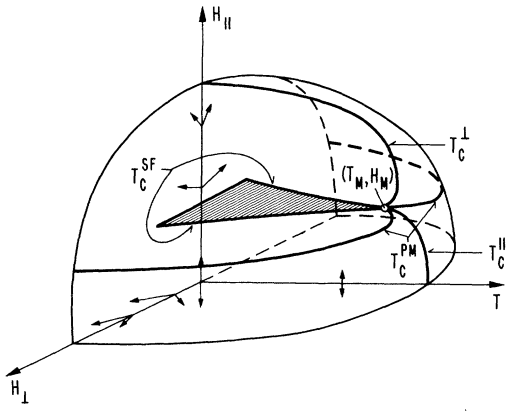

FIG. 1. Phase diagram of a uniaxial antiferromagnet in the space of uniform fields $H_\parallel$ and $H_\perp$ and temperature T. The bicritical lines $T_c^\perp$ and $T_c^\parallel$ and the tetracritical lines T_c^{SF} and T_c^{PM} meet tangentially at the multicritical point (T_M, H_M) (open circle). The shaded area is the shelf of first-order spin-flop transitions.

medium anisotropy. On the other hand, if $H_\perp$ points along the axis of hardest anisotropy, the topology of the phase diagram is qualitatively different.[9] The SF transition shelf then extends out to the PM boundary at all temperatures. In the $H_\perp$-T plane this gives a line of bicritical points intersecting the temperature axis at a right angle, rather than a tetracritical point. In the present experiment, $H_\perp$ was aligned along the axis of medium anisotropy within 0.5 deg. Crossover properties for arbitrary $H_\perp$ directions will be reported later.

A second point to be considered is demagnetization. Demagnetization corrections could be avoided in a disk with easy axis and $H_\perp$ in the disk plane. However, if the principal axes of demagnetization and anisotropy do not coincide, the resultant symmetry is not orthorhombic with new principal axes. Since the samples can only be shaped within an accuracy of some tenths of a degree, which is also the width of the SF transition shelf to be measured, the situation becomes unclear both theoretically and experimentally. This was avoided by using a sphere. Demagnetization corrections due to the parallel magnetization component are readily made; the perpendicular component $M_\perp$, however, could not be determined experimentally. Above T_M, the functional form of $T_c^{PM}(H_\perp)$ is unchanged by demagnization, since on the critical line $M_\perp \propto H_\perp$.[10] It is suggestive to assume the same proportionality between $M_\perp$ and $H_\perp$ on the spin-flop critical line T_c^{SF} below T_M. Numerical calculations confirm such a proportionality in the molecular-field approximation (MFA). It is not unreasonable to suppose that it might also apply beyond MFA as is, for instance, the case for the MFA relation between sublattice magnetization and parallel susceptibility.[11]

The phase boundaries were determined by measuring the susceptibility in the frequency range between 0.4 Hz (isothermal) and 53 kHz (adiabatic) with modulation fields of some milligauss. Initial alignment of easy axis and applied field was achieved within 0.05 deg. The final orientation of the applied field was controlled by an additional perpendicular-field component $H_\perp$ generated by a pair of Helmholtz coils.[9] The phase boundaries in the $H_\parallel$-T plane were located by the peaks in the direct isothermal susceptibility as described before,[4] making corrections[12] for the rounding of the asymmetric susceptibility peaks at the two λ lines.

The critical lines in the $H_\perp$-T plane are more difficult to determine. Below the tetracritical point, the susceptibility as a function of $H_\parallel$ for fixed $H_\perp$ exhibits a peak independent of whether the field scan leads through the SF transition shelf or past it. The peak of the isothermal susceptibility is small for field scans passing well outside the SF transition shelf, and grows rapidly when the field path approaches the spin-flop critical line T_c^{SF}. Close to T_M, the peak height of the susceptibility, $\tilde{\chi}_p$, is determined by the natural width of the transition and still increases inside the SF transition shelf because of the increasing magnetization discontinuity. However, at very low modulation fields and high frequencies, the stiffness of the domain walls reduces $\tilde{\chi}_p$ substantially inside the shelf. At lower temperatures, $\tilde{\chi}_p$ is limited by demagnetization, and $\tilde{\chi}_p = N^{-1}$ inside the shelf, where N is the demagnetizing factor. The additional reduction of $\tilde{\chi}_p$ due to domain walls leads to a pronounced minimum of $\tilde{\chi}_p$ for perfect alignment as shown in Fig. 2. The width of the transition shelf is then given by the flat part of $\tilde{\chi}_p(H_\perp)$ close to T_M and by the separation of the maxima of $\tilde{\chi}_p$ at lower temperatures.

Above T_M, the situation is less clear. When

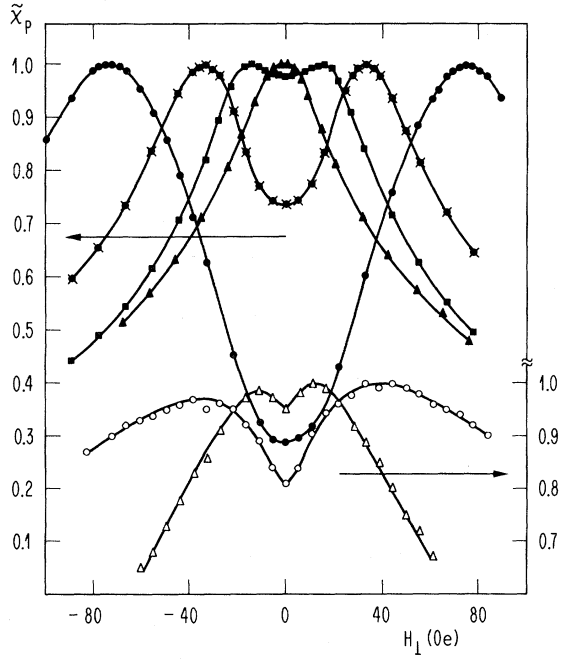

FIG. 2. Normalized height of the adiabatic susceptibility peak on or near the SF transition shelf as a function of $H_\perp$ below T_M at $T = 3.043$ K (●), 3.087 K (◙), 3.105 K (■) and 3.1219 K (▲), and above T_M at $T = 3.126$ K (△) and 3.1278 K (○). Below 3.11 K, $\tilde{\chi}_{p,\max} = N^{-1}$.

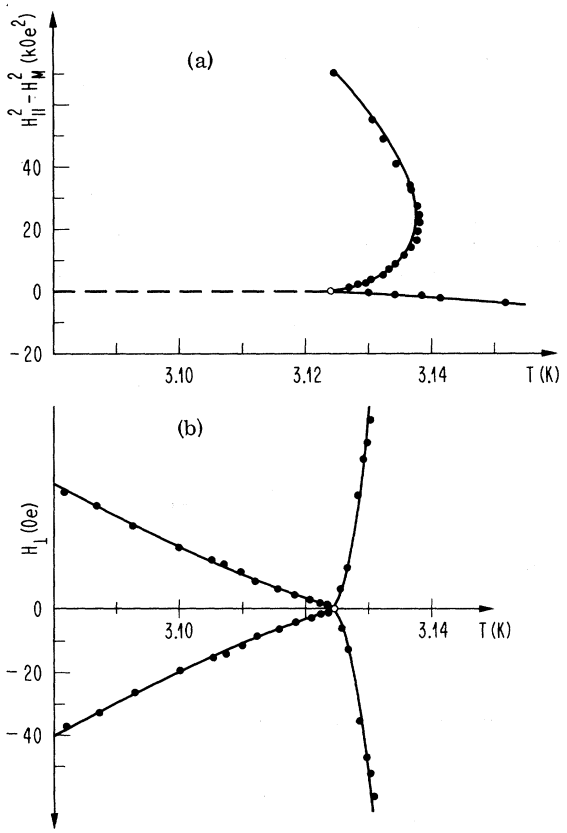

FIG. 3. Phase transitions near the multicritical point of $GdAlO_3$ at 3.1242 K, marked by the open circle. The solid lines represent the best fits to the experiment (filled circles). All fields plotted are external fields. (a) Bicritical behavior in the $H_{\parallel}$-T plane. The broken line is the SF transition line. (b) Tetracritical behavior in the $H_\perp$-T plane.

scanning $H_\perp$ at constant $H_{\parallel}$, the susceptibility is minimal for perfect alignment, as expected. But clear maxima at finite $H_\perp$ could only be observed for $H_{\parallel}$ close to the transition field to the PM state. However, an orientation dependence of $\tilde{\chi}_p$ similar to that below T_M (see Fig. 2) was observed when scanning $H_{\parallel}$ at constant $H_\perp$ but $\tilde{\chi}_p$ was independent of modulation frequency since no domain walls are present. We assumed that the maxima of $\tilde{\chi}_p$ map the two extreme critical lines in the $H_\perp$ direction. The small asymmetry of $\tilde{\chi}_p(H_\perp)$ is not explained at present.

The experimental critical lines are shown in Fig. 3. The best T_M for all three pairs of critical lines was $T_M = 3.1242$ K at $H_{M,\mathrm{ext}} = 12.494$ kOe. In the $H_{\parallel}$-T plane, the field at the bicritical lines scales with t^{φ}, where φ is the quadratic anisotropy crossover exponent.[1,2] With φ, the amplitudes of the critical lines, and the orientation of the skewed field-scaling axis[13] as fitting parameters, we obtain $\varphi = 1.17 \pm 0.02$ for the crossover exponent, and $Q = 0.9 \pm 0.2$ for the ratio of the critical line amplitudes, where the errors quoted correspond to a 10% increase in the standard deviation of reduced temperature of 2×10^{-4}. These values are in good agreement with the predicted $\varphi = 1.18$ and $Q = 1$ for an $n = 2$ component system.[1,2]

In the case of the tetracritical point, $H_\perp$ at the critical lines above T_M should also scale with t^{φ}.[10] This is in contrast to the zero-field tetracritical systems, with quartic anisotropy where $H_\perp^2 \propto t^{\varphi}$.[3,7] A least-squares fit to the experimental points gives $\varphi = 1.19 \pm 0.03$. Below T_M, $H_\perp$ at the edge of the spin-flop transition shelf scales with t^{ψ}, where $\psi = \varphi + |\varphi_v|$.[3,14] Assuming that $M_\perp \propto H_\perp$ at $T_c^{SF}(H_\perp)$ we obtain $\psi = 1.17 \pm 0.02$. If the demagnetization correction is derived from the MFA value of $M_\perp$, the resulting value of ψ is slightly changed to $\psi = 1.19 \pm 0.02$. Again, the errors indicate a 10% increase of the standard deviations $\sigma_{H_\perp} = 0.8$ Oe below T_M, and $\sigma_{H_\perp} = 2.2$ Oe above T_M. Comparison with φ obtained from the other four critical lines implies $\varphi_v = \pm 0.03$. In the $n = 3$ case, φ_v was estimated to be $0 > \varphi_v \geq -0.03$,[15] and φ_v might well have about the same value for $n = 2$[16] appropriate for $GdAlO_3$. The nonuniversal ratio of the critical line amplitudes above and below T_M is 25.

In conclusion, it has been shown experimentally that the spin-flop bicritical point of $GdAlO_3$ also appears as a tetracritical point in the $H_\perp$-T plane. The appropriate fields at the bicritical and tetracritical lines all scale with t^{1},[17] implying crossover exponents $\varphi = 1.17$ and $|\varphi_v| = 0.03$.

Stimulating discussions with A. Aharony, M. E. Fisher, and K. A. Müller and growth of the crystals by H. J. Scheel are gratefully acknowledged.

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High-Temperature Series Expansion for Complicated Level Systems*

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Based on a Green's function formalism, a high-temperature series expansion technique applicable to systems with complicated energy levels is developed. The application of the method to magnetic systems with crystal fields is discussed. As an example, we have obtained the high-temperature series expansion of the susceptibility for a spin-1 ferromagnet with anisotropic exchange interactions and with a uniaxial crystal-field potential.

In this Letter we present a high-temperature expansion technique which is applicable to systems with complicated energy levels. The original motivation for this research was to seek an accurate method to estimate the crystal-field effect on the critical temperature in *real physical* systems such as rare earths and actinides. Intensive research on these compounds has been carried out for twenty or so years.[1] Indeed, with today's experimental techniques, especially with the advancement of neutron-scattering spectroscopy, it is no longer a difficult task to measure accurately the critical temperature and the crystal-field energy scheme of a compound. In fact, even the exchange-interaction parameter can be accurately deduced. The theoretical part of the research, however, seems to lag behind in some respects. For example, when it comes to calculating the critical temperature, the mean-field approximation is used even though the accuracy of the results is known to be very poor. Recently a Green's-function approach[2] and a correlated mean-field method[3] have been proposed, and calculations of critical temperatures for spin systems with a uniaxial crystal-field potential of second degree have been carried out. The critical temperatures thus obtained are presumably quite accurate. It is not easy, however, to assess the accuracy of the results so obtained except by comparing them with the known values, nor is it a simple matter to carry out the calculations to higher orders.

Up to date the most accurate estimations of the critical temperatures are those made by high-temperature series expansion techniques.[4] Such calculations not only provide critical temperatures accurately (generally within 1% uncertainty), it allows estimations of other critical parameters if the series is sufficiently long. The applications of the high-temperature expansion techniques, however, have been limited to simple Ising and Heisenberg models. It is therefore highly desirable to develop a general high-temperature series expansion technique applicable to a more general Hamiltonian such as that which contains a crystal-field potential.