

Magnetic Ordering in PrB₆†

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We present measurements of the specific heat and resistivity ρ of PrB₆ at low temperatures. The extreme sharpness of the specific-heat anomaly at the antiferromagnetic ordering temperature indicates that PrB₆ may undergo a first-order transition of the type predicted by Wang and Cooper. A comparison of $d\rho/dT$ with the heat capacity in the critical region gives qualitative agreement with the theory of Fisher and Langer.

INTRODUCTION

Praseodymium hexaboride is a metal which orders antiferromagnetically at 6.9 K. In a previous investigation¹ an unusually sharply peaked specific-heat anomaly was observed at the ordering temperature, suggesting that perhaps there was a latent heat. Assuming the crystal field in cubic PrB₆ is dominated by the fourth-order contribution, the ground state of the Pr³⁺ ion is either a singlet (Γ_1) or a triplet (Γ_5).²

Magnetic systems with crystal-field singlet ground states were discussed first by Trammell and Bleaney³ and more recently by Wang and Cooper.⁴ The Wang-Cooper theory predicts that the magnetic ordering will be of first order under some conditions.

In order to examine this question more closely we have undertaken a measurement of the specific heat from 2 to 20 K, using techniques which are especially suited for the study of small samples and for the detection of latent heats. No latent heat was found, although the question of the order of the transition is not completely resolved.

We have also studied the resistivity anomaly at the transition, using the same sample. We correlate the temperature derivative of the resistivity, $d\rho/dT$, with the specific heat, and discuss the relevance of the correlation to the theory of resistance anomalies due to Fisher and Langer.⁵

SPECIFIC-HEAT MEASUREMENTS

The sample, prepared during the earlier study,¹ was made from Pr metal and elemental boron. The constituents were reacted on the water-cooled copper hearth of an arc furnace. X-ray diffraction patterns of powdered material gave a lattice constant $a=4.133$ Å, in excellent agreement with published values.⁶ In addition, the room-temperature resistivity of $15 \mu\Omega$ cm agrees well with the $20\text{-}\mu\Omega\text{-cm}$ value given by Post.⁷

Heat-capacity measurements were first made on the arc-melted button of PrB₆ using the pulse technique of Morin and Maita.⁸ In the region of the peak (see Fig. 1) where the heat capacity is large, the time required to establish thermal equilibrium after a heat pulse was applied was correspondingly large. It

was therefore desirable to examine the transition under conditions where the possible presence of a latent heat could be detected more easily.

In order to accomplish this two new methods were developed for measuring a small (30-mg) sample cut from the original button. The small size of the sample cuts down the internal equilibration time and minimizes thermal gradients; in addition it facilitates resistance measurements. The first of these methods is a dynamical temperature relaxation method, the other, a variant of the ac-temperature technique of Sullivan and Seidel.⁹

We use silicon bolometers to sense the temperature of the sample. These bolometers have been described elsewhere in detail.¹⁰ Briefly, they are silicon wafers with a thin diffusion-doped layer on one side. At low temperatures all of the wafer except the diffused layer is insulating. We use the layer resistance to measure the sample temperature. The sample itself is bonded to the insulating side by ultrasonic soldering.

Electrical contact and mechanical support for the bolometer is established with two 5-mil-diam gold wires. The wires are thermally anchored to a copper block whose temperature can be varied with a heater and sensed by a Au + 0.07-at.% Fe-versus-Cu thermocouple. The sample and bolometer are heated by a laser beam directed down a light pipe into the cryostat, which is evacuated and immersed in liquid helium (see Fig. 2).

In the first method, the laser beam is switched on suddenly. The time constant of the resulting thermal relaxation measures the heat capacity. If the bolometer is operated in a constant-current mode, the small, exponentially saturating temperature change produced by the incident light can be described by a time constant¹¹

$$\tau = C / (k - \alpha P), \quad (1)$$

where C is the total heat capacity of sample and bolometer, k is the thermal conductance linking bolometer to block, α is the temperature coefficient of bolometer resistance equal to $(1/R)(dR/dT)$, and P is the electrical power dissipated in the bolometer. In our case $k \gg \alpha P$, so that $\tau = C/k$, and in the absence

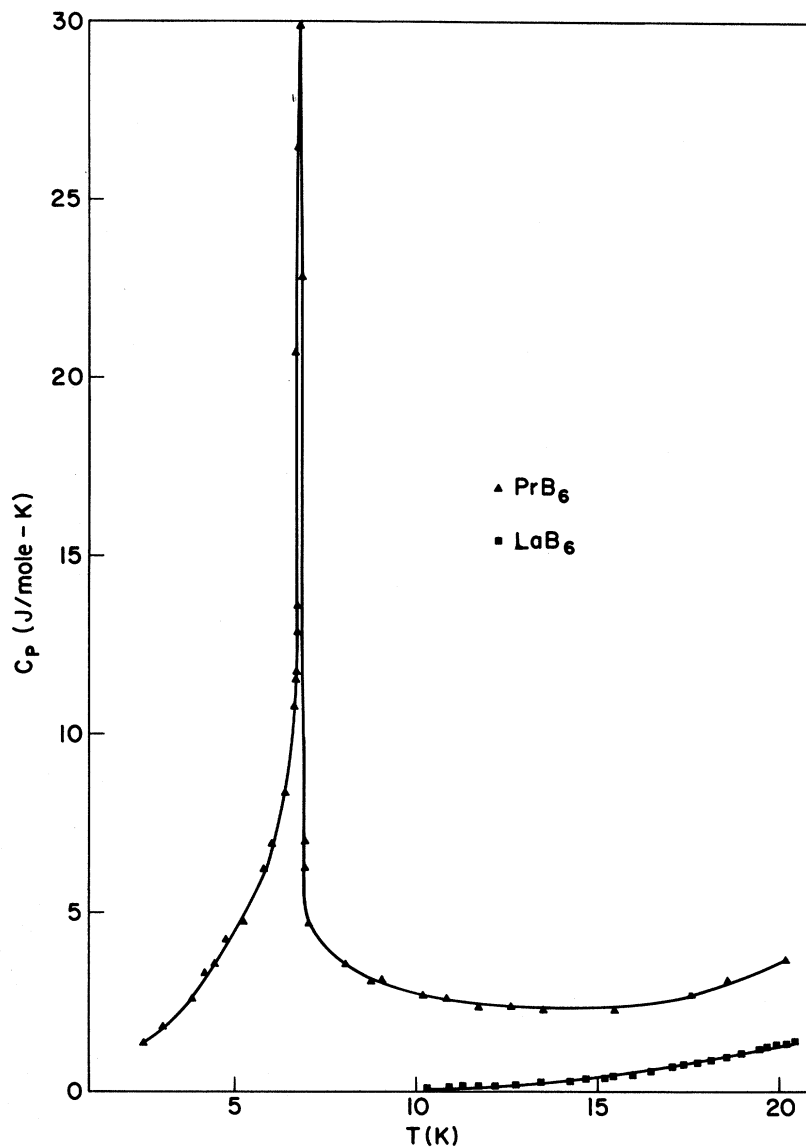


FIG. 1. Specific heat of PrB_6 from 2 to 20 K. The specific heat of LaB_6 represents contributions due to lattice vibrations and conduction electrons.

of laser light $T_{\text{bol}} = T_{\text{block}}$. The thermal conductance can be measured as a function of temperature by varying the electrical power dissipated in the bolometer

$$k = P / (T_{\text{bol}} - T_{\text{block}}). \quad (2)$$

A measurement of the time constant [Fig. 3(a)] then gives an absolute measurement of C .

The time constant, however, is a measure of the heat capacity only if thermal equilibrium between bolometer and sample is established in a time short compared to τ . To verify that this was indeed the case we turn to the second method.

Here we chop the laser light at a frequency ν (typically 5–300 Hz) and detect the ac component of the bolometer voltage using a lock-in amplifier. As Sullivan and

Seidel showed,⁹ the ν dependence of the ac signal measures both the internal time constant and C/k . Making such checks at several temperatures, we confirmed that the τ we measure is uninfluenced by internal equilibration processes.

The ac-temperature method provides a rapid and convenient means for measuring C over regions where C does not change rapidly.¹² Its shortcoming is that it does not provide an absolute determination. Most of the points we measured, except those near the transition, were done with the ac method; they were normalized at several points by absolute measurements of τ .

In the region of the transition the thermal relaxation is no longer described by a single time constant because

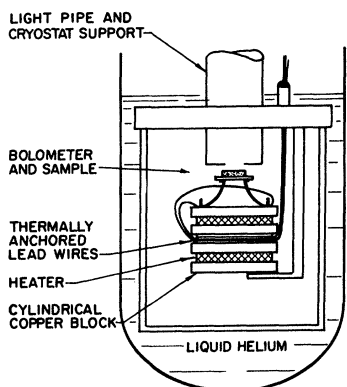


FIG. 2. Plan view of the cryostat used for measuring the specific heat by the dynamical temperature relaxation method and the ac-temperature method, as well as for measuring the resistivity.

of the rapid variation of the heat capacity. If one brings the light-off temperature close to but below the peak temperature, such that the light-on temperature is above the peak, then the temperature as a function of time takes the form shown in Fig. 3(b). The slope of this curve measures C according to

$$[1/(T_{\text{on}} - T)](dT/dt) = k/C(T). \quad (3)$$

Therefore a flat portion ($dT/dt=0$) of the curve implies a latent heat; one could estimate this latent heat by measuring the length of time for which the curve is flat. Figure 3(c) shows an expanded view of Fig. 3(b). There is always a finite slope: therefore there is no latent heat.

Our measurements are summarized in Fig. 1. For temperatures below 6.4 K and above 6.9 K, data were taken using the ac-temperature method. Points in the peak were deduced from an oscilloscope trace like Fig. 3(c), using (3). The over-all accuracy is about 5%. Points determined by the two new methods are in excellent agreement with those measured by the pulse technique, which uses the whole arc-melted button. The agreement at the peak is better than 3%. Below 10 K the heat capacity of the silicon bolometer (10.7 mg) is negligible; for points above 10 K it was subtracted using the values of Flubacher, Leadbetter, and Morrison.¹³ At all temperatures of interest the small amount of indium solder (~ 0.2 mg) used to bond the sample to the bolometer had negligible heat capacity.

For comparison we include data measured by the pulse method on the specific heat of LaB_6 . These values indicate the contributions from the hexaboride lattice and the conduction electrons, but exclude, of course, specific heat due to magnetic ordering and to the crystal-field splitting of the $4f$ electrons.

DISCUSSION

The salient feature of our data is the extremely sharp peak at the Néel temperature. If we compare the shape of the peak against specific-heat measurements in magnetic single crystals with second-order transitions, we find that, in reduced coordinates, our curve is both higher and narrower.

Pr^{3+} ions in PrB_6 are in a cubic environment with eight nearest-neighbor boron octohedra. These octohedra are known to be negatively charged^{6,7}; thus, if the boron framework were the main source of the crystal field, the fourth-order coefficient¹⁴ C_4^0 would be negative. With a predominantly fourth-order crystal field, this would imply a triplet Γ_6 ground state. Nickerson and White,¹⁵ however, have shown that the main contribution to the crystal field in the rare-earth hexaborides comes from the conduction electrons and is of opposite sign. On this basis they were able to calculate the magnetic susceptibility of CeB_6 ¹⁶; in addition, they could reproduce the crystal-field level structure of Nd^{3+} ions in NdB_6 , originally inferred from the specific heat of NdB_6 by Westrum *et al.*¹⁷

Thus, with a positive C_4^0 , the ground state of the Pr^{3+} ion in PrB_6 will be Γ_1 , the singlet. Additional evidence for this assignment may be found in the magnetic susceptibility of $\text{Y}_{0.957}\text{Pr}_{0.043}\text{B}_6$ measured by Fisk.¹⁸ Based on these data, Fisk suggested that the

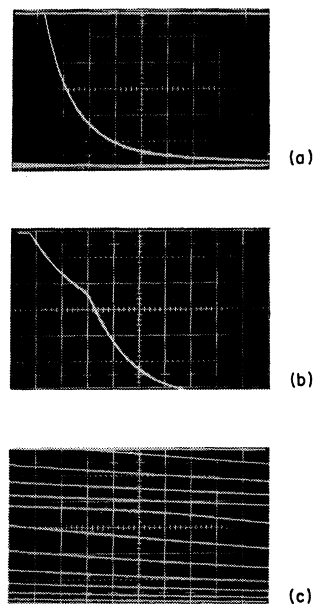


FIG. 3. Temperature as a function of time after the laser is suddenly switched on. Temperature increases downward, time to the right. The temperature swing is typically 0.1 K. (a) Normal case, in which C varies slowly on a scale of 0.1 K. Time scale 1 sec/(large division); (b) temperature swing through the transition, time scale 1 sec/(large division); (c) expanded view of (b), time scale 0.1 sec/(large division). Note that the slope of the curve is never zero during the swing.

ground state of the Pr³⁺ ion in the (isostructural) YB₆ host is a singlet.

The relevance of these considerations to the case of PrB₆ is confirmed by the value of the entropy at the ordering temperature. If the ground state were the magnetic triplet Γ_5 , the entropy under the ordering peak would be at least $R \ln 3 = 2.20$ cal/mole K. Replotting our data as c_p/T versus T , extrapolating to $T=0$ (a 2% correction), and numerically integrating up to 7 K, we find an entropy of 1.22 cal/mole K. The cutting off of the integration at 7 K is somewhat arbitrary and requires justification.

We believe that there is only a small amount of entropy above 7 K that is associated with the antiferromagnetic ordering, even though above T_N the specific heat does not fall to the lattice + conduction electron values represented by the specific heat of LaB₆. A similar excess heat capacity was found above the Néel temperature of NdB₆ by Westrum and co-workers.¹⁷ They attributed the excess to a broadened Schottky anomaly. We believe the same applies to PrB₆. The other alternative, that there is a large excess heat capacity due to short-range order above T_N , is ruled out by the sharpness of the ordering peak.^{19,20} Thus the small tail in the magnetic specific heat which we have not included in our estimate of the spin entropy would not make for an appreciable increase in the entropy.

Therefore, the low value of the entropy is compatible

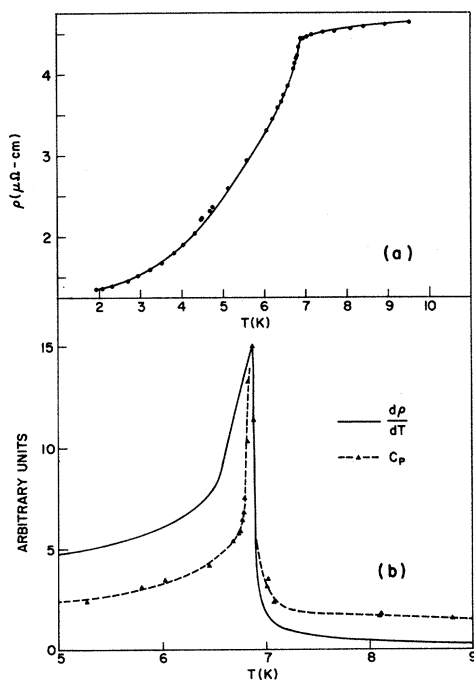


FIG. 4. (a) Resistivity of PrB₆ from 2 to 10 K; (b) Temperature derivative of the resistivity compared with the specific heat, normalized at the peak.

only with a Γ_1 ground state. A crystal-field singlet state can have a magnetic moment if the exchange interaction mixes in a higher level, the exchange field playing the role of an applied field in the theory of Van Vleck paramagnetism. In the Wang-Cooper model,⁴ this excited state is also a singlet, separated from the ground level by an energy Δ . Wang and Cooper studied such a system, assuming ferromagnetic coupling. They investigated the excitation spectrum using, first, the random-phase approximation (RPA) and, second, a more refined two-site correlation approximation (TSCA). Among their results:

(i) The magnetization (sublattice magnetization in an antiferromagnet) falls discontinuously to zero at $T_c(T_N)$. This implies that the ordering is thermodynamically of first order. In RPA this is true so long as $kT_c/\Delta \geq 0.1$. In TSCA this is always true, so long as the system orders at all.³

(ii) For $kT_c/\Delta \gtrsim 1$, the system approaches a molecular field magnet: The discontinuity in magnetization becomes small, and the transition is only weakly first order.

(iii) The Schottky anomaly in the specific heat, due to thermal excitation from the ground to the excited state, is broadened by the exchange interaction.

We have already dwelt upon the exceptional sharpness of the specific-heat peak, whose shape suggests a tendency toward a first-order transition. We leave it an open question, then, whether an unstrained single crystal of PrB₆ having perfect stoichiometry would display a latent heat of observable magnitude.²¹ Wang and Cooper⁴ note, however, that when the excited state is a triplet "the behavior becomes more complex (particularly the question of a first-order magnetic transition)."

The entropy value of 1.22 cal/mole K at 7 K indicates that the condition $kT_N/\Delta > 0.1$ is fulfilled. In fact, one can easily estimate Δ from this entropy value by considering only the ground state and the first excited state (Γ_4). We find $kT_N/\Delta = 0.36$. Taking into account only one state of the first excited triplet,³ the discontinuity in c_p at T_N is then 2 J/mole K. Our much enhanced value of ~ 25 J/mole K is further indication of the tendency toward a first-order transition.

RESISTIVITY ANOMALY

The extraordinary sharpness of the specific-heat peak prompted us to investigate the resistive anomaly at T_N , in the spirit of the Fisher-Langer theory.⁵

For the resistivity measurement we attached four gold wires to the sample. These leads were then soldered to insulated copper wires which were thermalized on the copper block. The sample was remounted on the bolometer with thermally conducting grease. The sample resistance was then measured using conventional lock-in techniques to detect the

resistive voltage. The resistivity, shown in Fig. 4(a), displays the usual growth of spin-disorder scattering as T increases to T_N , with a leveling off thereafter.

Fisher and Langer examined the exchange scattering of conduction electrons by constant localized moments. They argued that the resistive anomaly near a magnetic critical point is governed by scattering due to short-ranged spin fluctuations, and concluded on the basis of critical-exponent arguments that the derivative of the magnetic contribution to the resistivity $d\rho_m/dT$ should have the same temperature dependence as the magnetic specific heat c_m above the transition.

After plotting our data and drawing a smooth curve through the points, we determined $d\rho/dT$ graphically. The values of the slope scattered some 10–15% from the smooth curve presented in Fig. 4(b).

In Fig. 4(b) we compare $d\rho/dT$ with c_p , normalizing at the peak. There is a striking qualitative similarity. Within the 0.01 K accuracy of our absolute temperature scale, the two peaks coincide. Both $d\rho/dT$ and c_p fall off nearly vertically above the transition. As to the difference in leveling off above T_N , it was noted above that there is a large excess specific heat in this region which is not due to magnetic ordering. Since we were unable to subtract this nonmagnetic specific heat in an unambiguous way, we also did not bother to subtract the small temperature-dependent part of the nonmagnetic resistivity. Note that $d\rho/dT$ falls far below c_p for $T > T_N$. In terms of the Fisher-Langer theory, the low value of $d\rho/dT$ confirms the absence of appreciable short-range order above T_N .

Below the transition temperature $d\rho/dT$ and c_p scale, and for $4 < T < 6.7$ K, $d\rho/dT \propto c_p$ within our experimental resolution. This correlation, which is not predicted by Fisher and Langer, has recently been discussed by Zumsteg and Parks for the case of nickel.²²

Unlike the case of EuB_6 ,²³ it is not immediately obvious that the arguments of Fisher and Langer⁵ can be applied to PrB_6 because of the presence of crystal-field effects. As seen from the specific heat, the ground state of the Pr^{3+} ion in PrB_6 is nonmagnetic;

therefore the local moments are exchange induced, hence temperature dependent. In nickel the conditions of the Fisher-Langer model are not met either, because of the band character of the magnetism. However, in both cases the resistance anomaly follows the predictions of the Fisher-Langer theory, which emphasizes its qualitative generality.

CONCLUSION

We have measured the heat capacity of PrB_6 at low temperatures using heat-pulse and steady-state ac-temperature techniques. At the Néel temperature the specific heat exhibits an extremely sharp peak. We infer that the ground state of the Pr^{3+} ion is a crystal-field singlet. The model of Wang and Cooper⁴ provides a theoretical framework within which the sharpness of the peak may be interpreted as evidence of a tendency toward a first-order transition. We have, however, observed no latent heat, which might in part be due to sample imperfection.

The shape of the specific-heat anomaly, together with the fact that PrB_6 provides a clear-cut example of a system in which conduction electrons are exchange scattered by localized (exchange-induced) moments, prompted us to measure the resistive anomaly in the critical region. Comparison of $d\rho/dT$ with c_p gives qualitative agreement with the theory of Fisher and Langer⁵ for $T \geq T_N$. The presence of crystal-field effects seems not to affect seriously the conclusions of this theory.

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¹² In regions where C changes rapidly by large amounts the internal time constant, which is proportional to C , also changes rapidly. Consequently the useful range of ν in which the ac method measures the heat capacity shifts over narrow temperature ranges (see Ref. 9). In these cases the ac method is inconvenient.

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¹⁹ The internal energy of a magnetic system may be written in terms of the static spin-spin correlation function $\Gamma(R_s, T)$ as $U(T) = -\sum_s \nu_s g(R_s) \Gamma(R_s, T)$, where ν_s is the number of spins in the shell of radius R_s surrounding a local-moment site, and $g(R)$ is the Heisenberg exchange energy [see, e.g., Ref. 5]. In the case of nearest-neighbor interactions the sum reduces to $U(T) = -zg\Gamma(T)$, with z the number of neighboring magnetic moments, so that the heat capacity is $c_v = -zg d\Gamma/dT$. Thus a sharp heat-capacity peak implies that Γ is falling steeply toward zero at the ordering temperature. While this argument is correct only for nearest-neighbor coupling of constant local moments, the qualitative conclusion that short-range order is suppressed

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Domain Nucleation in Uniaxial Ferromagnets*

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We use linearized micromagnetic theory to calculate the nucleation field and the form of the nucleation mode for finite-thickness platelets of uniaxial ferromagnets in arbitrarily oriented uniform external magnetic fields. To carry out this calculation, we use the results of the theory in the limit of very thick platelets, a generalization of the switching theory of Stoner and Wohlfarth. The nucleation field and mode for smaller specimens are then found as first-order deviations from the corresponding quantities of thick platelets. The nucleation mode has the form of incipient strip domains parallel to the field component in the platelet plane.

I. INTRODUCTION

The domain structures formed in thin platelets of hexagonal ferrites and rare-earth orthoferrites have been observed in a variety of external-field geometries and demagnetization cycles.¹⁻⁹ Under many conditions, the patterns exhibit a striking regularity. Attempts to interpret the observations on the basis of micromagnetics have been confined to an analysis of domain nucleation in a field lying in the plane of the platelet^{10,11} or in a field lying along the easy axis of magnetization,^{12,13} and to a qualitative discussion of domain nucleation in a field inclined at a small angle to this plane.¹⁴

In the present work, we extend the theory to demagnetization in an arbitrarily oriented field. The theory is based on the linearized micromagnetic equations which treat deviations from uniform magnetization as small quantities. This micromagnetic problem is a self-consistent-field problem in the sense that the linearized equations contain the unknown orientations of the uniform magnetization at nucleation, and thus, in effect, require their own solution in order to be formulated.¹⁵ The calculation uses, as a starting point, the recently obtained solution for the nucleation field in the limit of thick specimens.¹⁶ Using these results as the zeroth-order approximation, the nucleation field and mode for smaller samples may be found as first-order deviations by treating the free-energy minimization as an eigenvalue problem.

In Sec. II, we summarize the procedure (given in

detail in Ref. 16) for obtaining the nucleation field function or switching threshold curves in the limit of thick specimens. This is done both for the convenience of reference and to provide a basis for showing, in a later section, the equivalence of this approach to the linearized micromagnetic equations under the appropriate limiting assumptions. Section III contains the solution of the micromagnetic problem of the uniaxial plate in an arbitrarily oriented uniform external magnetic field. It is shown that the nucleation mode has the form of incipient strip domains parallel to the component of field in the platelet plane. This invalidates the conjecture¹⁴ that a checkerboard pattern may be nucleated. The micromagnetic solution also provides the switching threshold curve for thinner specimens.

II. SWITCHING THRESHOLD CURVE FOR THICK UNIAxIAL FERROMAGNETS

We use a coordinate system whose axes coincide with the principal axes of an ellipsoidal specimen.¹⁶ The easy direction of magnetization is assumed to coincide with the x axis, the applied field lies in the x - z plane at an angle ϕ from the z axis, and the uniform magnetization lies in the x - z plane at an angle θ from the z axis (Fig. 1).¹⁷

The domain nucleation curve is obtained by equating to zero both the first and second variations of the free energy with respect to the magnetization vector \mathbf{M} . The calculation differs from the usual switching-

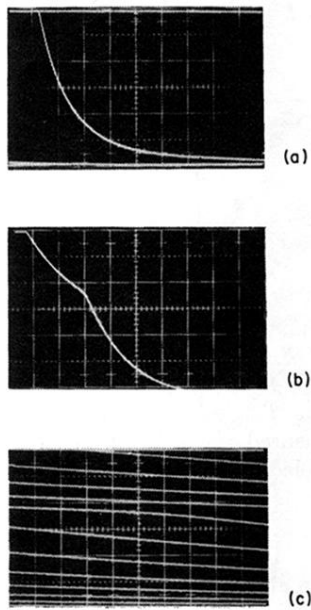


FIG. 3. Temperature as a function of time after the laser is suddenly switched on. Temperature increases downward, time to the right. The temperature swing is typically 0.1 K. (a) Normal case, in which C varies slowly on a scale of 0.1 K. Time scale 1 sec/(large division); (b) temperature swing through the transition, time scale 1 sec/(large division); (c) expanded view of (b), time scale 0.1 sec/(large division). Note that the slope of the curve is never zero during the swing.