Second-Order Nature of the Spin-Reorientation Phase Transitions in $YbFeO_3$†

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The specific heat of $YbFeO_3$ in the range 1.5-15 K exhibits spin-reorientation and Schottky anomalies. The magnetic field dependence of the reorientation anomalies is consistent with phenomenological descriptions which predict that two second-order phase transitions occur in the reorientation process. These transitions are quite different from typical first-order or λ-type phase transitions. The Schottky anomalies give values for the exchange splitting of the ground state of the Yb^{3+} ions.

In many of the ferrimagnetic rare-earth orthoferrites including $YbFeO_3$ the direction of the easy axis of magnetization is known to change from one crystallographic axis to another as the temperature is raised.[1] These so-called spin-reorientation phase transitions have recently been described phenomenologically[2-4] and with a microscopic model.[5] The descriptions all predict that the magnetization may change direction in either of two possible manners: (1) The easy axis jumps abruptly in a first-order phase transition, possibly exhibiting thermal hysteresis of the the transition temperature, or (2) as the temperature is raised the easy axis starts to rotate at one definite temperature T_L and ceases rotation when it reaches a new orientation at another definite temperature T_H. Second-order phase transitions occur at T_L and T_H. The rotation angle θ is a continuous function of but $d\theta/dT$ has infinite discontinuities at T_L and T_H. Our specific-heat measurements on $YbFeO_3$ were made in an effort to test the phenomenological description and in fact our results strongly support the second alternative mentioned above. Our results contrast with earlier specific-heat measurements at spin-reorientation transitions which either have shown no evidence of the phase transition[6,7] or have revealed a single peak in the specific heat which is not resolved well enough to lead to a unique interpretation.[8]

Our sample was a flux-grown single crystal weighing about 0.8 g and roughly cubical in shape. The temperature dependence of its specific heat is shown in Fig. 1. The spin-reorientation anomalies are the abrupt changes in specific heat which occur at about 6.5 K and 7.8 K.

In the reorientation region, the properties of the rare-earth orthoferrites have been found to be extremely sensitive to the orientation of applied magnetic fields.[9] Thus for our measurements in applied fields we oriented our sample with the x-z plane approximately in the plane of the magnetic field. The field was then rotated until an extremum in the magnetocaloric effect was found. In this way the x and z axes could be located to within $\frac{1}{2}°$ while the sample was inside our calorimeter. The y direction of $YbFeO_3$ is magnetically hard for both rare-earth and iron sublattices[10]; therefore, its orientation with respect to the field is not critical. In the orienting process and subsequent measurements no evidence of hysteresis was ever seen.

The application of a magnetic field H_x along the x axis produces three effects predicted by phenomenological models: (1) The onset temperature for spin reorientation, T_L, is shifted towards higher temperatures. The shift is proportional to H_x (at least for modest fields). (2) The abrupt jump in specific heat at T_L is reduced as H_x is increased. (3) The second abrupt jump in specific heat at T_H becomes a broad decline.

These effects result because the application of H_x is equivalent to the addition of an independent anisotropy field. The field favors the low-tem-

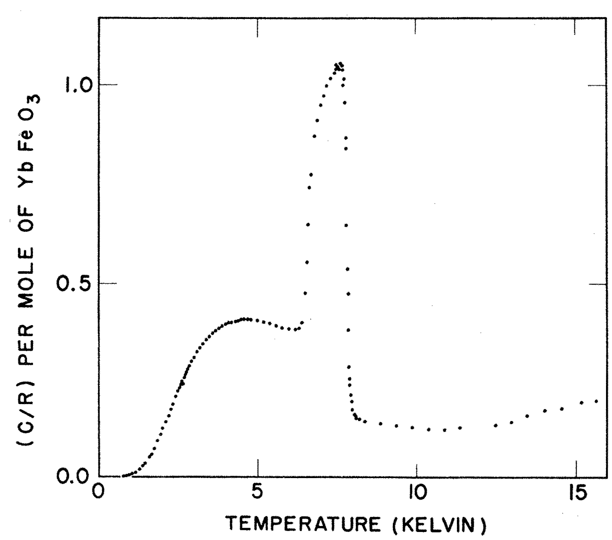

Fig. 1. Specific heat of $YbFeO_3$ from 0.4 to 15 K. Data from three different runs are included.

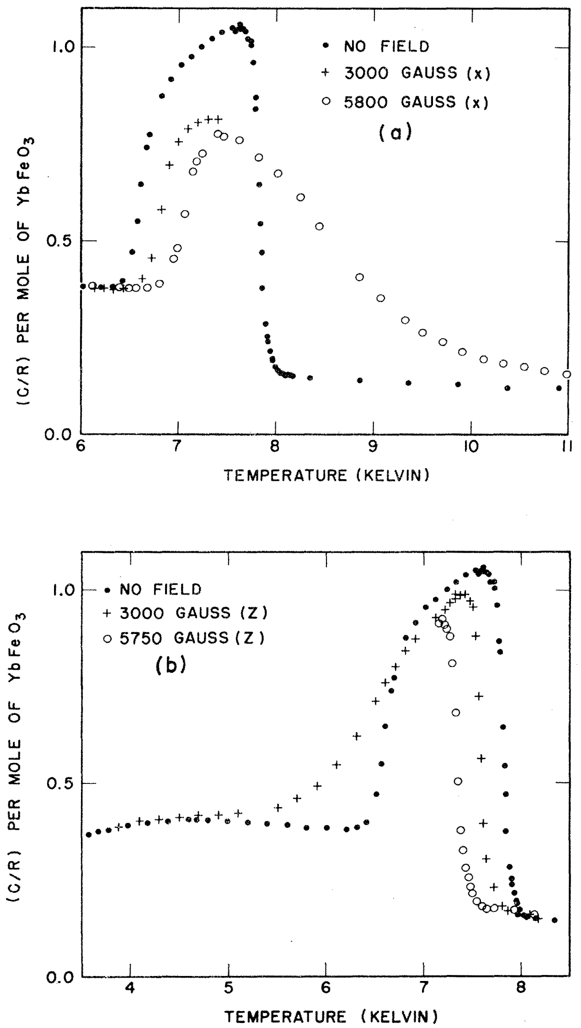

Fig. 2. Specific heat of $YbFeO_3$ in applied magnetic fields. (a) Specific heat with field applied along the x axis. (b) Specific heat with field along the z axis. The data scatter at the peak of the "no-field" curve reflects differences between different runs. For each run the data fall on a smoother curve.

perature phase causing the low-temperature phase to "hang on" longer. When reorientation finally does begin, the rate of change of $\sin\theta$ with temperature is diminshed. This leads to a reduced jump in specific heat. When H_x is present there is a component of magnetization in the x direction at all temperatures. Thus the reorientation towards the z axis never becomes complete, and hence there is no longer a second jump in the specific heat marking the completion of reorientation. All of these predicted effects are visible in Fig. 2(a). They are quite distinct from the effects of a magnetic field on a typical first-order or λ-type phase transition. They support the applicability of a mean-field description to the spin-reorientation transitions.

If we take T_L to be the temperature at which the specific heat is increasing most rapidly (about where the value $0.6R$ is attained), we find from the data shown and from data at 1000 G (not shown) that T_L is a linear function of H_x with a slope $dT_L/dH_x = 0.088 \pm 0.006$ K/kG. A graph of T_L vs H_x was extrapolated to $T_L = 6.55$ K at $H_x = 0$. This is our estimate for T_L in the absence of a field.

In an entirely analogous manner the application of a magnetic field H_z along the z axis leads to a reduction in T_H which is in proportion to H_z. It also leads to a reduction of the jump in specific heat at T_H and the disappearance of the transition at T_L. These effects are visible in Fig. 2(b).

Figure 2(b) displays the data taken with a field in the z direction. As predicted, T_H is reduced and the transition at T_L is broadened. We find that $dT_H/dH_z = 0.085 \pm 0.003$ K/kG and $T_H = 7.83$ K at $H_z = 0$ from the data shown and data at 1000 G. There is some evidence from the magnetization measurements of Clark and Belson[10] that the same linear dependence of T_H on H_z we observe extends to a field of at least 35 kG where T_H would be 4.5 K.

One of the predictions of the phenomenological model of Horner and Varma[2] is that $-dT_H/dH_z = dT_L/dH_x$. The fact that our results are consistent with this prediction is at first sight surprising since in their model the magnitude of the magnetization is independent of temperature while in fact the total magnetization of $YbFeO_3$ is known to decrease by roughly 40 % as the temperature is raised through the spin-reorientation region.[11] To identify $YbFeO_3$ with their model we may consider the nearly antiferromagnetic iron sublattices to be the system undergoing spin reorientation. Beaulieu[11] argues on the basis of a detailed model of $YbFeO_3$ and his magnetization studies that the small net iron moment does not change size in the reorientation region. This moment is in an effective field resulting from an exchange interaction with the Yb^{3+} ions as well as any applied magnetic field. The result $-dT_L/dH_x = dT_H/dH_z$ must imply that the application of a given magnetic field to the x direction in the low-temperature phase or to the z direction in the high-temperature phase will produce the same change in the magnitude of the effective field on the iron sublattices.

The simplest phenomenological model (e.g., Horner-Varma[2]) predicts that the ratio of the jumps in the specific heat at T_L and T_H is simply T_L/T_H. We observe a much smaller ratio which is consistent with the presence of a smaller exchange field at T_H than at T_L. This is expected if, as Beaulieu[11] argues, the dominant exchange constant is independent of temperature and the total magnetization decreases substantially through the reorientation region.

Outside the reorientation region, the zero-field specific-heat data from 8.2 to 15.5 K may be accurately described by the expression

$$C/R = 5\times 233 \times (T/320)^3 + (a/2T)^2. \qquad (1)$$

An order of magnitude estimate suggests the ferrimagnetic spin-wave contribution to the specific heat is much smaller than the lattice contribution. We recall that there are five atoms per $YbFeO_3$ molecule and find that the Debye temperature of our sample is approximately 320 K. We may subtract a Debye background from our data and estimate the magnetic contribution to the entropy of the Yb^{3+} ions. [We assume the $(a/2T)^2$ term in Eq. (1) may be extrapolated to high temperatures.] We find that $\Delta S/R = 0.650 \pm 0.007$. This is 6% less than the value ln2 expected from the complete ordering of a Kramers doublet in each mole. This 6% difference is puzzling. Our accurate measurements (±1%) extend down to 1.5 K. We were led to make additional measurements from 0.4 to 1.5 K but did not find any significant addition to the entropy. We are tempted to assume that 6% of the Yb in our sample is magnetically inactive for an unknown reason. A similar tentative conclusion has been drawn from specific-heat measurements of $DyFeO_3$.[6] (The Dy^{3+} ions undergo a λ-type transition at 3.7 K. The reported entropy change was 7% less than ln2.) Earlier measurements[3] on $YbFeO_3$ indicate an entropy change several percent smaller than the change reported here.

On the assumption that 7% of our sample is magnetically inactive, the coefficient a in Eq. (1) for a fully active sample becomes 6.0 K. This is close to the value 6.5 ± 0.3 K measured with far-infrared spectroscopy[12] and attributed to the ground-state splitting of the Yb^{3+} ion in the high-temperature phase of $YbFeO_3$.

As Fig. 1 suggests, the specific-heat data in the range from 1.5 to 6.0 K approximate a Schottky anomaly. To match the peak of the specific heat at 4.6 K to a Schottky anomaly arising from a two-level system one would have to assume that 9% of the sample is magnetically inactive. Even then, the decline in the specific heat on either side of 4.6 K is not quite as rapid as that expected from a Schottky anomaly. The peak at 4.6 K corresponds to a level splitting of 11.0 K. This splitting does not agree well with a 7.9-K line seen spectroscopically[12] and attributed to the exchange splitting of the Yb^{3+} ion in the low-temperature magnetic phase.

In summary, the results described above show that the spin-reorientation phenomenon in $YbFeO_3$ is well described by the Landau treatment of second-order phase transitions. First-order and λ-type phase transitions are ruled out. The behavior in an applied magnetic field, namely the linear shift of the transitions and the decrease in size of the anomaly without an accompanying change in shape, provides the definitive evidence for this conclusion.

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[1]R. L. White, J. Appl. Phys. 40, 1061 (1969).

[2]H. Horner and C. M. Varma, Phys. Rev. Lett. 20, 845 (1968).

[3]J. Sivardiere, Solid State Commun. 7, 1555 (1969).

[4]J. R. Shane, Phys. Rev. Lett. 20, 728, 1020(E) (1968).

[5]L. M. Levinson, M. Luban, and S. Shtrikman, Phys. Rev. 187, 715 (1969).

[6]A. Berton and B. Sharon, J. Appl. Phys. 39, 1367 (1968).

[7]R. W. Houghton, thesis, University of Minnesota, 1968 (unpublished).

[8]J. Peyrard and J. Sivardiere, Solid State Commun. 7, 605 (1969).

[9]R. C. LeCraw, R. Wolfe, E. M. Gyorgy, F. B. Hagedorn, J. C. Hensel, and J. P. Remeika, J. Appl. Phys. 39, 1019 (1968).

[10]A. E. Clark and H. S. Belson, in Proceedings of the Sixteenth Annual Conference on Magnetism and Magnetic Materials, November 1970 (to be published).

[11]T. J. Beaulieu, thesis, Stanford University, 1967 (unpublished).

[12]K. B. Aring as reported in Ref. 1.