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SPECIFIC HEAT MEASUREMENTS AT THE
SPIN-REORIENTATION TRANSITION
IN YbFeO_3

A THESIS
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ABSTRACT

The specific heat temperature dependence of a single crystal orthoferrite, YbFeO_3 , was measured from 2.55 K to 15.7 K. Measurements were made with no external magnetic field, and then with magnetic fields applied along the c-axis and a-axis having a field intensity of 1000, 3000, and 5800 Oe. Two specific heat anomalies were observed in this temperature range. One of these was a Schottky anomaly caused by the ground state exchange splitting of the Yb^{3+} , and the other was due to spin-reorientation of the Fe sublattice.

The spin-reorientation anomaly is well described by the phenomenological model of Horner and Varma¹ if one adds a magnetic interaction term $\vec{M} \cdot \vec{H}_r$, where $\vec{H}_r$ and $|\vec{M}|$ are constant in the transition region. The field $\vec{H}_r$ seems to be an effective residual field of about 430 G at an angle of 5° from the c-axis; however, in an applied field, $\vec{H}_a$, of the above intensities the parallel component of $\vec{H}_r$ appears to vanish. The magnetic interaction term becomes $\vec{M} \cdot \vec{H}_e$, where $\vec{H}_e \neq \vec{H}_a + \vec{H}_r$.

From the specific heat measurements, two characteristic temperatures², T_H and T_L , associated with the Horner and Varma model can be identified with the onset of spin-reorientation in YbFeO_3 .

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CHAPTER 1

INTRODUCTION

Magnetization is defined as the net magnetic moment per unit volume, and the net magnetic moment is determined by the degree of electron spin alignment. In many materials the magnetization is not an isotropic response to an external field, that is there exists a certain crystalline axis along which the electron moments prefer to align. This direction in the crystal is called the easy-axis of magnetization.

In many rare-earth orthoferrites, such as YbFeO_3 , it is observed that the easy-axis of magnetization changes from one crystal orientation to another orientation as the temperature of the material is raised or lowered through a transition region.³ The reorientation may take place suddenly with possible hysteresis of the transition temperature in a first-order phase transition, or reorientation may start at a lower transition temperature, T_L , and change continuously to its new orientation at a higher transition temperature, T_H , with second-order phase transitions at T_L and T_H .

The energy that causes the spins to align in a specific crystal direction is called the anisotropy energy.⁴ The modeled form of this energy which can explain continuous spin-reorientation has both a second-order anisotropy and a fourth-order anisotropy term.³ The model which will be looked at in detail which includes this fourth-order term is that of Horner

and Varma.¹

The free energy model of Horner and Varma is a phenomenological description of spin-reorientation systems. The free energy is expanded in a power series in the sine of an angle Θ ,

$$F = F_0 + K_1(T) \sin^2 \Theta + K_2(T) \sin^4 \Theta,$$

where Θ is the angle between the c-axis and the direction of magnetization, and where K_1 and K_2 are functions of temperature. The series is carried out only to the fourth-order term, and the odd powers are dropped for reasons of symmetry. In a material with orthorhombic structure,⁷ this expansion is believed to hold well.

The model of Horner and Varma is similar in many respects to the free energy expansion of Landau's description of phase transitions of the second kind. It is worth while comparing the two before going on into the details of the free energy model.

In the Landau theory it is assumed that near the phase transition a thermodynamic potential can be expanded in a power series in an order parameter that is small in the neighborhood of the phase transition. Such an expansion takes on the form⁸

$$\phi(P, T, \eta) = \phi_0 + \alpha \eta + A \eta^2 + B \eta^3 + C \eta^4 + \dots,$$

where α , A , B and C are functions of P and T . If the states where $\eta = 0$ and $\eta \neq 0$ are of different symmetry, it can be shown that $\alpha \neq 0$.⁸ Above the transition $\eta = 0$, $A > 0$ and below the transition $\eta \neq 0$ and $A < 0$ in order to have a stable state. This

implies that at the transition $A(T_c) = 0$. This, in fact, defines the transition temperature. The third-order term is generally considered identically zero and $C(P,T) > 0$. The expansion then takes the form

$$\phi(P,T,\eta) = \phi_0(P,T) + A\eta^2 + C\eta^4.$$

Comparing the Horner and Varma model to the Landau expansion above, it is seen that the term K_1 corresponds to $A(P,T)$, and K_2 corresponds to $C(P,T)$. In the Horner and Varma model it is assumed that K_2 is positive and temperature independent and that

$$K_1 = 2K_2 [(T-T_2)/(T_2-T_1)].$$

One would expect to define the order parameter as $\sin(\Theta)$ instead of Θ in accordance with the Landau theory, and the corresponding transition temperature T_2 defined by the zero of K_1 ; however, by letting Θ be the order parameter, two transition temperatures can be defined.

Defining Θ as an order parameter is somewhat misleading. An order parameter of zero implies complete randomness in some physical phenomenon of interest throughout the sample material, and a non-zero order parameter is a measure of ordering of this physical phenomenon. In YbFeO_3 it is not clear that the degree of ordering just above T_H is any different than just below T_H . It would seem, therefore, one should be cautious about making an exact analogy between the Horner and Varma model and Landau theory of second-order phase transitions.

The fourth-order equation describing anisotropy energy

can also be obtained from a microscopic model.¹⁰ Levinson, Luban, and Shtrikman write the spin Hamiltonian H as

$$H = H_0 + H_a,$$

where

$$H_0 = - \sum_{\substack{i,j \\ i \neq j}} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

is the isotropic Heisenberg Hamiltonian, and

$$H_a = \sum_i \kappa_2 (S_i^z)^2 + \sum_i \kappa_4 (S_i^z)^4 + \sum_{\substack{i,j \\ i \neq j}} \kappa_{ij} S_i^z S_j^z$$

represents the anisotropic contribution. By writing H_a in terms of spherical harmonic operators and transforming to a new set of spherical harmonics, Levinson et al. arrive at an explicit expression for H_a in terms of spherical harmonics,

$$\langle H_a \rangle = A_0(T) + A_2(T) \sin^2 \Theta + A_4 \sin^4 \Theta.$$

Writing the free energy as

$$F = F_0 + \langle H_a \rangle$$

one has the same expression as Horner and Varma.

The fourth-order phenomenological model, in addition to describing continuous spin reorientation, also predicts a discontinuity in the specific heat at T_L and T_H . Specific heat measurements on polycrystalline ErFeO_3 were unsuccessful in demonstrating this effect.³ A single crystal of YbFeO_3 was loaned to W. Weyhmann by Professor R.L. White to be used in testing the phenomenological model of Horner and Varma for the specific heat discontinuities. That which follows is a description

of the specific heat measurements of YbFeO_3 in the temperature range of spin-reorientation, and a comparison of the data to the phenomenological model of Horner and Varma.

CHAPTER II

THE PHENOMENOLOGICAL MODEL

2.1 HORNER and VARMA MODEL: NO FIELD

The model used to describe this experiment is the one offered by Horner and Varma as given above. The condition that the state described is stable is that the free energy be a minimum, that is

$$\partial f / \partial \Theta = 0 \text{ and } \partial^2 f / \partial \Theta^2 > 0 .$$

The first of these conditions gives the result¹

$$2K_1 \sin(\Theta) \cos(\Theta) + 4K_2 \sin^3(\Theta) \cos(\Theta) = 0 ,$$

and the second condition yields

$$2K_1 (2 \cos^2(\Theta) - 1) + 4K_2 \sin^2(\Theta) (4 \cos^2(\Theta) - 1) > 0 .$$

There are three solutions to $\partial f / \partial \Theta = 0$:

$$\Theta_1 = 0, \quad \Theta_2 = \pi/2, \text{ and } \Theta_3 = \arcsin \sqrt{-K_1/2K_2} .$$

In order that the solution be stable, the second condition requires that $K_1 > 0$ for Θ_1 , $K_1 < -2K_2$ for Θ_2 , and that $-2K_1(2 + K_1/K_2) > 0$ for Θ_3 . This last condition is satisfied for $K_1 < 0$ and $K_2 > 0$, but note that it is also satisfied for $K_1 > 0$ and $K_2 < 0$.

The temperature dependence of the free energy and Θ are

are determined by the behavior of $K_1(T)$ and $K_2(T)$. In this model it is assumed that K_2 is a positive constant as in the Landau theory discussed above, and that $K_1(T)$ is linear in the transition region having the form

$$K_1 = 2K_2[(T - T_H)/(T_H - T_L)] ,$$

where $T_H > T_L$. In keeping with Landau theory $K_1 = 0$ defines the transition T_H above which the order parameter Θ is zero. However, there is a second transition temperature, T_L , defined by $K_1 = -2K_2$. At this temperature and below Θ is $\pi/2$.

In summary, the above model describes a system in which the easy-axis of magnetization is at $\pi/2$ as the temperature is increased from zero to T_L . Then the easy-axis rotates continuously from $\pi/2$ to zero at T_H , and for $T > T_H$, Θ remains at zero. See figure 1.

The application of this model to the experiment is the derived behavior of the specific heat. The free energy is written in terms of temperature and magnetization, hence the corresponding specific heat is

$$C_H = -T(\partial^2 F / \partial T^2)_H . \quad (2.1)$$

The specific heat calculations in the three regions of interest corresponding to Θ_1 , Θ_2 , and Θ_3 are as follows: In the first region $\Theta_1 = 0$, $T > T_H$, and the free energy is

$$F = F_0 .$$

The specific heat is given by

Fig. 1. The angle of magnetization as a function of temperature derived from the Horner and Varma model.

Fig. 2. Specific heat from the Horner and Varma model, $H = 0$.

$$C_M^I = -T(\partial^2 F_0 / \partial T^2)_M.$$

In the second region $\Theta_2 = \pi/2$, $T < T_L$, and the free energy is

$$F = F_0 + \frac{2K_2(T - T_H)}{T_H - T_L} + K_2.$$

It follows that

$$C_M^{II} = -T(\partial^2 F_0 / \partial T^2)_M.$$

In the transition region, $T_L < T < T_H$,

$$F = F_0 - K_2(T^2 - 2TT_H + T_H^2)/(\Delta T)^2,$$

where $\Delta T = T_H - T_L$. The resulting specific heat is given by

$$C_M^{III} = -T(\partial^2 F_0 / \partial T^2)_M + 2K_2T/(\Delta T)^2.$$

An examination of the specific heat as a function of temperature shows that a discontinuous jump in specific heat of $2K_2T_L/(\Delta T)^2$ occurs at $T = T_L$ and $-2K_2T_H/(\Delta T)^2$ at $T = T_H$. See figure 2. Both discontinuities are representative of Landau-type second-order phase transitions.

2.2 APPLIED FIELDS: SPECIAL CASE

When an external magnetic field is applied to the crystal, one would expect a different behavior in the specific heat as a function of temperature than with no field applied. To under-

stand the system's response to an applied field in terms of the phenomenological model, an $\vec{M} \cdot \vec{H}$ term is added to the free energy. This additional term can be written as

$$-\vec{M} \cdot \vec{H} = -MH \cos(\theta_M - \theta_H),$$

where θ_M and θ_H are the angle from the c-axis for the magnetization and applied field respectively.

Before considering the general case of an arbitrary θ_H , it is of special interest to let $\theta_H = 0$ and $\pi/2$. Differentiation of the free energy with respect to θ_M and setting θ_H to zero gives

$$\partial F / \partial \theta_M = 2K_1 \sin \theta_M \cos \theta_M + 4K_2 \sin^3 \theta_M \cos \theta_M + MH \sin \theta_M = 0.$$

This equation has one solution for $\theta_M = 0$, and another solution given implicitly by

$$\cos^2 \theta_M (2K_1 + 4K_2 \sin^2 \theta_M) + MH = 0. \quad (2.2)$$

It can be seen that $\theta_M = \pi/2$ is not a solution when a magnetic field is applied along the c-axis. One also discovers that a new transition temperature, T_H , is found by using the linear form for $K_1(T)$ in Eq. (2.2). The new T_H is given by

$$T_H(H) = T_H(0) - (MH/4K_2)(\Delta T). \quad (2.3)$$

Likewise, differentiating the free energy as above and setting $\theta_H = \pi/2$, one finds that $\theta_M = \pi/2$ is a solution and that $\theta_M = 0$ is not. The lower transition temperature is given by

$$T_L(H) = T_L(0) + (MH/4K_2)\Delta T. \quad (2.4)$$

In summary, applying a magnetic field along the c-axis lowers T_H and smooths out the lower transition; whereas, applying a magnetic field along the a-axis raises T_L and smooths out the higher transition temperature. See figure 1.

2.3 APPLIED FIELDS: GENERAL CASE

In order to compare the data with the model, the general case of arbitrary Θ_H must be solved. Since we are interested in departure from the normal specific heat, F_0 in the free energy expression will be set equal to zero. If f_1 , f_2 , and f_3 are $\sin^2 \Theta_M$, $\sin^4 \Theta_M$, and $\cos(\Theta_M - \Theta_H)$ respectively, then the free energy is

$$F = K_1(T) f_1(\Theta_M(T)) + K_2 f_2(\Theta_M(T)) - MH f_3(\Theta_M(T), \Theta_H).$$

The specific heat is given by Eq. (2.1), and the problem at hand is to find the second derivative of F with respect to T . This derivative is given by the following expression:

$$\begin{aligned} \frac{\partial^2 F}{\partial T^2} = & \frac{\partial^2 K_1}{\partial T^2} f_1 + 2 \frac{\partial K_1}{\partial T} \frac{\partial f_1}{\partial T} + K_1 \frac{\partial^2 f_1}{\partial T^2} \\ & + K_2 \frac{\partial^2 f_2}{\partial T^2} - MH \frac{\partial^2 f_3}{\partial T^2}, \end{aligned}$$

and to be able to solve this equation, the chain rule must be used as given by

$$\frac{\partial f_i}{\partial T} = \frac{\partial f_i}{\partial \theta_M} \frac{\partial \theta_M}{\partial T} ,$$

and

$$\frac{\partial^2 f_i}{\partial T^2} = \frac{\partial^2 f_i}{\partial \theta_M^2} \left(\frac{\partial \theta_M}{\partial T} \right)^2 + \frac{\partial f_i}{\partial \theta_M} \frac{\partial^2 \theta_M}{\partial T^2} .$$

The result of a rather lengthy calculation is

$$\begin{aligned} \frac{\partial^2 F}{\partial T^2} = & \frac{4K_2}{\Delta T} \sin 2\theta_M \left(\frac{d\theta_M}{dT} \right) \\ & + \frac{2K_2}{\Delta T} (T - T_H) \left[2 \cos 2\theta_M \left(\frac{d\theta_M}{dT} \right)^2 + \sin 2\theta_M \left(\frac{d^2\theta_M}{dT^2} \right) \right] \\ & + 2K_2 \sin^2 \theta_M \left[(8 \cos^2 \theta_M - 2) \left(\frac{d\theta_M}{dT} \right)^2 \right. \\ & \quad \left. + 2 \sin \theta_M \cos \theta_M \left(\frac{d^2\theta_M}{dT^2} \right) \right] \\ & + MH \left[\cos(\theta_M - \theta_H) \left(\frac{d\theta_M}{dT} \right)^2 + \sin(\theta_M - \theta_H) \left(\frac{d^2\theta_M}{dT^2} \right) \right] . \quad (2.5) \end{aligned}$$

The specific heat equation is solved once the expressions for $d\theta_M/dT$ and $d^2\theta_M/dT^2$ are determined.

From the requirement that $\partial F/\partial \theta_M = 0$, an implicit equation for θ_M as a function of T can be written as

$$\sin^2 \theta_M + \frac{MH}{4K_2} \left[\frac{\cos \theta_H}{\cos \theta_M} - \frac{\sin \theta_H}{\sin \theta_M} \right] = \frac{T_H - T}{\Delta T}. \quad (2.6)$$

By letting $MH/4K_2 = A$, $\cos \theta_H = H_x$, and $\sin \theta_H = H_y$; and by differentiating Eq. (2.6) implicitly, the expression for $d\theta_M/dT$ becomes

$$\begin{aligned} \frac{d\theta_M}{dT} = & -\frac{1}{\Delta T} \left[2 \sin \theta_M \cos \theta_M + \frac{A H_x \sin \theta_M}{\cos^2 \theta_M} \right. \\ & \left. + \frac{A H_y \cos \theta_M}{\sin^2 \theta_M} \right]^{-1}. \end{aligned} \quad (2.7)$$

One more differentiation gives

$$\begin{aligned} \frac{d^2 \theta_M}{dT^2} = & \frac{1}{\Delta T} \left[2 \cos 2\theta_M + \frac{A H_x (\sin^2 \theta_M + 1)}{\cos^3 \theta_M} \right. \\ & \left. - \frac{A H_y (\cos^2 \theta_M + 1)}{\sin^3 \theta_M} \right] \left[\sin 2\theta_M + \frac{A H_x \sin \theta_M}{\cos^2 \theta_M} \right. \\ & \left. + \frac{A H_y \cos \theta_M}{\sin^2 \theta_M} \right]^{-2}. \end{aligned} \quad (2.8)$$

The specific heat for the general case is given by combining equations (2.5), (2.7), and (2.8) into Eq. (2.1). These are the equations used later in the computer simulation of specific heat as a function of $\vec{H}_a$ and T .

CHAPTER III

EXPERIMENTAL PROCEDURE

3.1 DESCRIPTION of SAMPLE and EQUIPMENT

The sample used in this experiment is a single crystal of the rare-earth orthoferrite YbFeO_3 . The crystal is a parallelepiped measuring $6 \times 4\frac{1}{2} \times 4$ mm, and it has a mass of 0.8136 gm. The molecular weight of YbFeO_3 is 276.89, hence the amount of sample is 2.938×10^{-3} moles.

The crystal axes are shown with respect to the crystal shape in figure 3. The longest axis is the c-axis; the a-axis bisects the obtuse angle; and the b-axis bisects the acute angle.⁵ the a-b face of the crystal is almost rectangular. The acute and obtuse angles are within 2° of a right angle.

The sample was held in a 6.822 gm copper block as shown in figure 4. The copper block was held in place by string attached to the block through holes in the tabs, and then it was attached to three posts in the flange in order to isolate the sample from the 4.2 K flange temperature. Tilting the block 45° allowed alignment of the magnetic field with the c- or a-axis by just rotating the magnet about the vertical axis. By observing a magnetocaloric effect while rotating the magnet, the alignment of the applied field and the crystal axes was assured to within $\frac{1}{2}^\circ$.

Two heater wires were wound around the copper block. The auxiliary heater was used to maintain a temperature base above

Fig.3. The crystal shape of YbFeO_3 and indicated crystal axes.

Fig. 4. Crystal holder assembly.

the ambient liquid helium temperature by balancing the heat loss through the lead wires. The test heater was used to input a small amount of energy, typically 0.8 m Joules, to the sample. The heater wires were 203.7 Ω /ft Evenohm which made connection to the electrical feed-through by way of a 3 cm, 49 Ω /ft manganin wire. This provided additional thermal resistance to the copper block. Also, a teflon plug was inserted into the tube that led to the vacuum can to prevent the sample from seeing the 300 K radiation from the top of the assembly.

A germanium cryoresistor was inserted into the copper block to be used as a thermometer. The calibration of the CryoCal thermometer was done by the manufacturer,⁹ and their computer fit generated a resistance - temperature function of the form

$$\ln R = \sum_{n=1}^8 \frac{A_n}{n} (\ln T)^n. \quad (3.1)$$

Since resistance was the parameter measured, the above equation presented a slight problem in determining the temperature. This will be discussed later.

The crystal and holder assembly was housed in a vacuum and surrounded by a liquid helium bath as shown in figure 5. By pumping on the liquid helium we were able to obtain temperatures in the bath below the λ - temperature of 2.17 K. To complete the experimental station, a large electromagnet, on tracks, was rolled into place and centered on the dewar assembly.

This concludes a brief description of the mechanical assembly of the experiment. The remaining part of this chapter will discuss

Fig. 5. System Mechanical Assembly.

the type of measurements taken to obtain our data, the electronics involved in these measurements, and the equations used in calculating the heat capacity.

The measured heat capacity of the sample is given by

$$C = \Delta E / \Delta T ,$$

where ΔE is the energy given to the sample by the test heater, and ΔT is the measured temperature change. It is assumed that ΔT is small enough that the above expression for C is equal to the true heat capacity midway in the temperature interval, ΔT . Since the resistance of the CryoCal indicates the temperature, the above equation for C becomes

$$C = \Delta E / \Delta R (dR/dT)_{\bar{R}} , \quad (3.2)$$

where dR/dT as determined from Eq. (3.1) is

$$dR/dT = (R/T) \sum_{n=1}^4 n A_n (\ln T)^{n-1} , \quad (3.3)$$

and $\bar{R}$ is evaluated midway in the resistance change. In order to measure the heat capacity, all that is needed is a way of establishing ΔE and measuring the corresponding ΔR . The above heat capacity really includes that of the copper block, CryoCal and grease used to hold the sample in the block. This background correction will be discussed below.

The energy given to the sample and holder assembly is

$$\Delta E = I^2 R_H \Delta t , \quad (3.4)$$

where I is the current in the effective test heater resistance, R_H , and Δt is the time the current flowed in the circuit. The time, Δt , was controlled by the gated output of a Monsanto 104 A

counter. This gate signal enabled a reed relay assembly that closed the circuit. The current was controlled by a ten turn potentiometer, and it was measured by the voltage generated across a $1\text{ k}\Omega \pm 0.02\%$ series resistor.

The resistance of the CryoCal was measured in an ac (100 Hz) bridge system using a PAR lockin amplifier, a precision decade resistance box, and a chart recorder. The data recorded was the starting and final resistance values of the decade box and an ohms/division calibration on the chart recorder taken before each data point. From this information ΔR and $\bar{R}$ were determined. A block diagram of the experimental system is shown in figure 6.

3.2 DATA REDUCTION and ERROR ANALYSIS

Errors and corrections in calculating the specific heat of YbFeO_3 due to the magnetic transition come from several sources. Specifically, there are corrections to be made for resistance measurements and background, and there are uncertainties in the change in energy, ΔE .

There are two corrections to be made on the measured resistance. One of the corrections to be made is for the effects of the strong magnetic fields on the ac resistance of the CryoCal. This correction for magnetoresistance was determined by Prof. M. Moldover. Three temperatures, 15.28 K, 10.88 K, and 6.87 K were used in this test, and the resistance vs applied field was observed at each temperature. However, the measurements were not completely reversible. Since this effect was more evident at lower temperatures, it was probably due to eddy

Fig. 6. Experimental system for measuring heat capacity of YbFeO_3 .

current heating of the copper block. As a result of these data, an empirical relationship between $R_{ac}(0)$ and $R_{ac}(H)$ is given by

$$R_{ac}(0) = R_{ac}(H) [1 - (2.254 - 11.877 R_{ac}(H)^{-\frac{1}{2}}) H^2 \times 10^{-10}]$$

and

$$R_{ac}(0) = R_{ac}(H) [1 - (2.245 - 5.939 R_{ac}(H)^{-\frac{1}{2}}) H^2 \times 10^{-10}] ,$$

where H is in gauss and R_{ac} is the ac bridge value in ohms.

The correction factor above agrees with the resistance-magnetic field data to within 10%. The largest correction made,

$(R_{ac}(0) - R_{ac}(H))/R_{ac}(0)$, is about 0.7%, and the corresponding temperature error is about 2mK, or about 0.03% in the temperature region of interest.

Since the manufacture's calibration of the CryoCal is based on a four point dc resistance, a second correction for resistance is a R_{ac} to R_{dc} conversion. This conversion is based on data taken by both G. Sjolander and M. Moldover. After working with some rather complicated empirical relations, a very simple linear form,

$$R_{dc} = 0.9822 R_{ac} - 13.0 ,$$

was used with good agreement to the data. This formula gave predicted results to within $\pm 0.2\%$ over the resistance range from 3000 Ω to 195 Ω , 4°K to beyond 15°K respectively, with a resulting temperature uncertainty of about 0.1%.

Once the dc resistance was calculated, there remained the

problem of inverting Eq. (3.1) to find the temperature. Of the several methods possible, it was decided that the least expensive approach would be to generate a table of $\ln R$ for $2.00 < T < 16.00$ K in steps of 0.01 K. For a given value of $\ln R$ a binary search of this table was generated, and a linear interpolation between two values of temperature, one above and the other below the given $\ln R$, gave the corresponding value of T .

The energy given to the sample and holder, Eq. (3.4), can also be written

$$\Delta E = (V^2/R_s) R_H \Delta t ,$$

where V is the voltage generated across the resistance standard, R_s . See figure 6. R_H and Δt are defined as before. The greatest source of error comes from the uncertainty in the effective test heater resistance, R_H . The effective resistance at liquid helium temperatures, as measured by M. Moldover, was 265.66Ω . This value was determined by measuring the heater resistance and then the lead resistance. It was assumed that half the power generated in the leads went into the sample. This value represents an upper bound, and R_H could be as low as 264Ω . These estimates lead to an error of about 0.7%, and it is the largest single error in the experiment. The errors associated with V , R_s , and Δt are all on the order of 0.1%, and the resulting overall error in ΔE is about 0.74%.

The background was determined by heat capacity measurements without the crystal in the holder. A least squares fit to the data gave the coefficients to the equation

$$H_{\text{bkg}} = \sum_{n=0}^5 A_n T^n$$

in the temperature range 3.1 K to greater than 15 K. This computed background was subtracted from the total heat capacity, and the result divided by the number of moles of YbFeO_3 to give the net specific heat of the sample.

CHAPTER IV

RESULTS and CONCLUSION

The data presented is representative of 285 points taken in 13 runs. Figure 7 shows the results of three runs in the temperature range of 2.5 K to 15.7 K with no external field applied. Two sharp transitions in the specific heat are seen at 6.6 K and 7.8 K. These transitions mark the beginning and end of the spin-reorientation region. A second anomaly at 4.6 K is a Schottky anomaly due to exchange splitting of the ground state Yb^{3+} ions. The investigation of the Schottky anomaly was done by M. Moldover, and it is discussed in reference 2.

External magnetic fields of approximately 1000, 3000, and 5800 Oe were applied along the *a*- and *c*-axes to see if the transition temperatures responded as predicted by the model, Eq. (2.3) and (2.4). Figures 10 and 11 show the results of these measurements. The details of these figures will be discussed later.

Since each transition has a finite slope, the transition itself can not be used to define the transition temperature. The method used was to define the transition temperature as the point of greatest slope (this turns out not to identify the transition temperature, but it is the best starting point) and to make a graph of $T_L(H)$ and $T_H(H)$ vs applied magnetic field.

Fig. 7. Specific Heat of YbFeO_3 with no magnetic field applied external to the sample.

A linear extrapolation to zero field gives the values of $6.59 \pm .04$ K and $7.82 \pm .03$ K for T_L and T_H respectively. The values reported earlier² were 6.55 K and 7.83 K. The slopes of the extrapolated lines are $dT_H/dH_z = .085 \pm .003$ K/kG and $dT_L/dH_x = .088 \pm .006$ K/kG.

A more detailed look at the zero field specific heat anomaly is shown in figure 8. The dashed line is the final fit to the data using the model of Horner and Varma with assumed zero field. The shape of the data as compared to the simple zero field model suggests trying to add a term $\vec{M} \cdot \vec{H}_r$, where $\vec{H}_r$ is an effective residual field. Since $dT_L/dH_x \approx dT_H/dH_z$, it is assumed that $|\vec{M}|$ is effectively constant in the transition region. This is in contradiction to data of T. J. Beaulieu.⁶ He shows that $|\vec{M}|$ changes from 12.8 to 8.8 emu/gm in the temperature range 6 to 8 K. This is a decrease in $|\vec{M}|$ of 30% as the sample is heated through the transition region. See reference 2. Nevertheless, in the following model the effective value of $|\vec{M}|$ is assumed constant as indicated by our data for dT/dH .

The equations used in the general model are (2.1), (2.5), (2.7), and (2.8). In order to implement this model, quantitative values for $K_2/\Delta T$ and M/K_2 are needed. To find approximate starting values for these terms, one can use experimental values given by the Horner and Varma model with zero field. This model predicts a jump in specific heat at T_H given by

$$\Delta C_H = -2K_2 T_H / (\Delta T)^2 .$$

From the data $\Delta C_H/R = 0.907$ and $\Delta T = 1.28$ K using T_L and T_H

Fig. 8. Specific heat of YbFeO_3 in a zero applied field. The dashed lines represent the zero³ field Horner and Varma model.

as originally reported.² This gives the value for K_2 as 0.789×10^7 ergs/mole. The value for M/K_2 can be obtained from Eq. (2.3) and the data, that is

$$dT_H/dH_2 = MAT/4K_2 = 0.085 \text{ K/kg}.$$

With these starting values, various values of H_r and Θ_r were tried, and with the aid of a CDC 6600, specific heat calculations were made. By matching the slope of the transition and general shape of the computed specific heat to the data, good results were obtained for $H_r = 430$ G and $\Theta_r = 5^\circ$. By using this fitting method it was found that a better value for T_L would be 6.615 K. The original value for T_H of 7.83 K remains the same. The final values for the parameters are listed as follows:

T_L	T_H	ΔT	$ \vec{N} $	K_2
6.615 K	7.83 K	1.215 K	7.6 emu/gm	0.750×10^7 ergs/mole
				or 2.04×10^6 ergs/cm ³
	H_r	Θ_r		
	430 G	5°		

The general model fit to the data in zero applied field, using the above parameters, is shown in figure 9. The dashed lines in figure 8 shows the fit for the same parameters except H_r is zero. With no residual fields, the model predicts that $\Delta C_H/R = .9555$ instead of the value .907 obtained from the data. The predicted value for $\Delta C_L/R$ is .8073.

Figures 10 and 11 show the effect of the applied magnetic

Fig. 9. Specific heat of YbFeO_3 in a zero applied field. The dashed line represents the general model that includes a residual field of 430 G at an angle of 5° from the c-axis.

fields along the c and a-axes respectively. The dashed lines represent the fit of the model to the data. The transitions themselves agree very well in temperature and slope, but in the remaining part of the curve where the other transition smooths out, especially for $H_a \hat{z}$, the fit is less successful. The vertical dashed lines indicate the predicted $T_L(H)$ and $T_H(H)$ based on the linear equations (2.3) and (2.4), and the horizontal dashed lines indicate where T_L and T_H cross the curve. The point to be made is that the transition $T(H)$ can not be identified by the maximum slope in the curve nor by a single value of C/R in the presence of a residual field not aligned with a crystalline axis. With off axis fields the identification of a single transition temperature becomes less meaningful; although, it is a useful parameter to be used in the model.

In figures 10 and 11 the transition curve and slope are calculated in the general model by the addition of the $\vec{M} \cdot \vec{H}_e$ term, where $\vec{H}_e$ is an effective field. It turns out that $\vec{H}_e \neq \vec{H}_a + \vec{H}_r$ for the model but rather $\vec{H}_e = \vec{H}_a + (\vec{H}_r)_\perp$, where $(\vec{H}_r)_\perp$ is the residual field component orthogonal to $\vec{H}_a$ in the orthogonal direction. That is, if $\vec{H}_a = H_a \hat{z}$ then

$$\vec{H}_e = H_a \hat{z} + (H_r)_x \hat{x}.$$

At first this seems like a strange kind of arithmetic, but it seems to be built into the construction of the model. The problem lies in the way T_H is determined. Instead of plotting $T_H(H_a)$ vs H_a , one should plot $T_H(\vec{H}_a + \vec{H}_r)$ vs the argument.

When this is done, a new $T_H(0)$ is found to be 7.85 K instead

Fig. 10. Specific heat of YbFeO_3 with magnetic fields aligned along the c-axis. The dashed lines are the general model fit as explained in the text.

Fig. 11. Specific heat of YbFeO_3 with magnetic fields aligned along the a -axis. The dashed lines are the general model fit as explained in the text.

of 7.83 K. The difficulty of finding $T_H(H)$ from the data has been pointed out, and in fact, both values for $T_H(0)$ are within the uncertainty of each other. The value of dT/dH remains the same for both cases. As of this writing, it is unclear whether or not the externally applied field adds to the effective residual field.

The general model and the resulting parameters were obtained by a hand fit from less than a dozen computer runs. Perhaps what should be done is to let the parameters of the model vary, including M , and fit the data with minimizing techniques to find the best values.

In conclusion, it is seen that two transition temperatures, T_L and T_H , can be identified with the beginning and ending of a continuous spin-reorientation of the iron sublattice. At these temperatures there is a jump in the specific heat consistent with a second-order phase transition. The introduction of an effective residual field not only describes the finite slope in the specific heat transition at T_L and T_H , but also is in agreement with the observed higher ground state splitting of the Yb^{3+} ions.²

The problem as to how $\vec{H}_g$ and $\vec{H}_r$ add is yet to be solved. Also, the bad fit of the model to the trailing part of the specific heat curve in the presence of an applied magnetic field suggests that there is a more complicated behavior in the system than is built into the model.

Aside from a few details, it is concluded that the behavior of specific heat data of YbFeO_3 is well described by the model.

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