Thermodynamic and Magnetic Properties of Ytterbium Iron Garnet

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(Received April 14, 1961)

Some low-temperature thermodynamic and magnetic properties of ytterbium iron garnet have been calculated as functions of temperature and orientation of the magnetization. The calculation is based on the spectroscopically determined splittings of the ground-state doublets of the ytterbium ions. The calculation accounts for the principal features of the observed torques and specific heats. It predicts a compensation point in the magnetization near 7.7°K which has since been observed. It also predicts a temperature change accompanying an adiabatic rotation in a saturating magnetic field.

INTRODUCTION

CONSIDERABLE progress has been made in the recent past in explaining the gross magnetic and thermodynamic properties of the insulating ferromagnets, especially the ferrites and yttrium iron garnet (YIG), in terms of the spectroscopic ground states of the individual constituent atoms. The insulating ferromagnets are primarily ionic crystals, implying that the electrons giving rise to the interesting magnetic properties remain largely localized on specific atoms. Many features of these materials can therefore be described by simple summations over the individual ion properties, without difficult band-structure problems arising as is the case in the ferromagnetic metals.

The rare-earth garnets, however, have not previously been satisfactorily treated on a single-ion model, owing primarily to the absence of adequate information on the detailed spectroscopic structure of the rare-earth ions in these crystals. Recently optical spectroscopic and paramagnetic resonance studies on the Yb^{3+} ion in the garnet structure have yielded sufficient information that a calculation of the properties of ytterbium iron garnet (YbIG) based on a single-ion model is now possible. The present paper presents the nature and results of this calculation.

THE CALCULATION

Wickersheim has determined the exchange splittings of the ytterbium ground-state doublets from spectroscopic studies of single-crystalline ytterbium iron garnet, $5Fe_2O_3 \cdot 3Yb_2O_3$.[1] The ytterbium ions occupy six inequivalent sites in this lattice and the ground-state doublet of each site is split anisotropically by the exchange field. For the magnetization lying in the (110) plane the number of inequivalent sites is reduced to the four whose splittings are shown in Fig. 1. The splittings are found to be nearly independent of temperature over the temperature range 4°K to 78°K. Since the first excited states lie approximately 500 wave numbers above the ground-state doublet, only the ground doublet of each Yb^{3+} ion is occupied at low temperatures and each of the six ytterbium sublattices may be taken to be a two-state system. The partition function and internal magnetic energy per ion are easily calculated for such a two-level system:

$$Z(\Theta,T)=2\exp(U_0/kT)\cosh[-\Delta(\Theta)/2kT], \quad (1)$$

$$U(\Theta,T)=\tfrac{1}{2}\Delta(\Theta)\tanh(-\Delta(\Theta)/2kT), \quad (2)$$

where Δ is the anisotropic exchange splitting of the ground doublet and the other symbols have their usual meaning. From these quantities can be calculated the total thermodynamic properties of the system such as total magnetic free energy of the ytterbium sublattice

$$F(\Theta,T)=\sum_i F_i=\sum_i -n_i kT\ln Z_i, \quad (3)$$

where n_i is the number of ions on the crystallographic site of type i and the summation is over the different kinds of sites.

Other properties such as magnetic torques, specific heats, etc., can be calculated in a similar fashion as detailed below. These calculations have been carried out using an analytical expression found by Wickersheim[1] for the Yb^{3+} energy splittings as functions of orientation

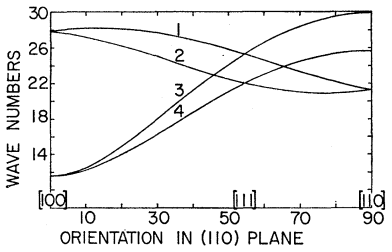

FIG. 1. The splittings of the four ground-state doublets of Yb^{3+} in ytterbium iron garnet.

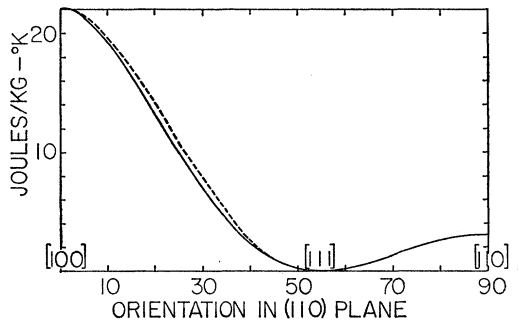

FIG. 2. The free energy of the ytterbium sublattice at 0°K. The solid curve is calculated from Eq. (3). The dashed curve is calculated from the anisotropy constants.

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[1] K. A. Wickersheim, Phys. Rev. 122, 1376 (1961).

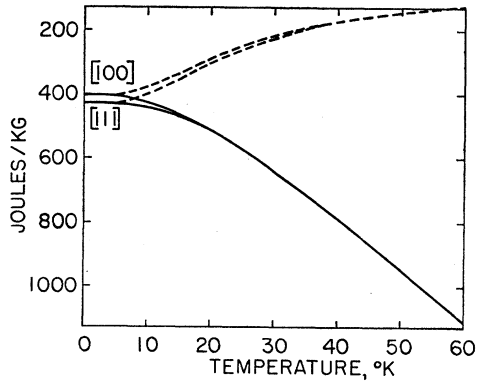

FIG. 3. The free energy (solid curves) and the internal energy of the ytterbium sublattice.

of the magnetization in the (110) plane. Numerical results have been obtained for a net of angles and temperatures using an IBM 709 computer. Some of the more informative results of these calculations are plotted in Figs. 2 through 14.

Figure 2 gives the magnetic free energy at 0°K due to the Yb^{3+} ions as calculated from Eq. (3). An arbitrary

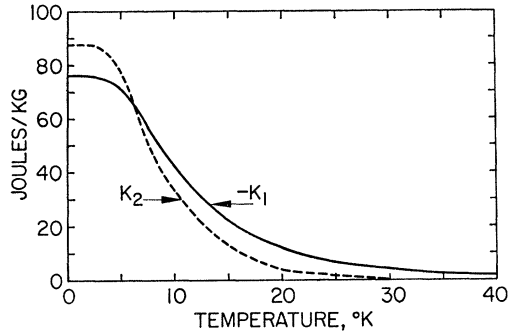

FIG. 4. The anisotropy constants.

constant is involved in the calculation of the free energy so ΔF, the variation in free energy with angle, is plotted. Figure 3 gives the variation of free energy and of internal energy as a function of temperature for two major-axis orientations of the magnetization. The anisotropic part of the free energy of a cubic material can be written

$$\delta F = K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_1^2\alpha_3^2)+K_2(\alpha_1^2\alpha_2^2\alpha_3^2)+\cdots, \quad (4)$$

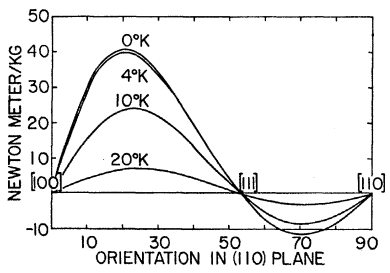

FIG. 5. The torque at various temperatures.

where $\delta F(\Theta)=F(\Theta,T)-F_{[100]}(T)$, K_1 and K_2 are the first and second anisotropy constants, the α_j are direction cosines of the magnetization with respect to the [100] direction, and higher order terms are ignored. Values of K_1 and K_2 chosen to make Eq. (4) predict accurately the calculated free energy in the three principal crystallographic directions are shown in Fig. 4. The angular variation of free energy at 0°K calculated from this two-constant approximation is also plotted in Fig. 2. It is worthy to note that at low temperatures K_1 is some two orders of magnitude smaller for pure YIG than for YbIG, and K_2 is negligible.

The torques required to align the magnetization in a given crystallographic direction can be calculated from

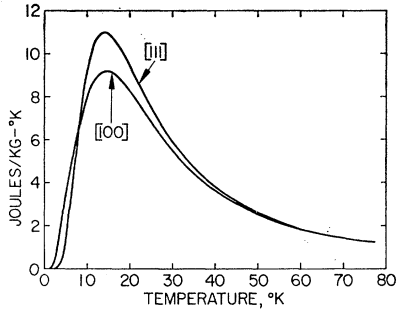

FIG. 6. The contribution to the specific heat due to the magnetization of the ytterbium sublattice.

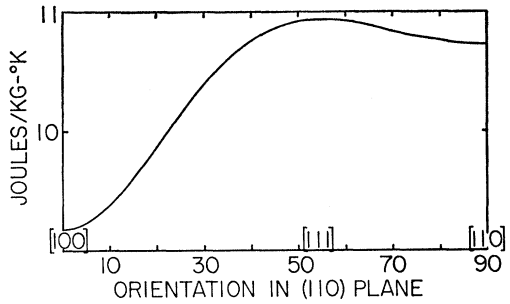

FIG. 7. The anisotropy of the magnetic specific heat at 15°K.

the free energy given in Eq. (3):

$$L(\Theta,T)=\sum_i \left.\frac{\partial F_i}{\partial\Theta}\right|_T = \sum_i \frac{n_i}{2}\frac{d\Delta_i}{d\Theta}\tanh\left(-\frac{\Delta_i}{2kT}\right), \quad (5)$$

where the summation is again over inequivalent sites whose contributions here tend to cancel. Torques calculated from this expression are plotted in Fig. 5.

The specific heat of the Yb^{3+} lattice can be calculated from the internal energy

$$C_\Theta=\left.\frac{\partial U}{\partial T}\right|_\Theta = \frac{1}{4kT^2}\sum_i n_i\Delta_i^2\,\mathrm{sech}^2\left(-\frac{\Delta_i}{2kT}\right), \quad (6)$$

and is presented in Figs. 6 and 7 as a function of temper-

ature and of orientation. Knowing total specific heats (as discussed below) and the angular dependence of free energy, one can calculate the cooling or heating of a sample upon adiabatic rotation of the magnetization:

$$\left.\frac{\partial T}{\partial \Theta}\right|_s = \frac{T}{C_\Theta}\frac{\partial L}{\partial T}\bigg|_\Theta = \frac{1}{C_\Theta}\sum_i \frac{d\Delta_i}{d\Theta}\frac{n_i\Delta_i}{4kT}\operatorname{sech}^2\left(-\frac{\Delta_i}{2kT}\right). \quad (7)$$

The resultant cooling is substantial, and is plotted in Figs. 8 and 9.

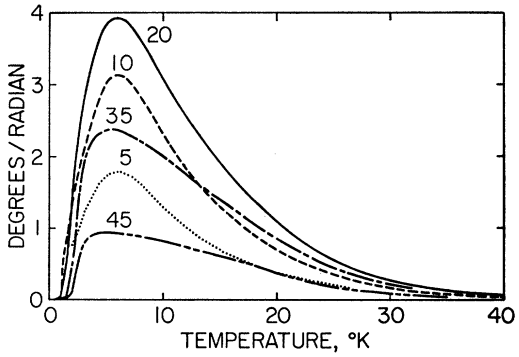

FIG. 8. The rate of cooling predicted for adiabatic rotation in a saturating magnetic field. The different curves show rates for various orientations in the (110) plane.

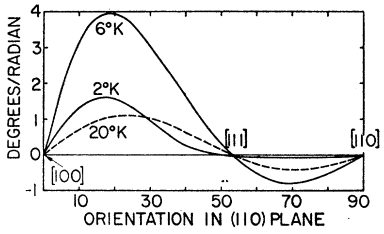

FIG. 9. Cooling rates for adiabatic rotation of the magnetization.

Finally, with one additional input, one can calculate the magnetic moment per ion of the ytterbium lattice.

$$M = \sum_i g_i \tanh(-\Delta_i/2kT), \quad (8)$$

where the newly introduced quantity, g_i, is the anisotropic g factor of the Yb^{3+} ion's lowest-lying doublet. For this calculation we have used the g tensor measured for Yb^{3+} in the yttrium gallium garnet by paramagnetic resonance techniques,[2] and the results are given in Figs. 10 and 11. The magnetization of the Yb^{3+} lattice is oppositely directed to that of the iron lattice, which has a nominal low-temperature value of 10 Bohr magnetons per formula weight. Hence our calculations predict a compensation temperature of 7.7°K, and considerable anisotropy of the net YbIG magnetization at low temperatures.

[2] J. W. Carson and R. L. White, J. Appl. Phys. **31**, 53S (1960). D. Boakes, G. Garton, D. Ryan, and W. Wolf, Proc. Phys. Soc. (London) **74**, 663 (1959).

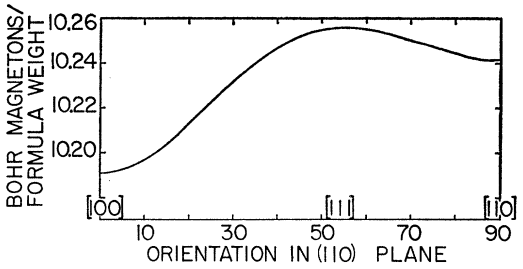

FIG. 10. The magnetic moment of the ytterbium sublattice at 0°K.

COMPARISON WITH EXPERIMENT

The theoretical results on YbIG can be compared with a number of experimental data. Measurements of the magnetic anisotropy in YbIG or in ytterbium-doped YIG have been made by both microwave and static torque techniques. The interpretation of the microwave data is at present unclear (problems arise as to the relative relaxation times of the precessing magnetization involved) so we shall make comparison with the static torque measurements of Pearson et al.[3] The experimental results of Pearson on a YIG sphere containing about two atomic percent substitution of Yb^{3+} for Y^{3+} are given in Fig. 12, together with the theoretical curve

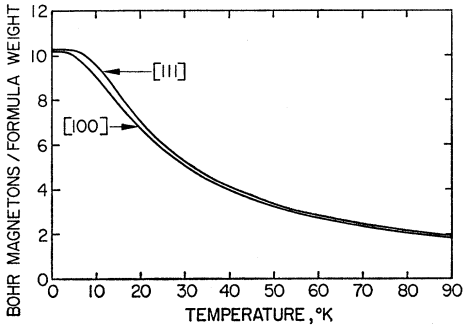

FIG. 11. The magnetic moment of the ytterbium sublattice.

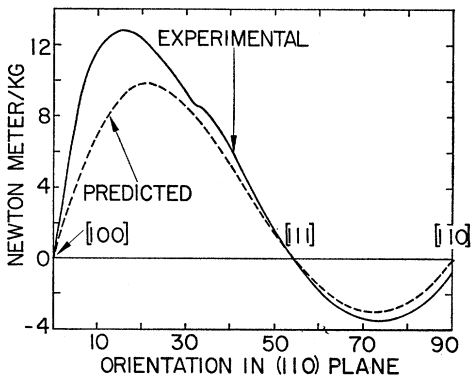

FIG. 12. Comparison of the experimental torque from reference 3 (solid curve) with our prediction (dashed curve) for a sample having 1.9% ytterbium in YIG. The temperature is 1.5°K.

[3] R. F. Pearson (private communication).

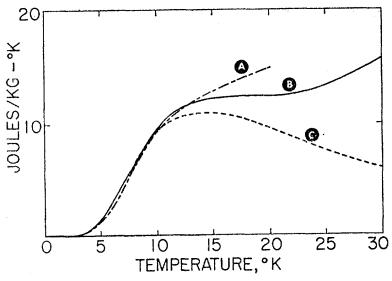

FIG. 13. Comparison of the measured specific heat from reference 4 (curve A), with our prediction (curve B). The prediction is the sum of the magnetic specific heat (curve C) and a reasonable T^3 phonon contribution.

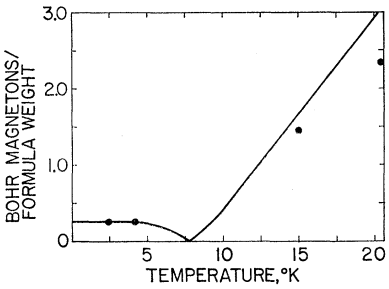

FIG. 14. The total predicted magnetic moment. The experimental points shown are from reference 6. These points taken alone do not indicate the presence of the predicted compensation point. A subsequent experiment has confirmed its presence near 7.6°K.

predicted on the basis of the preceding calculations. The total theoretical curve was obtained by adding 2% of the torque predicted by Eq. (5) to the torque curves for pure YIG. The torque contributed by the anisotropy of the pure YIG is about 20% of the total predicted value. The calculated torque is nearly correct in angular form and about 20% smaller in magnitude than the observed torque. Two possibilities for the discrepancy suggest themselves. First, the exact environment of the Yb^{3+} ion dilutely incorporated in YIG may be somewhat different than in YbIG, in which the spectroscopic splittings were determined. Second, the lattice distortion which minimizes the magnetoelastic energy has not been taken into account. A further important difference between the theoretical and experimental torques is the absence in the theoretical curve of the kink in anisotropy at about 30° from the [100]. This kink shows up as a large resonant field anomaly in the microwave resonance experiment, and its explanation probably requires an additional conceptual input above the single-ion model utilized here.

The specific heat of polycrystalline YbIG has been measured by Meyer and Harris,[4] who were able to deduce from it the correct mean value for the splitting in the easy [111] direction. Their results are shown in Fig. 13 together with our theoretical value for the [111] direction. For comparison purposes it is necessary to add to the calculated Yb^{3+} magnetic specific heat the specific heats attributable to the remainder of the lattice. In Fig. 13 only the phonon contribution has been added. The coefficient for this T^3 contribution has been taken as 3.6 ergs/g deg^4, a value which appears reasonable considering typical values for YIG.[5] The remaining discrepancy, not apparently attributable to spin waves, is currently unexplained. (For the purpose of computing the cooling effect mentioned above, a larger value of the T^3 coefficient, 7 ergs/g deg^4, was used to give a better empirical approximation of the measured specific heat.)

THE COMPENSATION POINT

In order to confirm the existence of the predicted compensation point in the magnetization, the following simple experiment was performed. A small single crystal sample of YbIG was suspended near a small permanent magnet. A calibrated carbon resistor thermometer was suspended in the same horizontal plane. This assembly was moved through the temperature gradient above a liquid helium bath. Below 5.9°K and above 8.6°K the sample was observed to attach itself to the magnet. Between these temperatures it was observed to swing free of the magnet. Assuming that the actual magnetization curve has the same form as the calculated curve, this measurement indicates a compensation point about 0.2°K below the predicted value of 7.7°K. This discrepancy, while within the experimental errors, may be due to the inaccuracy of the assumed g tensors. Figure 14 shows the calculated net magnetization together with Pauthenet's measured values.[6]

Experiments are also in progress in this laboratory to measure the cooling of a YbIG crystal upon adiabatic rotation in a magnetic field.

ACKNOWLEDGMENTS

The authors wish to thank Dr. K. A. Wickersheim and Prof. M. Tinkham for useful and stimulating discussions of the problem. They wish also to thank Dr. R. F. Pearson for permission to quote his experimental results and J. W. Carson for supplying the calibrated carbon resistance thermometer. The YbIG crystal used in the compensation point experiment was grown by Dr. R. A. Lefever and co-workers.

[4] Horst Meyer and A. B. Harris, J. Appl. Phys. **31**, 49S (1960).
[5] S. S. Shinozaki, Phys. Rev. **122**, 388 (1961).
[6] R. Pauthenet, Doctoral thesis, University of Grenoble, 1958 (unpublished).