Calorimetric Study of Yttrium and Rare-Earth Iron Garnets between 0.4 and 4.5°K*

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(Received 3 April 1969)

We present the results of a calorimetric study on iron-garnet polycrystalline samples of Y, Eu, Tm, Sm, and Yb between 0.4 and 4.2°K in zero magnetic field. Results for another sample of YIG between 0.7 and 4.2°K in magnetic fields up to 13 kOe are also presented. In YIG it is shown that in addition to the lattice vibration and acoustic spin-wave-mode contributions, C_L and C_{acous}, there is a residual specific heat $\mathfrak{R}(T)$ that is linear with temperature and somewhat dependent on magnetic field. This new term $\mathfrak{R}(T)$ is tentatively attributed to surface effects although its magnitude is much larger than that predicted for surface spin-wave modes in a ferromagnetic sintered sample with the same dispersion constant D. The data in YIG are compared with previous work, and it is shown that the analysis of the calorimetric data on this compound is more complex than was thought previously, and in particular that data on C_v in zero field are not suited for obtaining the value of D from the usual $C_v/T^{3/2}$-versus-$T^{3/2}$ plot. The same comments apply to EuIG, where a residual term, linear in temperature, was also obtained. From the nuclear specific heat of this compound, we obtain an rms magnetic field at the nucleus $H_N=597\pm5$ kOe, in excellent agreement with results from Mössbauer experiments. In TmIG, the effect of acoustical spin waves on C_v could be detected, and (as expected) there was no evidence of population of the optical modes. However, no firm conclusions could be reached about a residue, since it was difficult to estimate C_{acous} theoretically. The nuclear contribution $C_NT^2/R=(7.8\pm0.4)\times10^{-4}$ was found to be in good agrement with that predicted from Mössbauer data. In SmIG, the first excited electronic level was deduced to be $E/k_B=(38\pm3)$°K, in good agreement with predictions from White's theory. The nuclear specific heat of SmIG was analyzed as corresponding to an rms field at the nucleus $H_N=(2.2\pm0.2)\times10^6$ Oe, while an analysis of Mössbauer data had given $(2.8\pm0.15)\times10^6$ Oe. A broad anomaly in C_v centered at 2°K remains unexplained, but is possibly due to an unreacted samarium oxide impurity. It is responsible for the uncertainty in E and H_N. In YbIG, a sizable discrepancy remains below 3°K between the theory using the 12 low optical spin-wave modes and the experimental data. Apparently the dispersion curve of the exchange mode is significantly different from that calculated by Tinkham using a simple model. The nuclear specific heat in YbIG, $C_NT^2/R=(1.6\pm0.2)\times10^{-3}$, was in fair agreement with that predicted from the electron-nucleus coupling parameter and the ground-state electronic moment.

I. INTRODUCTION

THIS paper presents a systematic study of the specific heat C_v of two very pure samples of yttrium iron garnet (YIG) in external magnetic fields up to 13 kOe between 0.4 and 4.5°K. Calorimetric data are also presented over the same temperature range for several rare-earth iron garnets MIG, where M stands for Sm, Eu, Tm, and Yb. The results are expressed in terms of the molar unit $3M_2O_3\cdot5Fe_2O_3$. This paper is a continuation of specific-heat work on yttrium and rare-earth iron garnets presented previously by Harris and Meyer.[1] More recent short reports of work in this laboratory have been presented elsewhere.[2,3]

The principal purposes of the present paper are as follows: First, to clarify and eliminate the large discrepancies in the value of the dispersion constant D of YIG and EuIG as derived from the analysis of different types of experiments. It is found that a simple analysis of the specific heat at $H=0$ into a T^3 contribution from the lattice and a $T^{3/2}$ contribution from the spin-wave motion does not give the correct value of D obtained from more direct methods. Measurements of D for YIG in various magnetic fields resolve this difficulty to a great extent and confirm previous findings[3] that in addition to the above contributions, there is another one, $\mathfrak{R}(T)$, that is somewhat field-dependent and is linear in T. Tentatively this new specific heat is attributed to surface effects of the polycrystalline material such as boundary scattering of spin waves or surface modes. The garnets of Eu and Gd also show a specific-heat residue that is not accounted for and which may be possibly attributable to surface effects, although the situation is not clear.

The second purpose of the paper is to present data on the effective field H_N at the nucleus of some rare-earth ions in the garnets. The data so obtained are found to agree with those from the Mössbauer effect in EuIG and TmIG. However, in SmIG, there is disagreement between our analysis from C_v data and that

* Work supported by a grant from the U. S. Army Research Office (Durham) and a contract from the Office of Naval Research.

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[1] A. B. Harris and H. Meyer, Phys. Rev. **127**, 101 (1962).

[2] D. G. Onn, R. Gonano, and H. Meyer, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio*, edited by J. G. Daunt *et al.* (Plenum Press, New York, 1965), p. 897. Tabulations of C_v versus T for LuIG and GdIG between 0.4 and 4.3°K are available upon request.

[3] D. G. Onn, J. P. Remeika, H. Meyer, and A. J. Henderson, Jr., J. Appl. Phys. **38**, 1023 (1967).

from Mössbauer experiments. In YbIG the splitting derived from calorimetry agrees only reasonably well with that predicted theoretically.

II. THEORETICAL SURVEY

Since a theoretical analysis of specific heat in garnets has been presented in Ref. 1, only a brief survey will be given here.

We assume again that the specific heat can be expressed by

$$C=C_L+C_M+C_N, \tag{1}$$

where the symbols on the right-hand side refer to the contributions, respectively, from the lattice, from the interactions between unpaired electrons of the ions, and from the electron-nuclear spin interactions.

A. Lattice Specific Heat

For rare-earth garnets, the lattice contribution C_L can be calculated by interpolation of the Debye temperatures. $\Theta_D=500°$K for EuIG,[4] $\Theta_D=494°$K for GdIG calculated from velocity of sound measurements[5] and $\Theta_D=458°$K for LuIG from the analysis of specific-heat measurements.[1] A satisfactory interpolation consistent with the above values allows one to calculate for the other iron garnets

$$C_L(M\text{IG})=(\mathfrak{M}_M/\mathfrak{M}_{\text{Eu}})^{3/2}C_L(\text{EuIG}), \tag{2}$$

where $\mathfrak{M}$ is the mass of the rare-earth ion. This interpolation scheme was found to be more successful than the one in which the scaling factor contains the ratio of the molecular masses of the two garnets. The lattice specific heats so chosen are given in Table I where, for convenience, we also present the lattice contributions for other iron garnets referred to in this work. For all the rare-earth garnets described here, the uncertainty in the lattice specific heat is unlikely to introduce an appreciable error in the interpretation of the other specific-heat contributions.

For YIG, the most recent sound velocity measurements[4] give $\Theta_D=560°$K and hence

$$C_L/R=0.53\times10^{-4}T^3 \quad \text{per mole garnet.} \tag{3}$$

B. Nuclear Specific Heat

Neglecting nuclear electric quadrupole effects, the expression for the nuclear specific heat per mole garnet is

$$\frac{C_NT^2}{R}=6\sum_i \tfrac{1}{3}I_i(I_i+1)\left(\frac{\Delta_i}{k_B}\right)^2 \tag{4}$$

for $\Delta_i\ll k_BT$, where the summation is over the different isotopes i, and where

$$\Delta_i=g_{N,i}\beta_NH_{N,i} \tag{5}$$

is the separation between successive nuclear levels. I_i is the nuclear spin, $g_{N,i}$ is the nuclear splitting factor, β_N is the nuclear magneton, and $H_{N,i}$ is the field at the nucleus. It turns out that the nuclear specific heat of Fe^{57} in the temperature range above 0.4°K is negligible, because of the small splitting[6] $\Delta(Fe^{57})/k_B\approx3\times10^{-3}$ °K, and because of the low abundance of this isotope, 2.5%. Consequently, the only nuclear contribution we will consider is that of the rare-earth ions.

TABLE I. The lattice specific heat used for the different rare-earth garnets.

MIG	Θ_D	$10^4C_L/RT^3$
EuIG	500	0.75
SmIG	500	0.75
GdIG	494	0.78
TmIG	465	0.93
YbIG	460	0.96
LuIG	458	0.98

C. Magnetic Specific Heat

The magnetic specific heat of the garnets YIG, EuIG, and TmIG can be attributed entirely to the acoustical spin-wave modes, since their optical modes have too high an energy to be populated at low temperatures.[7,8]

For YbIG and SmIG, however, the magnetic specific heat is dominated by the contributions from the twelve low-lying optical modes[1,9] with energies $E_j(\mathbf{k})$ corresponding to the 12 inequivalent c sites in the unit cell. At liquid-helium temperatures where $E\gg k_BT$, the magnetic specific heat can then be written as

$$\frac{C_M}{R}=\frac{C_{\text{opt}}}{R}=\frac{V}{8\pi^3}\sum_j\int_{\text{BZ}}\left(\frac{E_j}{k_BT}\right)^2e^{-E_j/k_BT}d^3k, \tag{6}$$

where V is the volume element of the unit cell. In Sec. IV the analysis of C_{opt} for SmIG and YbIG will be discussed further.

For the acoustic modes, the specific heat can be calculated[10] from the approximate dispersion relation for an infinite crystal:

$$\hbar\omega=g\beta H_i+Da^2k^2, \tag{7}$$

where $a\approx12.4$ Å is the lattice constant of the unit cell containing 4 moles of garnet, D is the dispersion constant which is a linear combination of the exchange integrals in the garnet, g is the gyromagnetic ratio,

[4] W. G. Nilsen, R. L. Comstock, and L. R. Walker, Phys. Rev. **139**, A472 (1965).
[5] R. L. Comstock, J. J. Raymond, W. G. Nilsen, and J. P. Remeika, Appl. Phys. Letters **9**, 274 (1966).
[6] C. Robert, Compt. Rend. **251**, 2684 (1960).
[7] A. B. Harris, Phys. Rev. **132**, 2398 (1963).
[8] R. L. Douglass, Phys. Rev. **120**, 1612 (1960).
[9] A. J. Sievers II and M. Tinkham, Phys. Rev. **129**, 1995 (1963).
[10] J. E. Kunzler, L. R. Walker, and J. K. Galt, Phys. Rev. **119**, 1609 (1960).

and H_i is the effective internal field given by

$$H_i=H_0-\mathrm{NM}+H_A. \quad (8)$$

Here H_0 and H_A are the externally applied field and the anisotropy field, respectively, NM is the demagnetizing field, and M is the magnetization. The above dispersion relation neglects a dipolar term which, as has been pointed out,[1,10] changes C_M only by a small amount, and it also neglects terms of order $O(\mathbf{k}^4)$ and higher, which partly cancel out the dipolar effects. An unpublished numerical calculation by Edmonds shows that even at 0.8°K, the inclusion of dipolar effects depresses the spin-wave specific heat for fields up to about 12 kOe by only 2–3%, which for our purposes is negligible.

From the calculation in Ref. 10, one obtains for the magnetic entropy S_M, using Eq. (7),

$$S_M/R=S_{\mathrm{acous}}(x,T)/R=\alpha T^{3/2}B(x)$$
$$=\tfrac{1}{3\sqrt{2}}(k_BT/\pi D)^{3/2}[\tfrac{5}{2}f_{5/2}(x)+xf_{3/2}(x)], \quad (9)$$

$$C_M/R=C_{\mathrm{acous}}(x,T)/R=\tfrac{1}{3\sqrt{2}}(k_BT/\pi D)^{3/2}$$
$$\times[(15/4)f_{5/2}(x)+3xf_{3/2}(x)+x^2f_{1/2}(x)], \quad (10)$$

where

$$f_P(x)=\sum_{n=1}^{\infty}\frac{e^{-nx}}{n^P}$$

and

$$x=g\beta H_i/k_BT. \quad (11)$$

We note that over the range of temperatures and fields of interest in this paper, $0\leqslant x\lesssim 2$, one can represent Eq. (10) to an accuracy of better than 3% by the simple expression

$$C_M(x,T)/R=\tfrac{1}{4}\times 0.113(k_BT/D)^{3/2}e^{-0.45x}. \quad (12)$$

Since in our experiments we deal with small sized particles of garnets, the possible contribution ΔC_M of surface modes will be discussed. In two recent publications, ΔC_M was calculated for a Heisenberg ferromagnet.[11,12] Assuming a thin crystal of volume V bound by two parallel surfaces of total area A, the result is

$$\Delta C_M=[\zeta(2)/4\pi](A/a^2)(k_BT/D). \quad (13)$$

The ratio between the surface and bulk contribution for the "thin film" crystal is then

$$\Delta C_M/C_M\simeq(0.131/0.113)(aA/V)(D/k_BT)^{1/2}. \quad (14)$$

As a rough guess, we extend this argument to a cubic crystal with an edge of (1000 a) or ($\sim 1\,\mu$) and we obtain $\Delta C_M/C_M\approx 3\times 10^{-3}(D/k_BT)^{1/2}$. Assuming $D/k_B\approx 40$°K (which is close to the value for YIG) then the ratio at 1°K is of the order 2×10^{-2}.

Although the temperature dependence of the acoustic spin-wave term is the same in a ferromagnet and a ferrimagnet, it is possible that the numerical factors are quite different for a given absolute magnitude of the exchange integral. No calculations of the surface modes in a ferrimagnet have been found in the literature.

If spin-wave surface effects become important, one might expect lattice surface modes to become noticeable also, giving a term in T^2. Under these circumstances, an analysis of experimental specific-heat data might become still more complicated.

Another specific-heat contribution that is linear in T is that which is due to domain wall motion. Janak[13] applied his calculation to the case of YIG. Assuming one domain wall per micron, he found $C_{\mathrm{DW}}=0.5\,T$ erg/cm³ °K, which becomes per mole garnet

$$C_{\mathrm{DW}}/R=1.7\times 10^{-6}T. \quad (15)$$

This contribution is quite small and goes to zero in external fields above the saturation value.

III. EXPERIMENTAL

A. Apparatus

The cryostat, capable of operating between 0.35 and 4.3°K, used a heat switch and was the same as described in a previous paper.[14] Carbon resistors were used for thermometry and were calibrated at several external magnetic fields using the T_{62} He^3 and the 1958 He^4 vapor pressure tables. For temperatures below ~0.7°K, a McLeod gauge was used to measure the vapor pressure. In a separate experiment, the readings of this gauge were calibrated as a function of temperature using the susceptibility of cerium-magnesium nitrate. This calibration was thereby corrected for thermomolecular pressure effects.

The samples, having cylindrical or ellipsoidal shapes, were attached to a suspension system whose heat capacity was measured in separate experiments in several external-field values. As a test of the cryostat and the experimental techniques, we have measured above $T=0.7$°K the specific heat of a 117.6-g cylinder of ASARCO grade 58 copper (purity 99.999+%) kindly lent by Dr. D. W. Osborne of Argonne National Laboratory. Analysis of these data gave

$$C=0.710T+0.046T^3\ \mathrm{mJ/mole\ °K} \quad (16)$$

with a 0.5% rms scattering in the data over the range $0.7\leqslant T\leqslant 4.4$°K independent of magnetic field up to 13 kOe. Comparison with high precision measurements[15–17] shows our data to be 2% too high at 1°K, with this difference decreasing to less than 0.5% at 3°K and above; however, we have been unable to account for

[11] D. L. Mills and A. A. Maradudin, J. Phys. Chem. Solids **28**, 1855 (1967).
[12] T. Fujiwara, K. Ohtaka, and S. Yanagawa, J. Phys. Soc. Japan **25**, 1236 (1968).
[13] J. F. Janak, Phys. Rev. **134**, A411 (1964).
[14] D. C. Rorer, D. G. Onn, and H. Meyer, Phys. Rev. **138**, A1661 (1965).
[15] D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instr. **38**, 159 (1967).
[16] G. Ahlers, Rev. Sci. Instr. **37**, 477 (1966).
[17] D. L. Martin, Phys. Rev. **170**, 650 (1968).

this small difference. For the measurement of YIG in a magnetic field, the ellipsoidal sample was suspended rigidly by cotton threads in a cradle so as to avoid displacement through the forces exerted by the slight magnetic-field gradient. In this experiment a heater wire and a carbon resistance in a thin copper foil were glued directly on the sample; the specific heat of these addenda will be discussed in Sec. IV A.

B. Samples

All samples were polycrystalline and their mass varied between 50 and 100 g. Their density was checked and was found to be better than 95% of that expected from x-ray determinations of the lattice constant. The choice of polycrystalline rather than single-crystal samples was dictated by the following considerations. Since the specific heat was usually small, a larger block of material was needed than was available in the form of a single crystal. Furthermore, polycrystalline ceramic samples are free of impurity inclusions formed during the growth of large single crystals. Because of the small specific heat of YIG in particular, any impurities can have an important influence on the measurements.

The iron garnets of Tm and Yb were prepared in the Gordon McKay Laboratory, Harvard University, by Molea using a coprecipitation method of Wolf and Rodrigue.[18] The original reagents had a purity of at least 99.99%. The sample of SmIG was obtained from Microwave Chemical Associates and was of more recent preparation than the one described in Ref. 1.

The samples of EuIG and of YIG were prepared by one of us (J. P. R.) and had less than 5 ppm total rare-earth impurities.[19] The approximate diameter of the individual garnet crystallites obtained after firing was of the order of 5 to 10 μ for YIG and 20 μ for EuIG.

In addition to a search for impurity by fluoroscopic methods, all the samples were subjected to an intensive x-ray analysis to check for traces of unreacted oxides, but none were found. This check was particularly necessary for SmIG because a previous sample[1] had shown an unusual anomaly in the specific heat near 2°K, which was attributed to some unreacted oxides. It should be noted that Sm^{3+} is the lightest rare earth fitting into the iron garnet lattice and therefore it is more difficult to prepare in the pure garnet phase than the other iron garnets.

In a recent paper,[3] specific-heat data of a sample of EuIG were presented and it was found out afterwards that a portion of the oxides had not reacted to form the final garnet phase. These results on the early EuIG sample and their analysis have to be discarded and are replaced by the data in this paper.

[18] W. P. Wolf and G. P. Rodrigue, J. Appl. Phys. **29**, 105 (1958).
[19] The ultrapure starting materials were obtained from American Potash and Chemical Corp., Whittier, Calif.

IV. RESULTS AND DISCUSSION

A. YIG

Two samples were used in the experiments. The first one (YIG I) with a mass of 55.15 g was measured only in zero field, and its shape was that of a cylinder. YIG II, with a mass of 56.37 g, was measured in zero field and in external applied fields, and had an approximately ellipsoidal shape with an axis ratio $c/a=1.55$. The field from a current regulated electromagnet could be varied up to 13 kOe and was applied perpendicular to the c axis of the ellipsoid. To obtain data in magnetic fields, measurements were carried out at fields of $H_0=0$, 5.7, and 13 kOe between 0.7 and 4.3°K. From Eq. (8) these correspond to internal fields of $H_i=0.2$, 4.9, and 12.2 kOe, respectively, given $H_A=170$ Oe,[20] and the magnetization M is 195 Oe.[21] For YIG II, the demagnetizing field was calculated to be 980 Oe. Isotherms of C_v versus H_i were taken at 0.745, 0.82, 1.45, 1.54, and 1.78°K. The curve at 1.45°K was taken to allow comparison with that given in Ref. 10. Because of some difficulties in the current regulation of the magnet in small fields, and especially because of large irreversible heating effects in this range (see, e.g., Ref. 10), no data were taken between 0 and 4 kOe.

The results for both samples in zero field are presented in Table II and are also shown in Fig. 1 as a familiar $C/T^{3/2}$ versus $T^{3/2}$ plot. As can be seen, there is some

TABLE II. Smoothed specific heat of YIG I and YIG II, expressed as 10^3 (C/R) at different internal fields in kOe.

T(°K)	(YIG I) $H_i=0.2$	(YIG II) $H_i=0.2$	$H_i=4.2$	$H_i=12.2$
0.5	0.087			
0.6	0.116			
0.7	0.148	0.119	0.106	0.093
0.8	0.183	0.143	0.132	0.115
0.9	0.221	0.172	0.162	0.141
1.0	0.266	0.204	0.196	0.172
1.1	0.312	0.242	0.234	0.205
1.2	0.362	0.285	0.276	0.244
1.3	0.418	0.331	0.323	0.287
1.4	0.480	0.386	0.375	0.336
1.5	0.545	0.444	0.432	0.389
1.6	0.611	0.506	0.495	0.450
1.7	0.690	0.574	0.563	0.515
1.8	0.770	0.648	0.638	0.587
2.0	0.955	0.814	0.806	0.752
2.2	1.17	1.010	1.004	0.95
2.4	1.41	1.24	1.23	1.19
2.6	1.69	1.50	1.49	1.45
2.8	1.99	1.79	1.79	1.76
3.0	2.34	2.12	2.12	2.08
3.2	2.73	2.49	2.49	2.47
3.4	3.18	2.93	2.93	2.89
3.6	3.68	3.40	3.39	3.36
3.8	4.25	3.92	3.90	3.87
4.0	4.88	4.45	4.45	4.44
4.2	5.60	5.03	5.04	5.04
4.4		5.68	5.70	5.68

[20] G. P. Rodrigue, H. Meyer, and R. V. Jones, J. Appl. Phys. **31**, 376S (1960).
[21] See for instance E. E. Anderson, Phys. Rev. 134, A1581 (1964).

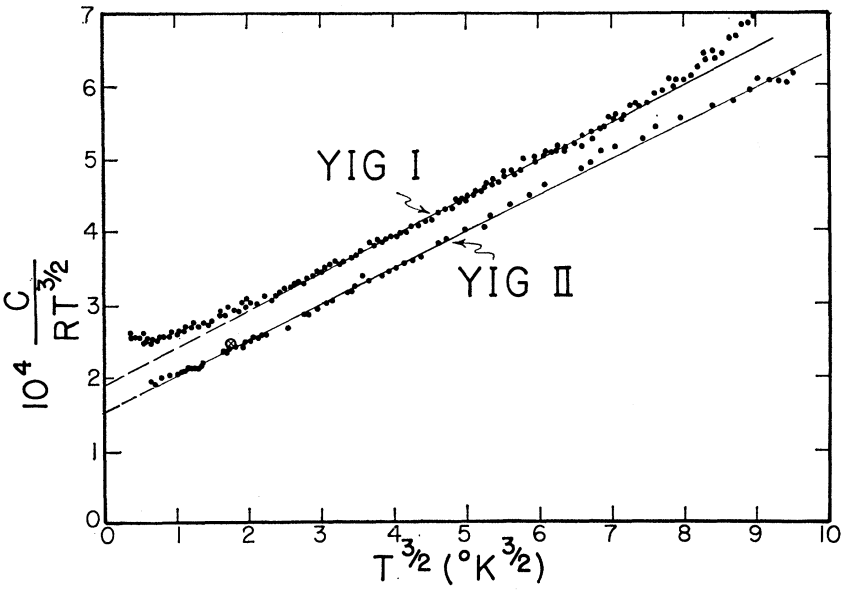

FIG. 1. Plot of the experimental specific-heat data for YIG I and YIG II in zero applied field, expressed as $C/RT^{3/2}$ versus $T^{3/2}$. The symbol ⊗ denotes the point by Kunzler *et al.* (Ref. 10).

difference between these two samples which were measured under the same conditions. The support and heat switch components (addendum AI) for both samples were the same, and their heat capacity had been determined several times to within a few percent. At 1 and 4°K the heat capacity of AI was 100 and 55%, respectively, of that of the garnet sample. Since we estimate an accuracy of 1–2% in the heat-capacity measurements, there is an estimated possible systematic uncertainty of up to ~3% in that of YIG. As mentioned before, sample YIG II was measured a second time with a much smaller addendum (AII) that included only the Evanohm heater and carbon resistor in a copper foil directly glued onto the sample so as to minimize the extra specific heat. This procedure was made necessary to achieve the best sensitivity in measuring the field dependence of the specific heat. In a further experiment, to check the heat capacity of the addendum (AII), a measurement was made of the garnet plus two identical addenda (AII). From the difference between the results of these two experiments, the heat capacity of (AII) was found to be about 15% of the sample over the whole temperature range, and moreover was found to be field-independent. The C_V of YIG was then computed by subtracting the (AII) contribution and in zero field it was found to agree better than 3% with that measured using the support (AI).

To avoid confusion, we plot on a different graph (Fig. 2) the results obtained by previous authors.[1,10,22] None of these data extend below 1.45°K. We note that our sample YIG I shows a C_v systematically higher than all the others. Sample YIG II agrees with that of Kunzler *et al.*[10] It should be noted that the 10-g sample (S1) of Shinozaki[22] is the same as that used by Kunzler *et al.*, yet the extrapolation of the (S1) data to 1.45°K shows a value about 10% lower than Kunzler *et al.* obtained. This again illustrates the difficulty in making measurements with samples having a small heat capacity, and still more the difficulty in extrapolating the data to $T=0$ to obtain D. No estimation or discussion of the heat capacity of support, heater, etc., were given in Ref. 22.

An analysis of the data of YIG I and YIG II from the plot of Fig. 1 using the expression

$$C/R=\tfrac{1}{4}\times 0.113(k_BT/D)^{3/2}+9350(T/\Theta_D)^3 \quad (17)$$

would give values of D and Θ_D. These are presented in Table III and, as can be seen, there is substantial disagreement between the value of D obtained from such an analysis and that from microwave instabilities, magnetostatic modes, and sublattice magnetization. The D from the heat-capacity measurements is con-

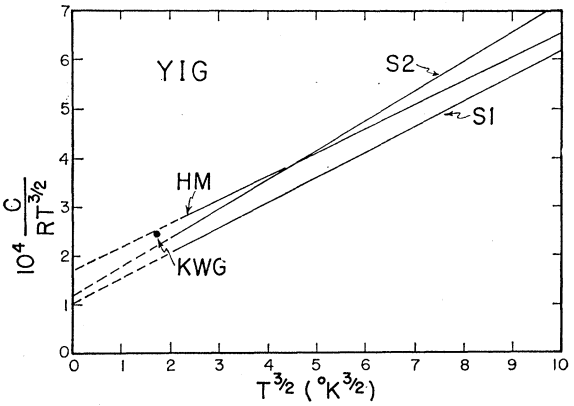

FIG. 2. Plot of specific-heat data of YIG obtained by previous authors, expressed as $C/RT^{3/2}$ versus $T^{3/2}$. S1 and S2 denote Ref. 22, HM denotes Ref. 1, KWG refers to Ref. 10.

[22] S. S. Shinozaki, Phys. Rev. **122**, 388 (1961).

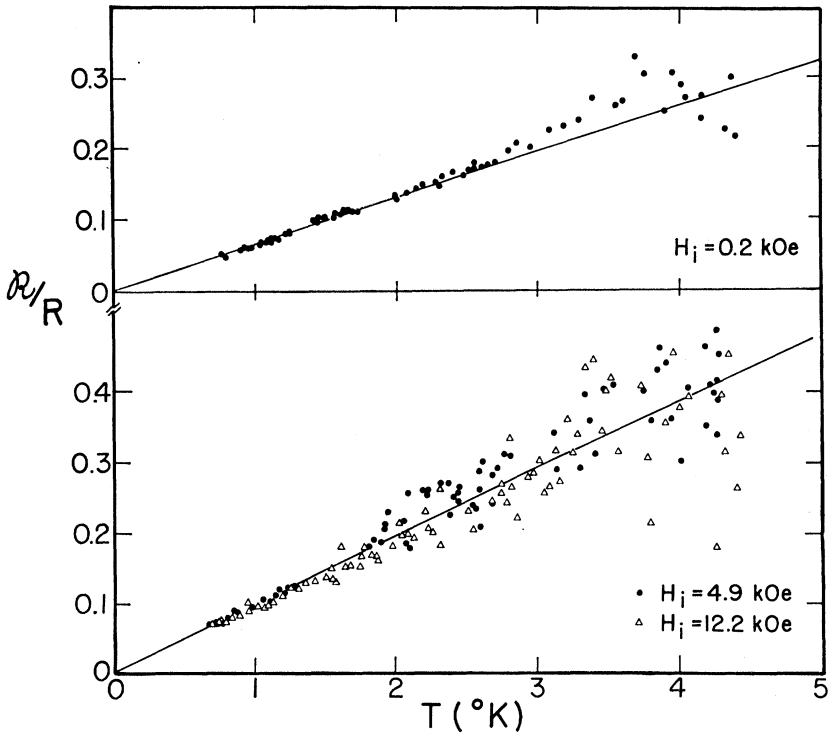

FIG. 3. The residue $\mathcal{R}(T)/R$ in YIG II obtained via Eq. (18) for several magnetic fields. *Note added in proof*: The vertical scale should read $10^3 \times \mathcal{R}/R$.

sistently lower, and hence the total $C_v(H=0)$ would seem to be too large for YIG I, YIG II, and the samples of Refs. 1 and 10. However, the agreement of Θ_D with that determined from the velocity of sound is reasonable.

In order to investigate the possibility of an excess in the heat capacity data, (C_L+C_M) was calculated using $\Theta_D = 560 \pm 5°\text{K}$ and $D = 30 \pm 1$ cm^{-1}, which are believed to be the most reasonable average values from previous measurements (see Table III). This quantity was then subtracted from the data points to form a residue

$$\mathcal{R}(T) = C_{\text{tot}} - (C_L + C_M). \qquad (18)$$

In Fig. 3 plots of $\mathcal{R}(T)$ at three values of constant field are shown. The residue for the choices of Θ_D and

TABLE III. Value of the dispersion constant D and the Θ_D of iron garnets from various experiments. The values between parentheses are those obtained via Eq. (17).

Garnet	Method	D(cm^{-1})	Θ_D(°K)	Reference
YIG	Neutron scattering	13.2		30
	Sublattice magnetization	30.0		23
		30.7		24
	Magnetostatic modes	30		25
	Microwave instabilities	29.5		26, 27
		27		4
	Specific heat (isotherm)	27.1	510	10
	S1, S2	(26.4, 27.8)	(567, 538)	22
	HM	(21)	(572±14)	1
	YIG I	(20)	(568±8)	This work
	YIG II	(23)	(568±6)	
	YIG II (isotherms)	33±3		
	Sound velocity		565	a
			560	4
EuIG	Sublattice magnetization	28.4±0.8		37
	Microwave instabilities	33±1.5		4
	Specific heat	(14.2±1.5)		This work
	Sound velocity		500	4
GdIG	Sublattice magnetization	8.2		b
	Microwave instabilities	9.6		5
	Specific heat	(7.3±0.6)		2
	Sound velocity		494	5
TmIG	Specific heat	(21)		This work
LuIG	Sublattice magnetization	27.3		23
	Specific heat	(27)	458	1,2

[a] H. J. McSkimin (private communication, 1961).

[b] S. M. Myers, J. R. Gonano, and H. Meyer, Phys. Rev. 170, 533 (1968).

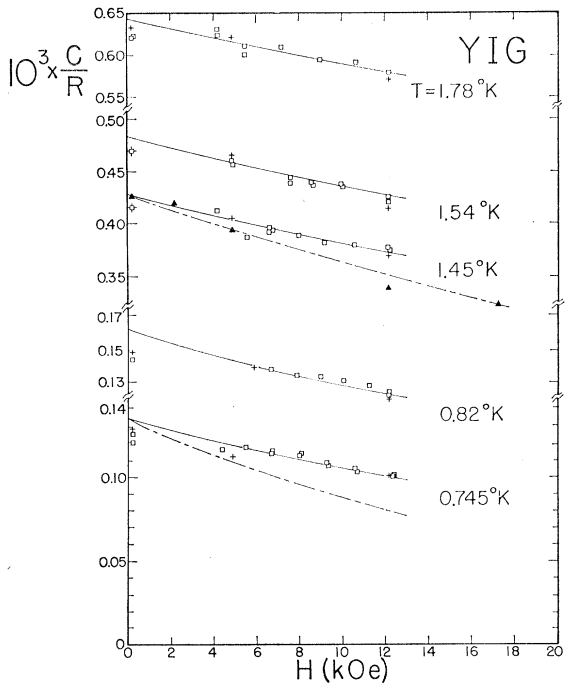

FIG. 4. Specific-heat data of YIG II along isotherms as a function of H_i, and comparison with data by Kunzler *et al.* (Ref. 10). The solid lines are the theoretical curves, obtained as explained in the text for $D=34$ cm^{-1}. The dashed curves are for $D=27$ cm^{-1}. Note the scale change for the various isotherms. □: Points taken along an isotherm. +: points from smoothed data taken at constant field as a function of temperature. ▲: data of Ref. 10.

D within the quoted errors can be represented very well by a linear term in the temperature, $\mathfrak{R}(T)/R=\epsilon T$. One finds $\epsilon=(6.4\pm1.5)\times10^{-5}$ at $H=0$, and $\epsilon=(9.0\pm2)\times10^{-5}$ for $H>4$ kOe. This compares with $\epsilon=1.1\times10^{-4}$ found for YIG I[3] at $H=0$. At 1 and at 4°K, the residue accounts for $\sim35\%$ and $\sim6\%$, respectively, of the total specific heat, which explains the increase of the scatter in the residue with increasing temperature.

Figure 4 shows isotherm data on YIG II as a function of internal magnetic field, and the calculated C_M [Eq. (9)], to within an additive constant, for $D=34$ cm^{-1}. At all temperatures the field variation of this calculated isotherm fits the data within the scatter except at $H=0$. The somewhat better fit for $D=34$ cm^{-1} rather than the $D\simeq30$ cm^{-1} found by other experiments,[23–27] and the fact that the $H=0$ points all lie too low may both have their explanation in a field dependence of $\mathfrak{R}(T)$ as indicated also by Fig. 3. This would have the tendency to flatten the field dependence of the isotherm data and hence to decrease D. It is clear furthermore that the very low values of D obtained previously[1] by the method of Eq. (17) are erroneous.

At present the origins of the residue $\mathfrak{R}(T)$ are not understood. Using Eq. (14) and taking 10 μ as the average dimension of the crystallites, it appears that $\mathfrak{R}(T)$ is much too large to be accounted for by surface modes. Furthermore, any contribution from domain walls must disappear at fields larger than the saturating one, $H_{\text{sat}}\approx1000$ Oe. Hence $\mathfrak{R}(T)$ cannot be caused by domain walls either. Also, since the garnets are electric insulators, no electronic specific heat is expected. We believe magnetic impurities cannot be blamed for $\mathfrak{R}(T)$ since great care was taken to work with very pure materials, as outlined before, and also impurities would be unlikely to give a term linear in T. The difference between samples might be ascribed to the preparation and the size of the crystallites. Certainly the difference in C_v for YIG I and YIG II is much larger than can be attributed to uncertainty in the specific-heat measurement or in the thermometer calibration. Apparently the sample of Kunzler *et al.*[10] also showed an excess specific heat, since in zero field their specific heat agrees with that of YIG II and Ref. 1. As the field increases, there is a systematic discrepancy from our data (Fig. 4) that is unexplained. These authors obtained $D=27$ cm^{-1} and they attributed the difference $(C_{\text{tot}}-C_M)$ entirely to the lattice contribution and hence obtained $\Theta_D=510$°K, while acoustic measurements[4] give $\Theta_D=560$°K. The adiabatic magnetization data[10] have been re-examined by us to check for consistency with the linear-residue hypothesis. Combining the Eq. (21) of Ref. 10 with our Eq. (18), one can write the total entropy as

$$S/R=\alpha T^{3/2}B(x)+\beta T^3+\epsilon T. \tag{19}$$

The invariance of the entropy $\delta S=0$ during an adiabatic process allows one to write

$$\delta[T^{3/2}B(x)]/\delta T=(\beta/\alpha)(\delta(T^3)/\delta T)+\epsilon/\alpha. \tag{20}$$

In this form, a plot of the data should be a simple linear function allowing one to extract the ratios β/α and ϵ/α. If one assumes $\Theta_D=560$°K and that the addenda contribution to the specific heat was approximately $1.6T^3$ erg/cc°K in that experiment,[10] one can determine α and ϵ. In spite of some ambiguity due to the scatter in the data, a reasonably good fit could be made for a value of α corresponding to $D=28.5\pm2$ cm^{-1} and for $\epsilon=(7\pm3)\times10^{-5}$. It seems probable then that the systematic deviations observed by Kunzler *et al.*[10] in the fit to their data (Fig. 4) and attributed to impurities are due to the presence of the linear residue.

Because of these surprising findings, it is of interest to comment on the Fe^{57} NMR longitudinal relaxation measurements at 4.2°K that were carried out in YIG I and YIG II in zero applied external field by means of

[23] R. G. Gonano, E. Hunt, and H. Meyer, Phys. Rev. **156**, 521 (1967); R. G. Gonano, E. Hunt, H. Meyer, and A. B. Harris, J. Appl. Phys. **37**, 1322 (1966).
[24] D. Litster and G. Benedek, J. Appl. Phys. **37**, 1320 (1966).
[25] I. Solt, J. Appl. Phys. **33**, 1189S (1962). The measurements were analyzed in Ref. 23.
[26] E. H. Turner, Phys. Rev. Letters **5**, 100 (1960).
[27] R. C. Le Craw and L. R. Walker, J. Appl. Phys. **32**, 167S (1961).

pulse techniques.[28] The measurements showed nonexponential recovery from saturation with relaxation times T_1, 0.9 sec and 0.4 sec, respectively, for the two samples. This contrasts with 200 sec in zero applied field for a single-crystal sphere of comparable purity.[29] For this single crystal T_1 at the saturation field was found to be only about 10% larger than at $H=0$, which shows that domain walls apparently do not appreciably help the relaxation process. The experiment was repeated with several crystals of about 0.2 cm^3 packed in the rf coil with random orientations. The results were the same as for the single crystal. We conclude that effects of the crystallite size and boundary relaxation are apparently very important in the spin dynamics of polycrystalline sintered YIG, and may therefore affect the specific heat.

One might ask how the magnetization is affected by such possible surface effects. This question is difficult to answer because the variation of M with temperature between 1 and 5°K is so small in YIG as to be hardly observable, even with sensitive methods. It should be noted, though, that the sublattice magnetization on both a and d sublattices, as evidenced by Fe^{57} NMR frequency, is the same within experimental error in both YIG I, YIG II, and in the single crystal YIG sphere between 4 and 77°K, where the comparison was carried out. Hence surface effects, if any, have not been detected.

In summary, the calorimetric work on YIG, which covers a greater temperature range than research reported previously, shows clearly that a reasonably straight line obtained from a $C_vT^{-3/2}$ versus $T^{3/2}$ plot over a limited temperature interval in zero field can give an incorrect value of D, since the specific heat is apparently more complex than Eq. (17) would indicate. As we shall see, there are indications that a residue $\Re(T)$ is also present in other iron garnets. The presence of this residue makes the interpretation of the YIG data in magnetic fields more difficult. However, we feel that there is basically no serious discrepancy between the D obtained from various experiments[4,23–27] and from specific-heat isotherms. Only the neutron scattering results[30] disagree, and it would be most useful to clear up this discrepancy by a reanalysis of the neutron data and by the performance of scattering experiments that determine the acoustic dispersion curve.

It is possible that the residue would account for the apparent disagreement[31] between the value of D in magnetite as obtained by specific-heat measurements, neutron scattering experiments, and analysis of the Curie temperature. These specific-heat experiments[31] were made with an addendum whose heat capacity was large in comparison with that of the sample. Although the reproducibility of the results was poor, it is felt that the disagreement is significant.

TABLE IV. Abundance, nuclear spin, nuclear moment μ_N (in nuclear magnetons), nuclear specific heat C_N (experimental), calculated nuclear quadrupole specific heat C_{QQ}, and effective field at the nucleus H_N (in MOe) for rare-earth ions in several iron garnets studied. Data in columns 2, 3, and 4 are those given in *The American Institute of Physics Handbook* (McGraw-Hill Book Co., N. Y., 1963), pp. 8–11 unless otherwise specified.

M	%	I	μ_N	$10^3(C_NT^2/R)$	$C_{QQ}T^2/R$	H_N(10^6 Oe)
Sm^{147}	14.87	$\frac{7}{2}$	−0.807[a]	(2.6±0.4)	3×10^{-5} [b]	2.2±0.2
Sm^{149}	13.82	$\frac{7}{2}$	−0.665[a]			
Eu^{151}	47.86	$\frac{5}{2}$	3.419[c]	9.07	4×10^{-7} [d]	0.598
Eu^{153}	52.14	$\frac{5}{2}$	1.507[c]			
Gd^{155}	15.1	$\frac{3}{2}$	0.24			
Gd^{157}	15.7	$\frac{3}{2}$	0.32			0.37[e]
Tm^{169}	100	$\frac{1}{2}$	−0.229	0.79		0.81[f] / 1.70
Yb^{171}	14.4	$\frac{1}{2}$	0.45	1.8±0.1		1.8±0.15
Yb^{173}	16.2	$\frac{5}{2}$	−0.65			
Lu^{175}	97.41	$\frac{7}{2}$	2.9	0.52		0.13[g]
Lu^{176}	2.59	7	4.2			

[a] F. M. Dichanik, R. E. H. Sandars, and G. Woodgate, Proc. Roy. Soc. (London) **A257**, 277 (1960).
[b] Estimated from the data in Ref. (a).
[c] Reference 41.
[d] Estimated from the data in Ref. 41.
[e] Calculated from data by J. Budnick, Bull. Am. Phys. Soc. **8**, 439 (1963); S. M. Myers, J. R. Gonano, and H. Meyer, Phys. Rev. **170**, 513 (1968).
[f] Reference 47.
[g] Reference 2.

B. EuIG

In its ground state, the Eu^{3+} ion has $J=0$ and the first excited state lies about 500°K above the ground state.[32] Hence no low-lying optical modes are expected for this ion and only an acoustic spin-wave mode should contribute to the specific heat at liquid-helium temperatures. Hence Eq. (10) is to be used for C_M, where we take $g=1.1$ and $H_A=5020$ Oe, as determined from microwave measurements of Le Craw *et al.*[33] This leaves the parameter D to be determined from the analysis of the data. The nuclear specific heat is due to the hyperfine splitting of the nuclear levels of the two stable isotopes Eu^{151} and Eu^{153}, both with $I=\frac{5}{2}$ and with nuclear moments and relative abundances as indicated in Table IV. Since the anisotropy field is in a [111] direction, there are two types of magnetically inequivalent c sites[34] with equal abundance. Accordingly, the fields at the Eu nuclei for these two types of sites will be different. In the temperature region where the energy of the splittings is much smaller than k_BT and Eq. (4) is valid, specific-heat data can measure only rms values of the fields. In the analysis that follows, we shall neglect the quadrupolar contribution to C_N,

[28] S. M. Myers (private communication).
[29] S. M. Myers, H. Meyer, and J. P. Remeika, Bull. Am. Phys. Soc. **13**, 668 (1968).
[30] G. A. Ferguson and A. W. Saenz, Phys. Rev. **156**, 632 (1967).
[31] M. Dixon, F. E. Hoare, and T. M. Holden, Phys. Letters **14**, 184 (1965).
[32] See for instance J. H. Van Vleck, *The Theory of Electric and Magnetic Susceptibilities* (Oxford University Press, London, 1932).
[33] R. C. Le Craw, W. G. Nilsen, J. P. Remeika, and J. H. Van Vleck, Phys. Rev. Letters **11**, 490 (1963).
[34] J. F. Dillon and L. R. Walker, Phys. Rev. **124**, 1401 (1961).

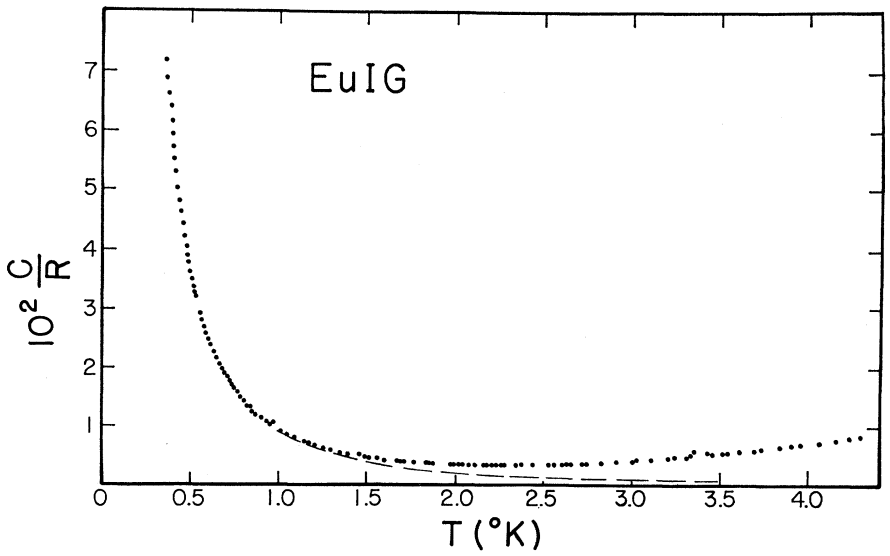

FIG. 5. Specific-heat data of EuIG. The dashed curve is that of C_N/R.

estimated to be $C_{QQ}T^2/R=4\times10^{-7}$ using data from Mössbauer experiments.[35]

The experimental data are presented in Table V and Fig. 5 and were analyzed as follows: After subtracting the lattice contribution (Table I) from the total specific heat, the remainder was fitted to an expression of the form

$$(C_N+C_M)/R = AT^{-2}+\tfrac{1}{4}\times0.113(k_BT/D)^{3/2}\,e^{-0.45g\beta H_A/k_BT}. \quad (21)$$

At temperatures below 1°K, the nuclear specific heat is by far the dominant one and the value of A was found from data below this temperature to be $(9.07\pm0.1)\times10^{-3}$. This gives an effective rms field of 598 ± 5 kOe, which is in excellent agreement with that obtained from Mössbauer experiments (600 kOe,[35] and more recently 596 kOe[36]).

We further obtain $D=(14.2\pm0.5)$ cm^{-1}, but in the same sample, Myers *et al.*[37] have obtained a value of $D=(28.4\pm0.5)$ cm^{-1} from NMR measurements of Fe^{57}. Once again, one is faced with a large disagreement in the values of D, as already experienced with YIG (see Table III). Hence it was decided to carry out a "residue" analysis in EuIG, as was done with YIG data. In this analysis, the constant A and the calculated lattice specific heat were the same as before but the value of $D=28.4$ cm^{-1} was used. Then the residue was obtained and could be represented satisfactorily by the expression $\mathfrak{R}(T)/R=(0.23\pm0.03)\times10^{-3}T$. This function is of the order of 15% of the total specific heat above 2°K, but becomes negligible below 1.2°K. Its magnitude is comparable to C_M.

[35] P. Kienle, Rev. Mod. Phys. **36**, 372 (1964).
[36] M. Stachel, S. Hüfner, G. Crecelius, and D. Quitmann, Phys. Letters **28A**, 188 (1968); and Phys. Rev. (to be published).
[37] S. M. Myers, J. P. Remeika, and H. Meyer, Phys. Rev. **170**, 520 (1968).

C. GdIG and LuIG

We now comment briefly on the specific heat of two garnets, reported previously.[1,2] In GdIG, where the analysis of the specific heat is complicated by the presence of optical spin-wave modes, there appears also to be an extra contribution $\mathfrak{R}(T)$ to the specific heat. This can be seen from the fact that D obtained from an analysis using Eq. (17) including anisotropy and dipolar corrections is smaller than that obtained

TABLE V. Smoothed data of the specific heat per mole of rare-earth iron garnet, expressed as $10^3(C/R)$.

T (°K)	SmIG	EuIG	TmIG	YbIG
0.40	19.0	57.4		
0.45	16.4	43.5		8.54
0.50	14.4	36.2	3.13	7.01
0.55	13.0	29.9	2.48	5.89
0.60	11.8	25.0	2.10	5.73
0.70	10.4	18.7	1.66	4.01
0.80	9.81	14.4	1.38	3.22
0.90	9.84	11.4	1.20	2.64
1.0	10.1	9.38	1.07	2.28
1.1	10.5	7.86	0.978	2.00
1.2	10.8	6.64	0.930	1.80
1.3	11.1	5.88	0.920	1.70
1.4	11.3	5.25	0.930	1.67
1.5	11.5	4.74	0.970	1.68
1.6	11.7	4.35	1.02	1.76
1.8	11.9	3.86	1.18	2.08
2.0	12.0	3.58	1.38	2.76
2.2	12.0	3.45	1.67	3.80
2.4	12.1	3.51	2.04	5.48
2.6	12.3	3.68	2.46	7.88
2.8	12.8	3.94	2.95	11.7
3.0	13.4	4.27	3.51	17.6
3.2	14.2	4.72	4.02	25.9
3.4	15.4	5.24	4.80	37.2
3.6	17.1	5.85	5.55	52.4
3.8	19.1	6.51	6.58	72.1
4.0	21.6	7.26	7.70	96.5
4.2	24.8	8.16	9.02	128.
4.4	28.5			167.
4.6	33.1			

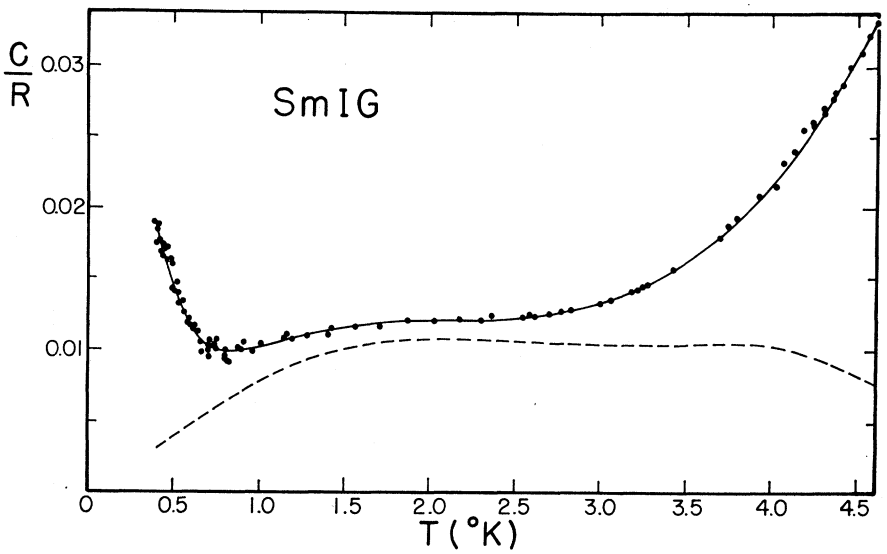

FIG. 6. Specific-heat data of SmIG. The dashed line shows the specific heat that cannot be accounted for by C_N and the excited optical modes. The rise of C below 1°K is attributed to the nuclear contribution C_N.

from NMR and microwave instability data. Here the absolute value of $\mathcal{R}(T)$ is smaller than for YIG and its temperature dependence is less well established, although it is very roughly linear. In LuIG, where the velocity of sound has not yet been measured, the lattice specific heat cannot be calculated exactly and therefore any estimate on the residue cannot be made yet. Analysis of the specific-heat data according to Eq. (17) gives a value of D that is close to the same as that obtained from NMR data. However, we consider this agreement somewhat fortuitous, pending further experiments with other LuIG samples.

D. SmIG

Recently, White[38] has calculated the splittings between the two lowest levels in the $J=\frac{5}{2}$ manifold due to exchange and crystalline fields. The calculation was done for a cubic crystalline-field symmetry with a rhombic distortion, and the axis of easy magnetization was taken to be [110] following experimental evidence from torque anisotropy data.[39] Magnetization measurements by Nowlin[40] also show the [110] direction to be that of easy magnetization below about 60°K. Hence there will be three inequivalent c sites for the Sm^{3+} ions, with an abundance ratio of 1:4:1, and White[38] has calculated the energy levels to be $E/k_B=32$, 73, and 79°K, on the basis of the specific-heat measurements of Ref. 1. At temperatures below about 8°K, the early SmIG data showed an anomaly from an impurity, probably a nongarnet phase, that made an unambiguous detection of the lowest level of 32°K difficult.

The sample investigated in the present work shows a smaller specific heat than in the first sample, yet an important fraction of C_v between 1 and 3°K cannot be accounted for, and it is not clear whether the quantity denoted by the area under the dashed curve in Fig. 6 is entirely due to an unreacted oxide phase or if it is partially an acoustic spin-wave mode contribution. Conceivably small undetected amounts (0.1–0.5%) of unreacted samarium oxides would give a magnetic transition in the range of 1 to 2°K which would be broadened by size effects and inhomogeneous local fields.

At temperatures above 3°K, the rise in C_v was attributed to a single level occupied by $\frac{1}{6}$ of the Sm^{3+} ions, as in White's theory. The data could be fitted approximately with the low-temperature approximation for a Schottky anomaly,

$$C_M/R=\tfrac{1}{6}(E/k_BT)^2e^{-E/k_BT}, \qquad (22)$$

with $E=(38\pm3)$°K, in good agreement with White's prediction. It should be noted that the higher levels for the two other sites are expected to give a negligible contribution to the specific heat at these low temperatures. That a relatively small error is claimed for E in spite of the uncertainty in C_v is due to the exponential dependence of C_v on E/k_BT. For $E/k_BT\gtrsim0.1$, an uncertainty of 30% in C_v gives an uncertainty in E of about 3% or less.

The increase in the specific heat with decreasing temperatures below 1°K was attributed to the nuclear hfs contribution and below 0.7°K it could be expressed by $C_NT^2/R=(2.6\pm0.4)\times10^{-3}$ where the large uncertainty arises from the broad anomaly centering at 2°K. The quadrupolar contribution has been calculated from molecular beam experiments and from Mössbauer experiments[41,42] and was found to be of the order of

[38] J. White, Proc. Phys. Soc. (London) **90**, 1095 (1967).
[39] R. F. Pearson and R. W. Cooper, J. Phys. Soc. Japan **17**, Suppl. B1, 369 (1962).
[40] C. H. Nowlin, Harvard University Cruft Laboratory Scientific Report No. 7, 1963.
[41] G. Woodgate, Proc. Roy. Soc. (London) **A293**, 117 (1965).
[42] S. Ofer and I. Nowick, Nucl. Phys. **A93**, 689 (1967).

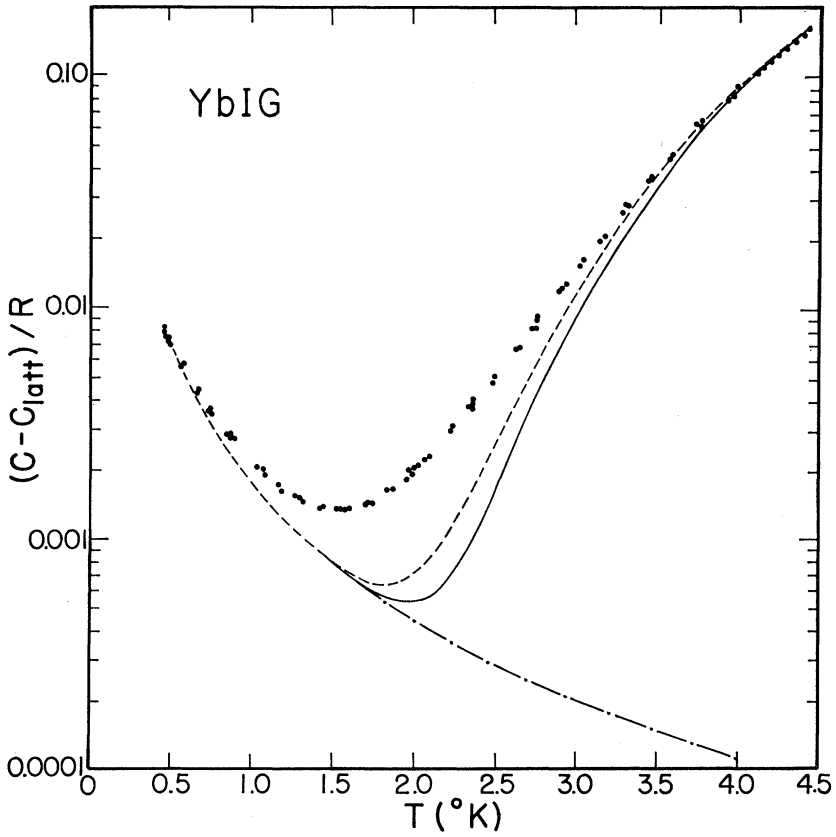

FIG. 7. Specific-heat data of YbIG after subtraction of C_L. ●: experimental data. Dot-dash dot curve: nuclear contribution C_N/R. Solid curve: Theoretical curve for the Tinkham spin-wave model, including the contribution of C_N. Dashed curve: theoretical curve for the optical and exchange spin-wave modes using Eq. (23).

$C_{QQ}T^2/R=3\times10^{-5}$, which is negligible in comparison with the observed total nuclear specific heat.

The rms value of H_N was found to be $(2.2\pm0.2)\times10^6$ Oe using the values of Table IV and Eq. (4). This value can be compared with that from a recent interpretation[43] of Mössbauer data,[44] where a unique value of H_N was assumed for all c sites and which gave $H_N=(2.8\pm0.15)\times10^6$ Oe. The discrepancy, which is well outside the combined experimental errors, remains unexplained. Effects from impurities in our sample with strong hfs specific heat, such as Ho^{3+}, would have given too large an H_N, and have to be ruled out. Also x-ray analysis does not show evidence of unreacted oxides, which if present would make H_N appear to be smaller.

E. TmIG

From magnetization measurements of this compound,[45] it appears that the first excited level of Tm^{3+} becomes significantly populated only above 30°K, which indicates that the energy of this level is of the order of 100°K, as shown by Schieber *et al.*[46] Hence at helium temperatures, only the acoustical spin-wave mode will contribute to the magnetic specific heat.

The nuclear specific heat is caused by the effective field at the Tm^{169} nuclei. Assuming the magnetization of this garnet to be in a [111] direction, there will be two different types of c sites with equal abundance, as in EuIG. The fields at the Tm^{169} nuclei are different for the two types of c sites, as shown by Cohen from Mössbauer experiments,[47] being 1700 and 810 kOe, respectively. The calculated specific heat is then given by $C_NT^2/R=7.5\times10^{-4}$. The results of the measured specific heat are presented in Table V. The low-temperature limit of the specific heat was attributed to the nuclear hfs splitting and found to be $C_NT^2/R=(0.78\pm0.04)\times10^{-3}$, in good agreement with the value expected from Mössbauer data. A further analysis of the specific heat is prevented by the uncertainty on the value of D, which cannot be extracted in a simple way from total magnetization or sublattice magnetization measurements. It is sufficient to say that the quantity $(C_{tot}-C_N-C_L)$ which represents the magnetic contribution plus a possible "residue" term linear in T, is approximately the same as for EuIG and YIG.

It should be noted that the analysis gave no evidence of a Tm^{3+} optical level becoming populated at tem-

[43] I. Nowik and S. Ofer, J. Appl. Phys. **39**, 1252 (1968).
[44] S. Ofer, E. Segal, I. Nowik, E. R. Bauminger, L. Grodzins, A. J. Freeman, and M. M. Schieber, Phys. Rev. **137**, A627 (1965).
[45] S. Geller, J. P. Remeika, R. C. Sherwood, H. J. Williams, and G. P. Espinoza, Phys. Rev. **137**, A1034 (1965).
[46] M. M. Schieber, C. C. Lin, and J. H. Van Vleck, J. Phys. Chem. Solids **27**, 1041 (1966).
[47] R. L. Cohen, Phys. Letters **5**, 177 (1963).

peratures below 4.5°K, as expected from the work of Schieber *et al.*[46]

F. YbIG

The calorimetric measurements were made with a different sample from that described in Ref. 1. The purpose was to test the reproducibility between samples and to extend the measurements to lower temperatures in order to obtain an accurate value for the rms field H_N. The easy magnetization axis of YbIG is in the [111] direction[48] and the exchange fields at the two inequivalent c sites are almost the same, as shown most clearly by infrared absorption measurements.[9] Hence one can assume that the fields at the Yb nuclei are also closely the same on both types of c sites. The data are presented in Table V, and agree well with those of Ref. 1 below 3°K. Apparently there is a small difference in the exchange splittings between the two specimens and this has a drastic effect on the specific heat, which depends on this splitting in an exponential manner.

After subtracting the appropriate C_L (See Table I), the specific heat below 1°K, attributed to nuclear hfs was found to be $C_N T^2/R = (1.6 \pm 0.3) \times 10^{-3}$. Subtraction of any effects from an impurity with a large nuclear specific heat such as HoIG should give $C_N T^2/R$ not less than about 1.55×10^{-3}. This specific heat corresponds to an rms field of $(1.8 \pm 0.15) \times 10^6$ Oe. Our experiments compare with the value $C_N T^2/R = 1.9 \times 10^3$ calculated using the hf coupling constants and the electronic moment of the ground state, $10.0 \mu_B/6$ per Yb^{3+} ion, assuming no canting. For a canting of about 20° from the [111] direction[49] one calculates $C_N T^2/R = 2.1 \times 10^{-3}$. Since the fit of a T^{-2} law to the experiment (Fig. 6) is only moderately good, a canting of the Yb^{3+} moments cannot be proven with certainty from specific heat data. In HoIG however, the comparison between the calculated and experimental nuclear specific heat[1] shows strong evidence of a canting of about 30°.

The rise of the specific heat with temperature above 2°K is due to the population of the 12 low-lying optical modes. Tinkham[50] has shown from a simple model that eleven modes should have very nearly the same energy, which is independent of $\mathbf{k}$, with an average value of $E/k_B = 33.9$°K.[1,9] The 12th mode is an exchange mode, the frequency of which is lower at the center of the BZ and tending to that of the other modes as $\mathbf{k}$ approaches the zone boundary.[50] The energy of the 12th mode at $\mathbf{k}=0$ was measured to be $E/k_B = 20.2$°K.[9] The specific heat calculated from Tinkham's dispersion curve, with $(E/k_B)_{k=0} = 20.2$°K for the twelfth mode and an average energy of $(E/k_B)_{k=2\pi/a} = 33.9$°K for all 12 modes, does not agree well with the experiment. This is seen in Fig. 7 where the lattice contribution has been subtracted. A somewhat better agreement can be found by assuming a dispersion relation for the 12th mode which weights the lower energies more heavily than does the Tinkham model. A crude approximation to such a dispersion curve is that of a linear increase of E with k, taking the limiting values of E in the center and at the BZ boundary as indicated before, namely

$$E/k_B = 20.2 + 13.7(a/2\pi)k. \tag{23}$$

It should be pointed out that the contribution of this mode is dominant over that from the eleven other optical modes below about 2.5°K, and hence the influence of its dispersion curve on thermodynamic data is quite sensitive. From the substantial disagreement remaining between the experiment and the theoretical fit, one must conclude that the energy of the exchange mode increases even less with increasing k than given by Eq. (23). Possibly there may also be a residue $\mathfrak{R}(T)$, but its existence cannot be cleared up until a direct determination of the dispersion curve for this mode is obtained by means of another method, such as neutron scattering.

ACKNOWLEDGMENTS

The authors are indebted to G. R. Brown for help with some of the experiments. They acknowledge several informative discussions with Professor A. B. Harris, and with Dr. R. L. Walker, who also read the manuscript. Thanks are due to Dr. D. W. Osborne for his loan of the copper ASARCO sample. An informative correspondence with Professor D. L. Mills is gratefully acknowledged.

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