Calorimetric Study of Several Rare-Earth Gallium Garnets*

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Specific-heat measurements on the gallium garnets (GaG) of Nd, Sm, Gd, Er, Dy, Ho, and Yb between 0.35 and 4.2°K are presented. The transition to the ordered state for the garnets of Nd, Sm, and Er is studied in detail, the transition temperature T_N being, respectively, 0.516, 0.967, and 0.789°K. Another Sm sample had a transition at $T_N=0.921$°K. From this study, the exchange coupling parameter J_{cc} between the rare-earth ions situated on the c sites is derived in different ways, namely, from T_N, the magnetic energy, and the high-temperature specific-heat "tail." These determinations are found to be reasonably consistent. The entropy and magnetic energy are found to be approximately those of a Heisenberg system with spin $\frac{1}{2}$. For GdGaG, the rounded specific-heat maximum is interpreted in terms of a Schottky anomaly. The specific-heat anomaly can be well fitted by a calculated curve assuming a cubic crystalline field. Unexpectedly, the splitting is much larger than that obtained for the diluted garnet from ESR data. For HoGaG, the specific heat shows the population of the first excited singlet at $E/k=7.4$°K and a second-order hyperfine splitting at temperatures below 1°K. For YbGaG, the specific heat increases as the temperature decreases, and from the temperature region where the magnetic contribution is proportional to T^{-2}, the transition to an ordered state is expected at about 0.3°K. The DyGaG shows a maximum specific heat at about 0.36°K, but no satisfactory analysis could be carried out on this compound.

I. INTRODUCTION

THERE have been a number of experiments and discussions in recent years on the exchange interaction in rare-earth garnets.[1–3] In the rare-earth iron garnets, the exchange J_{ad} between the a and d sites is found substantially larger than the exchange parameter J_{aa} and J_{dd} within the same sublattice, and research on these parameters is being pursued in this laboratory.[4] The coupling J_{ac} and J_{dc} between the Fe^{3+} ions and the rare-earth ions, located on the c sublattice, depends on the rare earth in question and is much smaller than J_{ad}.[1] It is usually of such magnitude that the rare-earth spins are practically aligned at liquid-helium temperatures.

In this paper we wish to investigate the coupling parameter J_{cc}, usually neglected in comparison with the other exchange parameters. This study is concerned with several garnets with gallium on the a and d sites. Previous studies on several rare-earth gallium garnets (GaG) have been carried out by means of electron-spin-resonance,[5] susceptibility,[6] and specific-heat[7] measurements above 1.5°K. The susceptibility data[6] were analyzed in terms of a Curie-Weiss law showing an antiferromagnetic coupling for most garnets. An attempt[7] was made to separate the observed specific heat into lattice and magnetic contributions C_L and C_M.

In the present work the transition into an ordered magnetic state is studied in detail for several garnets. An estimate for the respective contributions to the specific heat is obtained, and these are analyzed in terms of exchange and dipolar coupling. For the garnets investigated, in particular SmGaG, NdGaG, and YbGaG, exchange rather than dipolar interaction is believed to be the dominant factor in the transition.

A short account of this work has been presented elsewhere.[8]

II. EXPERIMENTAL

The calorimeter and techniques for operating between 0.35 and 4.3°K were the same as in a previous work.[9] The samples were glued with a small amount of

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[1] See, for instance, L. Néel, R. Pauthenet, and B. Dreyfus, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1965), Vol. 4, p. 344.

[2] E. A. Anderson, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and The Physical Society, London, 1964), p. 660; P. J. Wojtowicz, *ibid.*, p. 11.

[3] P. M. Levy, Phys. Rev. **147**, A311 (1966).

[4] R. Gonano, E. Hunt, H. Meyer, and A. B. Harris, J. Appl. Phys. **37**, 1322 (1966); R. Gonano, E. Hunt, and H. Meyer, Phys. Rev. **156**, 521 (1967).

[5] M. Ball, G. Garton, M. J. M. Leask, D. Ryan, and W. P. Wolf, J. Appl. Phys. **32**, 267S (1961); Proc. Phys. Soc. (London) **74**, 663 (1959); W. P. Wolf, M. Ball, M. T. Hutchings, M. J. M. Leask, and A. F. G. Wyatt, J. Phys. Soc. Japan **17**, Suppl. BI, 443 (1962).

[6] M. Ball, G. Garton, M. J. M. Leask, and W. P. Wolf, in *Proceedings of the Seventh International Conference on Low Temperature Physics, 1960* (University of Toronto Press, Toronto, 1960), p. 128; W. P. Wolf, M. Ball, M. T. Hutchings, M. J. M. Leask, and A. F. G. Wyatt, J. Phys. Soc. Japan **17**, Suppl. BI, 443 (1962).

[7] C. Bailey, Clarendon Laboratory, Oxford University, Technical Report AF 61 (052)–125, edited by B. Bleaney, 1963 (unpublished).

[8] D. G. Onn, H. Meyer, and J. P. Remeika, Ann. Acad. Sci. Fennicae **6**, 218 (1966).

[9] D. C. Rorer, D. G. Onn, and H. Meyer, Phys. Rev. **138**, A1661 (1965).

grease to thin copper strips that were a part of a support. The specific heat of this support was measured in a separate experiment.

For samples not showing a transition, approximately 200 specific-heat points were taken between 0.35 and 4.5°K with an accuracy of about 2%. The samples which showed a lambda-type specific heat were warmed very slowly through the transition by steps of a quarter of a millidegree. The temperature resolution was about 5 μdeg, which is more than adequate considering the broadness of the maximum (approximately 5 mdeg). For these samples, up to 500 points were taken.

Most of the samples were prepared by one of us (J. P. R.). The rest were prepared by C. Quadros at the Gordon McKay Laboratory, Harvard University, using the coprecipitation technique.[10] ErGaG, GdGaG (Sample II), YbGaG (II), and SmGaG (II) were in the form of single crystals of approximately 0.2–0.5 g each. The sample was usually made up of 2 g of crystals. The gallium garnets of Sm (I), Nd, Dy, Ho, Yb (I), Gd (I) were sintered materials in the shape of two thin disks of approximately 1 g each, sawed off a cylinder 2 cm in diameter. Copper strips in contact with the carbon resistance thermometer were sandwiched between the two disks, a small amount of grease providing thermal contact. The copper strips in contact with the heater and the support were fastened on the outside of the sandwich. The samples in powder form were checked by x-ray diffraction and only the garnet phase was detected. The YbGaG(I) sample mentioned previously[8] gave results believed erroneous because of possible impurities. It will not be discussed any further.

III. RESULTS AND DISCUSSION

The quantity of interest in this research is the magnetic specific heat C_M. This quantity is obtained by subtracting the lattice contribution C_L from the total measured specific heat. In order to estimate C_L, we have used the data for NdGaG and YbGaG (II) obtained in the present research. Our data are consistent with those of Bailey[7] in the temperature region where they overlap. The advantage in using these compounds is that susceptibility measurements[6] indicate that there are no excited levels for energies less than 100°K. Also for these compounds, the transition temperature T_N is low enough so that we can expect that in the region above about 3°K the total specific heat per mole rare-earth ion is given by the expression

$$C/R=A/T^2+BT^3, \quad (1)$$

the second term representing C_L. We find for these two compounds the same slope $B=2.8\times10^{-5}$ within experimental error. This corresponds to a Debye temperature of about 380°K. It is then safe to assume that the lattice specific heat of the gallium garnets with molecular weights between those of YbGaG and NdGaG will be close to $C_L/R=2.8\times10^{-5}T^3$. Since C_L is relatively small in comparison with C_M (5–10% at 4.2°K except for YbGaG) any error in the calculation of C_L will affect only slightly the determination of C_M from the difference $C_{\text{total}}-C_L$. The contribution of the nuclear specific heat C_N resulting from electron-nucleus interaction was calculated to be negligible in comparison with C_M above 0.35°K for all the garnets used in this research, except for HoGaG. For ErGaG, for example, one estimates C_N from the known values[6] of g_z, g_y, g_x and the ratio $A_x/g_x=A_y/g_y=A_z/g_z$ of the hyperfine coupling parameters.[11] One then obtains $C_NT^2/R\approx1\times10^{-3}$.

A. SmGaG, ErGaG, and NdGaG

Our measurements show the absence of any Schottky anomaly in these compounds. Therefore, only the lowest Kramers doublet of the rare-earth ion is occupied at temperatures of liquid helium, and the ion has an effective spin of $\frac{1}{2}$. These three garnets show a sharp transition with a maximum of the specific heat at $T_{\max}=0.960$, 0.786, and 0.514°K, respectively. The other sample SmGaG (I) showed a maximum specific heat at $T_{\max}=0.918$°K. This sample was made up of sintered material and it is possible that surface effects[12] are partly responsible for lowering the transition. The difference in the technique of sample preparation may also account for the lower $T_{\max}$.

The question of the selection of the actual transition temperature is by no means well resolved. One may define T_N in such a way that the specific heat, plotted against the log of the relative temperature difference $|T-T_N|/T_N$ gives over a certain temperature region two "parallel" straight lines which correspond to tem-

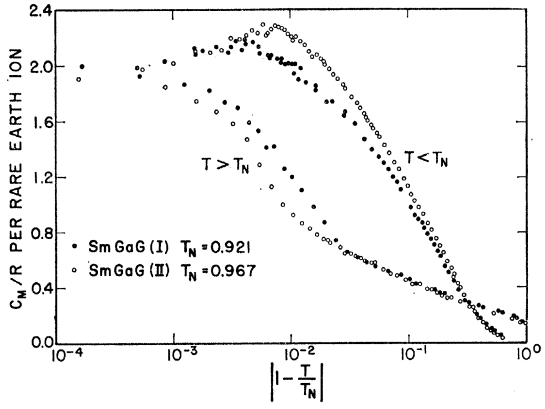

FIG. 1. Magnetic specific heat of two samples of SmGaG plotted as C_M/R versus $\log_{10}|1-T/T_N|$. SmGaG (I) was sintered, SmGaG (II) consisted of several single crystals.

[10] W. P. Wolf and G. P. Rodrigue, Croft Laboratory, Harvard University, Scientific Report No. 9, 1957 (unpublished).

[11] K. D. Bowers and J. Owen, Rept. Progr. Phys. **18**, 304 (1955).

[12] C. P. Poole, J. Phys. Chem. Solids **24**, 781 (1963).

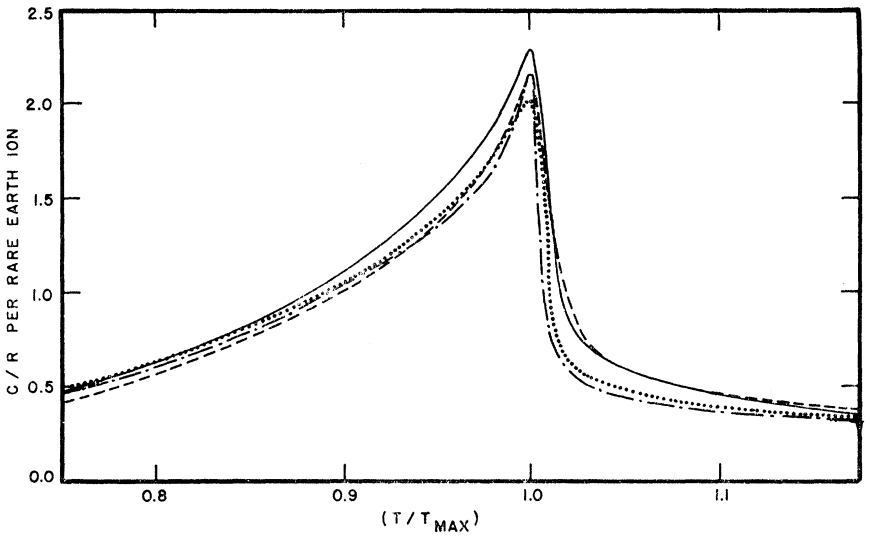

FIG. 2. Reduced plot of C_M of SmGaG (I), dashed line; SmGaG (II), solid line; NdGaG, dash-dot line; and ErGaG dotted line as a function of T/T_N.

peratures above and below T_N. Such a plot,[13,14] typical for the three compounds, is shown in Fig. 1 for SmGaG. The parameters of the plot

$$C_M = \alpha \log_{10}|1-T/T_N| + \Delta_{\pm}$$

are presented in Table I. From this plot we have determined $T_N = 0.967$, 0.790, and 0.516°K, respectively, for SmGaG (II), ErGaG, and NdGaG, slightly higher than the $T_{\max}$.

Because of the rounded maximum of the specific heat, a relation[15] of the form $(T-T_N)^{-\alpha}$ or $(T-T_{\max})^{-\alpha}$ for $T>T_N$ could not represent the data any better than did the logarithmic plot. We tentatively chose T_N as the transition temperature because several authors have done so previously.[13,14] However this choice is still rather arbitrary. Figure 2 shows a plot of the specific heat as a function of the reduced temperature T/T_N for the four samples. The maximum is less sharp than that for dysprosium aluminum garnet (DyAlG), where $C_{\max}/R$ was found[16] to be of the order of 5. Mattis and Wolf[17] have pointed out that the electron-nucleus interaction for the isotopes having a nuclear spin might broaden out the transition. These authors proved theoretically that for DyAlG, which is a nearly perfect Ising system, the nucleus-electron interaction does not cause broadening. As will be seen below, our own garnets behave nearly like a Heisenberg system, which is to be expected, since the electronic g values are more nearly isotropic[18,5] than in DyAlG. Therefore, the broad maximum may be attributed, at least in part, to the mechanism suggested in Mattis and Wolf. Other sources of broadening in magnetic transitions have recently been examined by Yamamoto *et al.*[14]

In Table II we have computed the entropy and magnetic energy for the three compounds using the notation of Domb and Miedema.[19] Since we find that the specific heat for $T/T_N<0.5$ follows closely a T^3 dependence,[20] we have extrapolated it from 0.35°K to $T=0$ assuming such a dependence. This should be a good enough approximation because the relative contribution to the energy and entropy below 0.35°K is small, except for NdGaG. At high temperatures, the specific heat is taken to be proportional to T^{-2} and the limiting entropy S_∞ is found to be close to $R\ln 2$, the value for a system of spin $\frac{1}{2}$. Over the temperature range covered experimentally, the entropy change was approximately 90–95% of the limiting $S_\infty - S(T=0)$.

TABLE I. Summary of λ-point analysis. $C_M/R = \alpha \log_{10}(|1-T/T_N|)+\Delta_{\pm}$.

Sample	α	Δ_+	Δ_-	$\Delta_+-\Delta_-$
SmGaG(I)	−1.2	−1.2	−0.2	1.0
SmGaG(II)	−1.5	−2.2	−0.5	1.7
ErGaG	−1.25	−1.8	−0.2	1.6
NdGaG	−1.2	−1.8	−0.2	1.6

[13] See, for instance, J. Skalyo and S. Friedberg, Phys. Rev. Letters **13**, 133 (1964); J. Skalyo, A. F. Cohen, and S. Friedberg, in *Low-Temperature Physics LT9*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yagub (Plenum Press, Inc., New York, 1965), p. 884.

[14] T. Yamamoto, O. Tanimoto, Y. Yasida, and K. Okada, Natl. Bur. Std. (U. S.) Misc. Publ. **273**, 86 (1966).

[15] C. Domb, in *Magnetism*, edited by H. Suhl and G. T. Rado (Academic Press Inc., New York, 1965), Vol. IIA.

[16] M. Ball, M. J. M. Leask, W. P. Wolf, and A. F. G. Wyatt, J. Appl. Phys. **34**, 1104 (1963).

[17] D. C. Mattis and W. P. Wolf, Phys. Rev. Letters **16**, 899 (1966).

[18] The g values for Sm^{3+} in the garnet have not yet been measured. However, Sm^{3+} in other compounds has g values that are fairly isotropic and close to 0.6. [See for instance W. Low, in *Solid State Physics*, edited by Seitz and Turnbull (Academic Press Inc., New York, 1960), Suppl. 2.]

[19] C. Domb and A. R. Miedema, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (John Wiley & Sons, Inc., New York, 1964), Vol. 4.

[20] Such a temperature dependence might be fortuitous. For $T \ll T_N$, however, this temperature dependence is expected from the spin-wave theory for an antiferromagnet without anisotropy field.

TABLE II. Entropy and internal energy.

Sample	$\frac{S_\infty-S_0}{R}$	$\frac{S_\infty-S_c}{R}$	$\frac{S_c-S_0}{R}$	$\frac{S_\infty-S_c}{S_c-S_0}$	$\frac{E_\infty-E_0}{RT_N}$	$\frac{E_\infty-E_c}{RT_N}$	$\frac{E_c-E_0}{RT_N}$	$\frac{E_\infty-E_c}{E_c-E_0}$
NdGaG	0.72	0.264	0.46	0.58	0.91	0.554	0.36	1.58
SmGaG (I)	0.699	0.304	0.395	0.77	0.944	0.625	0.319	1.96
SmGaG (II)	0.689	0.272	0.417	0.65	0.869	0.526	0.343	1.53
ErGaG	0.700	0.271	0.429	0.63	0.923	0.582	0.341	1.70
Heisenberg (fcc) ferromagnet $S=\frac{1}{2}$[a]	0.693	0.265	0.428	0.62	0.736	0.439	0.297	1.48
As above but corrected as antiferromagnet $S=\frac{1}{2}$	0.693	...	...	...	0.785	...	...	...
Ising (fcc) ferromagnet $S=\frac{1}{2}$[a]	0.693	0.107	0.586	0.18	0.629	0.169	0.460	0.37
DAG[b]	0.693	0.204	0.489	0.42	0.612	0.213	0.399	0.53

[a] Reference 15.
[b] Reference 16.

For comparison, the value for the entropy and the energy at the Néel temperature calculated for an Ising[15] spin-$\frac{1}{2}$ system in a fcc lattice[21] and for a Heisenberg model spin-$\frac{1}{2}$ is also shown in Table II. As can be seen, all three garnets have values very close to those for a Heisenberg antiferromagnet. One might have expected ErGaG, which has rather anisotropic g values[5] to be closer to an Ising model. The ratio $(E_\infty-E_N)/(E_N-E_0)$ is larger than unity, which is a feature of the Heisenberg coupling.[15,19]

The ratio C_MT^2/R is plotted in Fig. 3 as a function of T for these four samples. For ErGaG, a constant value for this ratio has not yet been reached at 4°K, but it can be estimated by extrapolation. A reduced plot of $C_M(kT/J)^2$ versus (kT/J) gives approximately the same behavior for all three garnets, with a minimum near $(kT/J)=2$. The behavior of SmGaG (I) at temperatures above 1°K is not well understood, and therefore this sample will not be analyzed in detail.

It is interesting to compare the magnetic specific heat expressed as C_MT^2/R with that expected theoretically from a power expansion in T^{-1}. According to

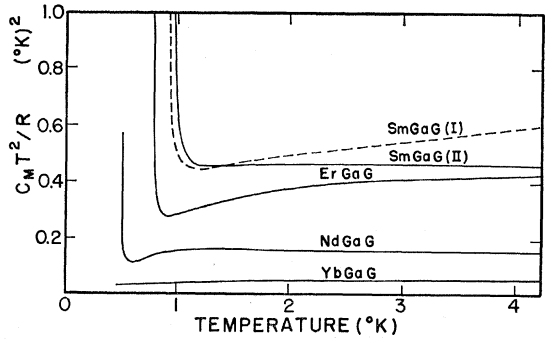

FIG. 3. Magnetic specific heat of SmGaG, ErGaG, NdGaG, and YdGaG plotted as C_MT^2/R versus T.

[21] It should be mentioned that the garnets do not have an fcc structure. This comparison with the models having this structure is made because there exist no estimates for entropy and energy for the garnet structure.

Domb,[15] the expression is of the form

$$\frac{CT^2}{R}=A\left(1+\sum_{i=1}^{\infty}a_i/T^i\right). \tag{2}$$

Unfortunately calculations of the constants in Eq. (3) have not been published for the garnet structure.

Before deriving the exchange parameter J_{cc}, it will be instructive to estimate the relative importance of exchange and dipole-dipole interaction in the specific heat. For temperatures such that kT is much larger than the dipolar energies, the corresponding specific heat C_{dip} can be obtained by expansion in powers of T^{-1}. Such an expansion was derived by Daniels[22,23] for several paramagnetic compounds in terms of the splitting factors g_x, g_y, and g_z and the appropriate lattice sums. For the rare-earth garnets one has to distinguish between six inequivalent sites, as shown by Wolf and co-workers.[24] Therefore, the summation over the different types of sites has to take into account the relative orientation of the local axes relative to the crystal axes. For the simple situation $g_z\gg g_y, g_x$, the extension of Daniel's expression becomes

$$\frac{C_{\text{dip}}T^2}{R}=\frac{g_z^4\beta^4}{32k^2}\left[\sum_{\substack{\text{sublattices}\\1,2}}\left(\frac{1}{r^3}-\frac{3z^2}{r^5}\right)^2+\sum_{\substack{\text{sublattices}\\3-6}}\frac{9x^2z^2}{r^{10}}\right], \tag{3}$$

where in sublattices 1 and 2 the local z axes are parallel to the crystal z axis (a certain ⟨100⟩ direction). In sublattices 3 to 6, the local z axes are perpendicular to the crystal z axis. The lattice sums for the six sublattices

[22] J. M. Daniels, Proc. Phys. Soc. (London) **66**, 673 (1952).
[23] The total magnetic specific heat is in general not simply the sum of the respective contributions from dipolar and nondipolar interactions. There are terms that contain cross products from both types of interaction. Only in the special case where the nondipolar forces are isotropic exchange and the g values are isotropic (a case not likely in the garnets) and in the temperature range where CT^2=constant, will there be simple additivity of both contributions [W. P. Wolf (private communication)].
[24] D. Boakes, G. Garton, D. Ryan, and W. P. Wolf, Proc. Phys. Soc. (London) **74**, 663 (1959).

have been computed by Landau.[25] For ErGaG, we use $g_x=0$, $g_y=0$, and $g_z=11.0$, and we then obtain $C_{\rm dip}T^2/R=0.13$.

In actual fact, the assumption of $g_z \gg g_x, g_y$ is only justified for a few garnets. In the more general case, a more involved formula than Eq. (3) must be derived.[22] An order-of-magnitude calculation gives $C_{\rm dip}T^2/R<10^{-2}$ and $<10^{-5}$ for NdGaG and SmGaG, respectively. This is much smaller than the measured specific heat C_M in the temperature range where C_MT^2 is constant. Therefore, we come to the conclusion that the dipolar contribution is probably less than 30% of C_M for ErGaG and negligible for NdGaG and SmGaG. The cooperative transition in these two compounds can hence be ascribed to nondipolar forces.

The exact form of the nondipolar Hamiltonian is not known, and it is quite possible that the exchange is anisotropic to some extent.[3] In order to obtain an order of magnitude estimation of these forces, we will assume the exchange to be of the Heisenberg type

$$\mathcal{H}=-2J_{cc}\mathbf{S}_1\cdot\mathbf{S}_2, \tag{4}$$

since extensive calculations have used this model and since the entropy and energy results (Table II) seem to favor this model over that of Ising.

The exchange parameter is obtained from three relations:

1. The specific heat for $T\gg T_N$ given by the expression for a Heisenberg-type interaction

$$\frac{C_{\rm ex}T^2}{R}=\tfrac{2}{3}qS^2(S+1)^2\left(\frac{J_{cc}}{k}\right)^2, \tag{5}$$

where q is the number of nearest neighbors, which is 4 from an inspection of the garnet lattice, but it is possible that second- or third-nearest neighbors might also contribute substantially to the exchange.

2. The transition temperature T_N from a high-temperature expansion of the susceptibility. For a Heisenberg ferromagnet, Domb and Sykes[26] obtained $2kT_c/qJ=0.695$ for a fcc lattice, 0.61 for a sc lattice. Extrapolating graphically their results to the case of a lattice with four nearest neighbors, one obtains a ratio

$$\frac{T_c}{0.55}=2qS^2\left(\frac{J_{cc}}{k}\right)=2\left(\frac{J_{cc}}{k}\right). \tag{6}$$

Rushbrooke and Wood[27] have derived the relation between the transition temperature T_c for a ferromagnet and that for an antiferromagnet. They obtain

$$\frac{T_N}{T_C}=1+\frac{0.67}{q(S+1)S}\simeq 1.22. \tag{7}$$

Combination of Eqs. (6) and (7) gives J for a given T_N.

3. The magnetic energy of an antiferromagnet, which is given by[28]

$$\frac{E}{R}=S^2q\left(\frac{J}{k}\right)\left(1+\frac{\gamma}{qS}\right). \tag{8}$$

The factor γ has not been calculated for the garnet structure. It is 0.6 for simple cubic and bcc.[29] Since this factor is dimension-dependent but almost independent of q we take $\gamma=0.6$ for the garnet lattice. In these three ways of deriving J, we have assumed that the specific heat and energy are entirely due to exchange, which, as we have seen, is well justified for Sm and Nd garnet, and to a lesser extent for ErGaG. There is no clear way of subtracting the dipolar contribution except under special circumstances.[23] The values of J so derived are presented in Table III. It is to be noted that the numbers obtained from method 2 are consistently highest.

TABLE III. Values of the exchange constant J/k derived from Eqs. (5), (8), and (7).

Sample	C_MT^2/R	J/k (°K)	E/R	J/k (°K)	T_N (°K)	J/k (°K)
NdGaG	0.16	0.32	0.47	0.36	0.516	0.38
SmGaG(I)	0.60	0.63	0.87	0.67	0.918	0.68
SmGaG(II)	0.47	0.56	0.84	0.64	0.967	0.72
ErGaG	0.43	0.53	0.73	0.56	0.789	0.58

Capel[30] has predicted the transition temperature for several rare-earth aluminum and gallium garnets. He used a Weiss molecular field approach and obtained expressions for T_N in terms of dipolar coupling and exchange. Using the g values from the ESR data of Wolf and co-workers,[5] and neglecting exchange, he calculated T_N for ErGaG to be 0.94°K, assuming an antiferromagnetic transition, in fair agreement with unpublished specific-heat results of Vivet and Carara and our own. He has further discussed refinements of his calculations using the Bethe-Peierls method and finds a transition temperature of 0.82°K assuming dipolar interactions only. His analysis of the susceptibility shows, however, that the Weiss constant calculated for dipolar interaction only is half of the total measured value of 0.3°K. This is consistent with the specific-heat data where the $C_{\rm dip}$ is found to be less than $C_{\rm ex}$. Capel concludes that exchange may play an important role in the cooperative transition. Therefore the agreement between the calculated 0.82°K [30] and experimental value of T_N is somewhat fortuitous.

[25] We are very indebted to D. Landau for communicating his tabulations prior to publication.
[26] C. Domb and M. F. Sykes, Proc. Roy. Soc. (London) **A240**, 214 (1957).
[27] G. S. Rushbrooke and P. J. Wood, Mol. Phys. **6**, 409 (1963).
[28] P. W. Anderson, Phys. Rev. **83**, 1260 (1951).
[29] T. Nagamiya, K. Yosida, and R. Kubo, Advan. Phys. **4**, 1 (1955).
[30] H. Capel, Physica **31**, 1152 (1965).

For NdGaG, the highest transition temperature calculated[30] for dipolar interaction only is 0.10°K, appreciably below the observed transition. This result is consistent with the deduction that exchange plays the dominant role in the ordering in this compound.

B. YbGaG

This compound shows a magnetic specific heat rising monotonically as the temperature is lowered, and no transition has been found down to 0.35°K. At temperatures above 2.5°K, one obtains $C_M T^2/R = 0.061$. The constancy of this ratio confirms the absence of any excited level for energies of less than about 100 cm^{-1} as shown by susceptibility[6] and optical data.[31] The ratio $C_M T^2/R$ is plotted as a function of temperature in Fig. 3. It also shows a decrease with T similar to that of the Sm, Er, and Nd garnets. An estimate of the dipolar specific heat, based on Eq. (3) and the g values of Wolf and co-workers[5] in a "diluted" Yb garnet gives $C_{\text{dip}} T^2/R < 10^{-2}$. Therefore, exchange interactions seem to dominate the dipolar ones. From Eq. (5), we derive $J_{cc}/k = 0.2$°K and therefore predict from Eqs. (6) and (7) a transition temperature in the region of about 0.27–0.3°K. This is higher than the temperature 0.18°K, predicted by Capel *et al.*[32] for dipolar interaction only. These authors also expect a ferrimagnetic structure below the transition. From our own measurements, any conclusions about such a structure are not possible at present.

C. DyGaG

For this compound, the specific heat also increases steadily as the temperature decreases. A maximum was detected near the lower limit of our temperature range at 0.35°K, and this is shown in Fig. 4. The effect of an excited doublet with an energy $E/k = 34$°K was detected near the high-temperature end and was subtracted from the total C_M. Nevertheless, the remaining ratio $C_M T^2/R$ was not constant above 2.5°K, and

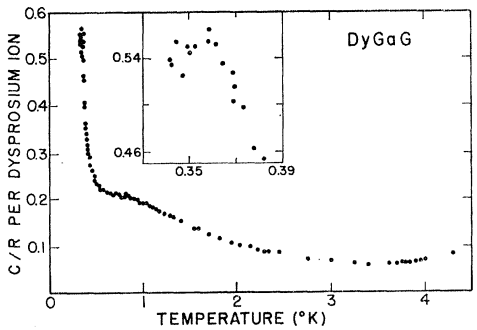

FIG. 4. Specific heat of DyGaG versus T.

appreciably larger than one would have expected in view of the low transition temperature.

It is possible that impurities may have influenced the experimental results somewhat. More samples, preferably single crystals, must be investigated in order to check for reproducibility of these strange results. [*Note added in proof.* Recent measurements by J. Henderson and one of the authors (H.M.) on DyGaG single crystals show a well-resolved broad maximum near 1°K, instead of the flattening-off exhibited by the sintered sample. Below about 0.5°K, there is again a sharp rise in the specific heat. Perhaps the maximum at 1°K can be related to the transition predicted by Capel *et al.*[32] at 0.7°K leading to a ferrimagnetic structure. But then the sharp rise at lower temperatures would indicate another transition.]

D. GdGaG

The experimental data for two samples are shown in Fig. 5. This compound shows a specific heat that can be

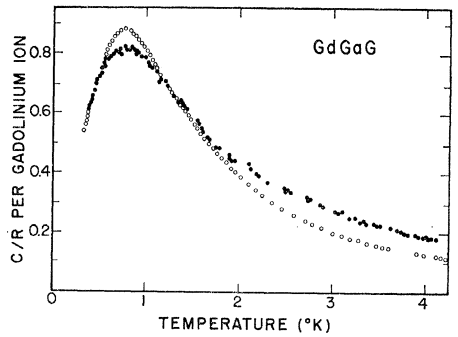

FIG. 5. Specific heat of two samples of GdGaG. ● Sintered sample, ○ cluster of single crystals.

interpreted as a Schottky anomaly resulting from the crystal field splitting the eightfold degeneracy of the ground state. From a rough estimate, these splittings appear to be of the order of several degrees Kelvin, an order of magnitude larger than the splittings obtained from ESR spectra in GdGaG diluted in YGaG and LuGaG.[33] It is rather surprising that dilution should change the electric-field splitting parameters by so large an amount. Analysis of susceptibility data[6] is also puzzling: from the data above 1.5°K, one obtains a Curie-Weiss constant of the order of 2°K, and therefore one might expect a high antiferromagnetic transition temperature. However, more recent measurements[34] down to 0.5°K do not show the maximum in the susceptibility expected for such a transition. Therefore specific heat and susceptibility from Curie's law might be attributed to the depopulation of levels with a high

[31] R. Pappalardo and D. L. Wood, J. Chem. Phys. 33, 1734 (1960).

[32] H. W. Capel, R. Bidaux, P. Carrara, and B. Vivet, Phys. Letters 22, 400 (1966).

[33] G. Overmeyer, E. A. Giess, M. J. Freiser, and B. A. Calhoun, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962,* edited by W. Low (Academic Press Inc., New York, 1964), Vol. II, p. 431.

[34] D. Thorp and A. H. Cooke (private communication).

S_z into the ground-state doublet. The resultant effect then is that the effective Curie constant becomes smaller. This has been observed clearly in compounds with comparable splittings, for example, Fe^{3+} in methylammonium sulphate,[35] which shows a specific-heat maximum and appreciable deviation from Curie's law near 0.5°K.

Since the surroundings of a rare-earth ion have an (admittedly distorted) cubic symmetry, we have tried to fit the specific heat to a system of levels obtained from a cubic crystal-field Hamiltonian[36] for $4f$ electrons:

$$\mathcal{H}=B_4(O_4^0+5O_4^4)+B_6(O_6^0-21O_6^4). \quad (9)$$

The energy levels in zero field, if the doublet Γ_6 is assumed to have zero energy, are[36,37]

$$\begin{aligned} &\Gamma_8 \text{ (quadruplet)} \quad E_8=3c-9d, \\ &\Gamma_7 \text{ (doublet)} \quad\quad E_7=8c-2d, \end{aligned} \quad (10)$$

where $c=240B_4$ and $d=5040B_6$. The fit was made assuming that at the low-temperature end there would be an additional contribution, roughly proportional to T^{-2} which accounts for exchange and dipolar specific heat. After trying several combinations of energy levels, the best fit, within $\pm 5\%$ above 0.8°K was found by taking $c=0.8$ and $d=0.04$°K for the sintered sample. This gives $E_8/k=2.04$°K and $E_7/k=6.32$°K. For the single crystals we obtain $c=0.55$, $d=-0.03$°K, which corresponds to $E_8/k=1.92$°K and $E_7/k=4.46$°K. The position of the maximum of C_M shows that E_8 has changed only little from one sample to the other. Because so many levels are involved, the above assignments may not be unique. The quadruplet will be split by an axial or orthorhombic component of the crystalline field, but energies quoted above give the order of magnitude, probably within, say, 10%, as suggested by the sensitivity of the fit when the parameters c and d are varied.

It was not possible to obtain a satisfactory fit assuming an axial field only. Overmeyer *et al.*[33] had found that for diluted Gd in YGaG and LuGaG, axial and rhombic fields gave the most important contribution to the splittings. In the concentrated Gd garnet, where the splittings seem so much larger, there is no reason to assume *a priori* that axial and rhombic crystal fields are the dominant ones.

The experimental data for the sintered sample together with the theoretical fit assuming cubic field only are shown in a previous paper.[8]

E. HoGaG

The specific heat of HoGaG is presented in Fig. 6. The magnetic specific heat can be analyzed in terms of

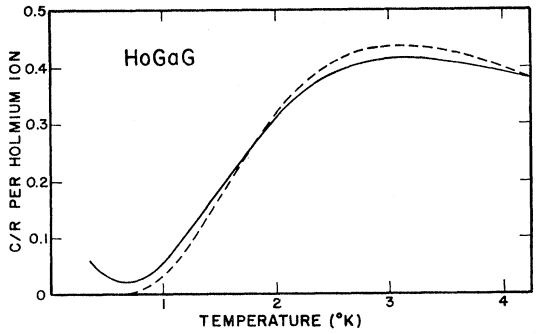

FIG. 6. Specific heat C_M of HoGaG. The solid line is a smoothed reproduction of the data, which scatter around this line by about 1%. Dashed line is calculated Schottky anomaly for $E/k=7.4$°K.

two electronic singlet levels separated by an average energy of $E/k=7.4$°K. There might be a certain distribution of splittings through the lattice since the fit of a simple Schottky anomaly to the experimental points is not perfect, especially at the low-temperature end where the specific heat is particularly sensitive to E. Other effects like dipolar and exchange coupling might affect C_M as well. The effect of the higher excited[38] levels at 26.5 and 30.5 cm^{-1} only accounts for a few percent of C_M at 4°K. Holmium is made up entirely of Ho^{165} with nuclear spin $I=\frac{7}{2}$ and one observes a contribution $C_NT^2/R=7.8\times10^{-3}$ which is to be attributed to nucleus-electron interaction. Unfortunately, a quantitative analysis in terms of the hyperfine interaction parameters[39] A, B, and P cannot be calculated at the present time because of the lack of information on the g values for Ho^{3+} in the garnet.

A qualitative argument can be made to justify the energy-level interpretation. The two electron levels cannot be doublets, because then C_N would be expected to be much larger, of the order of that for the non-Kramers doublet in Holmium ethylsulphate,[39,40] where, $CT^2/R=0.2$. For singlets separated by an energy E, the nuclear splitting becomes a second-order effect or pseudoquadrupolar splitting, inversely proportional to E. A simple calculation based on the Hamiltonian given in Eq. (3) of Ref. 36 shows that the expected nuclear specific heat is of the same order of magnitude as that observed. Because the wave functions of the ground state are not known, detailed quantitative calculations cannot yet be made.

IV. CONCLUSIONS

A detailed calorimetric study has been made of the magnetic transition in several rare-earth gallium gar-

[35] A. H. Cooke, H. Meyer, and W. P. Wolf, Proc. Roy. Soc. (London) **A237**, 404 (1956).

[36] For the explanation of the symbols and calculation of eigenvalues, see K. R. Lea, M. J. M. Leask, and W. P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).

[37] M. M. Abraham, E. J. Lee, and R. A. Weeks, J. Phys. Chem. Solids **26**, 1249 (1965).

[38] A. J. Sievers and M. Tinkham, Phys. Rev. **129**, 1995 (1963).

[39] J. M. Baker and B. Bleaney, Proc. Roy. Soc. (London) **A245**, 156 (1958).

[40] D. G. Onn, R. Gonano, and H. Meyer, in *Low Temperature Physics LT9*, edited by J. G. Daunt, D. O. Edwards, F. J. Milford, and M. Yaqub (Plenum Press, Inc., New York, 1965), p. 897.

TABLE IV. Specific heat of rare-earth gallium garnets expressed in C/R per mole rare-earth ion. The Roman numerals are sample numbers.[a]

T (°K)	Nd	Sm (II)	Gd (II)	Er	Dy	Ho	Yb (II)
0.35		0.0196	0.54	0.0621	0.551	0.0634	
0.4	0.583	0.0329	0.606	0.1105	0.364	0.0493	
0.45	0.911	0.0534	0.668	0.1770	0.270	0.0383	0.136
0.5	1.565	0.0868	0.734	0.2636	0.241	0.0313	0.1205
0.55	0.408	0.1340	0.784	0.385	0.225	0.0271	0.1060
0.6	0.327	0.2005	0.826	0.535	0.215	0.0248	0.0930
0.65	0.287	0.293	0.854	0.736	0.210	0.0243	0.0815
0.7	0.257	0.413	0.873	1.009	0.209	0.0253	0.0715
0.75	0.233	0.563	0.881	1.43	0.208	0.0281	0.0634
0.8	0.214	0.754	0.880	0.678	0.207	0.0323	0.0570
0.85	0.198	1.014	0.871	0.412	0.203	0.0376	0.0515
0.9	0.185	1.386	0.858	0.341	0.200	0.0439	0.0467
0.95	0.177	2.073	0.840	0.306	0.195	0.0516	0.0425
1.0	0.152	0.642	0.820	0.281	0.190	0.0662	0.0391
1.2	0.109	0.320	0.720	0.213	0.170	0.105	0.0289
1.5	0.071	0.205	0.567	0.150	0.143	0.182	0.0201
2.0	0.0402	0.116	0.385	0.0942	0.103	0.311	0.01320
2.5	0.0261	0.075	0.272	0.0641	0.0782	0.387	0.00955
3	0.0183	0.0527	0.202	0.0459	0.0648	0.420	0.00738
3.5	0.0139	0.0395	0.156	0.0357	0.0603	0.415	0.00622
4.0	0.0115	0.0308	0.126	0.0289	0.0676	0.395	0.0055
4.2	0.0109	0.0286	0.118	0.0271		0.387	0.0054

[a] Extensive tabulations of all the results, except for GdGaG (II) and YbGaG (II) are presented in the Ph.D. thesis of D. G. Onn, Duke University, 1966 (unpublished). In the region of the transition, the specific heat is tabulated in steps of 1 mdeg. Tabulation of the other two samples and the second sample of DyGaG will be supplied upon request.

nets. Smoothed values of the data are presented in Table IV. These compounds have the advantage that in the available temperature range of 0.35 to 4.2°K, the lattice specific heat is relatively small. Therefore the high-temperature tail of C_M could be investigated in detail. In that region, theoretical calculations by means of power-series expansions in T^{-1} can be made[15] and it is hoped that a comparison of theory and experiment for Heisenberg antiferromagnets with garnet structure can be made in the near future.

While such a calorimetric study can say little on the mechanism of the exchange or its exact form, the assumption of a Heisenberg exchange coupling gives values of the parameter J_{cc} that are reasonably consistent. Dipolar forces appear smaller than exchange in ErGaG and YbGaG, and negligible in NdGaG and SmGaG. In a recent study,[41] it was found that in dysprosium aluminum garnet also, nearest and next-nearest neighbors can almost entirely account for the cooperative phenomena.

The results near the transition were very similar for all three compounds and could not be fitted to any of the theoretical singular functions. Rounded maxima of a few millidegrees were obtained for all samples.

Estimates of the splittings for the lowest excited levels in GdGaG have been made on two samples. A cubic crystalline field splitting fits the data well, but the mechanism that creates these large splittings in the concentrated garnet is not understood. It is quite possible that other effects than purely crystalline fields affect the energy levels, and that exchange forces even split the doublets, but there is nevertheless no observed transition above 0.35°K. For HoGaG, the splitting between the lowest singlets has been measured and a second-order hyperfine specific heat observed.

There are indications that the way of preparation of the garnets affects the properties of the sample. It is therefore necessary to carry out other measurements like susceptibility, magnetization, etc., on these same samples. We hope to perform such experiments in the near future.

In spite of the difficulties in exactly reproducing results from sample to sample, several phenomena are clearly observed, that need further study. The most unexpected ones are the large splittings in GdGaG and the strange behavior of DyGaG.

ACKNOWLEDGMENTS

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[41] B. Schneider, D. P. Landau, B. E. Keen, and W. P. Wolf, Phys. Letters (to be published).