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Specific heat of europium, praseodymium, and dysprosium gallium garnets between 0.4 and 90°K

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The specific heat of single crystals of europium gallium garnet (EuGaG) and dysprosium gallium garnet (DyGaG) and of a sintered polycrystalline sample of praseodymium gallium garnet (PrGaG) has been measured between 0.4 and 90 °K. For EuGaG the results can be described by the lattice contribution alone between 2 and 55 °K. Schottky anomalies observed in PrGaG and DyGaG are explained by crystal-field splittings, with the best fit in both cases being obtained with a Gaussian distribution of energy levels rather than single values. In DyGaG anomalies below 2 °K suggest a possible reassignment of crystal-field levels, and magnetic ordering below 0.4 °K.

INTRODUCTION

The rare-earth gallium garnets provide an interesting opportunity to study crystal-field effects and rare-earth interactions throughout a sequence of isostructural compounds of moderate complexity in crystal structure. Many rare-earth gallium garnets have been studied by a variety of techniques in recent years, as have the properties of the rare-earth ions in dilute form in diamagnetic garnet hosts. While the literature is extensive, we note particularly the measurements of specific heat[1] and magnetic susceptibility[2,3] of the concentrated garnets, paramagnetic resonance,[4] and optical-absorption[5-7] studies of the dilute forms as typical and particularly relevant to the present work, which is intended to supplement and extend the referenced studies. We have determined the specific heat of two previously unmeasured garnets, europium gallium (EuGaG) and praseodymium gallium (PrGaG) between 0.4 and 90 °K, the former being a good single-crystal sample. We have also measured the specific heat of a good single crystal of dysprosium gallium garnet (DyGaG) over the same temperature range and compared the results with previous measurements of a sintered sample determined only up to 4.2 °K.[1]

The rare-earth gallium garnets have the formula $3R_2O_3 \cdot 5Ga_2O_3$, where R is the rare earth. The crystalline structure is well known,[8] the molar unit above containing forty ions, of which six are the rare-earth ions located on the c sublattice. Magnetic ordering arising from the rare-earth–rare-earth interactions is observed in the gallium garnets of erbium, samarium, and neodymium.[1,3] There is some evidence of ordering in DyGaG from the behavior of the specific heat and the magnetic susceptibility.[1,3] In many of the rare-earth garnets the crystalline field arising from the near cubic environment of the rare-earth ions gives rise to observable electronic energy levels in the temperature region up to 100 °K. These have been determined by specific-heat measurements in holmium gallium garnet (HoGaG) where the splitting is reduced to 7.4 °K by the presence of large nuclear spins.[1] For other rare-earth ions the splittings have been determined for dilute concentrations in garnet hosts[4-6,9,10] and for ions in the concentrated salts.[11,12]

We are able to analyze the specific heat of the three garnets measured here in terms of only two identifiable contributions, C_L due to the lattice and C_E due to the electronic contribution. There is no clear evidence of a nuclear specific-heat contribution C_N. We can then write the specific heat as

$$C_{\text{tot}} = C_L + C_E \,. \tag{1}$$

The electronic specific-heat contribution can generally be described by a Schottky anomaly of the form

$$C_E = R\left(\frac{\Delta}{T}\right)^2 \frac{g_0}{g_1} \frac{e^{\Delta/T}}{[1+(g_0/g_1)e^{\Delta/T}]^2} \,, \tag{2}$$

where R is the gas constant, Δ is the energy level splitting, g_0 is the degeneracy of the ground state, g_1 is the degeneracy of the first excited state, and T is the temperature. Although we could determine values of Δ for PrGaG and DyGaG, this simple form did not describe the results exactly. Rather a Gaussian distribution of energy levels is needed, as previously observed in[1] HoGaG and in other rare-earth salts such as praseodymium ethylsulphate.[12] In addition all three materials show anomalous behavior below 4.2 °K. In DyGaG this behavior is probably indicative of an ordering transition, but no unique explanation is possible for EuGaG and PrGaG.

EXPERIMENTAL

The thermal capacity of our samples was measured in a cryostat with an operating range of 0.3–100 °K. The cryostat was equipped with a remote pressure-operated heat switch and has been described in detail elsewhere.[13] The samples were attached to thin copper strips with a very small amount of N-grease[14] and monofilament thread. This assembly was suspended in the cryostat with monofilament nylon line.

Measurements were made by putting a known heat pulse into the sample by means of a noninductive wire-wound heater attached to the addenda. Power dissipation in the heater was determined by four-wire measurement of the current and voltage using a digital voltmeter with 1-μV resolution. Heating periods were measured to within ±0.02 sec. The temperature change of the sample due to the heat pulse was monitored by carbon and germanium resistors mounted on the addenda just above the sample. The resistances were determined by an ac bridge with lock-in detection and monitored by a strip chart recorder. A separate resistance bridge was used to control the temperature of the sample's environment. Approximately 300 data points were taken for each sample. The width of the data points varied from 1 mK at 0.4 °K to 2 °K at 90 °K. The thermal capacity of the addenda was measured in a separate experiment.

A calibration of the carbon and germanium resistors was made after each run, before returning to room temperature. For temperatures below 1.5 °K the resistors were calibrated against the vapor pressure of ^{3}He corrected for thermomolecular pressure effects.[15] The vapor pressure in this region was measured with a calibrated capacitance manometer.[16] For temperatures above 1.5 °K each resistor was calibrated against a four lead germanium thermometer[17] using the equation

$$\log T = \sum_{n=0}^{8} A_n \log\left(\frac{R-R_0}{100}\right)^n , \qquad (3)$$

where R_0 is the lead resistance and A_n are the coefficients to be determined by a multiple regression analysis. The fit to Eq. (3) was carried out over several short overlapping temperature intervals (e.g., 0.3–2.0 °K, 1.0–5.0 °K, etc.) to reduce high-frequency components detected in wide interval fits to Eq. (3). The final calibration was checked by specific-heat measurements of a 57-g sample of 99.99% pure platinum for which a plot of C/T vs T^2 was a good straight line, the slope and intercept agreeing with values obtained in other laboratories.[18]

Europium gallium garnet (EuGaG)

The sample measured was a single crystal, slightly elongated, with a mass of 5.71 g. Because of the low mass, the thermal capacity of the sample at the very lowest temperature was comparable to that of the various addenda, which limited the precision of determination, particularly at the lowest temperatures. Precision varied from ±10% at 0.6 °K to ±5% at 80 °K. The specific heat for the temperature range 0.6–90 °K is shown in Fig. 1 in smoothed form and tabulated in Table I. The small discontinuity in the region of 65 °K was reproducible and may arise from inclusions of the oxide EuO which is known to undergo a magnetic ordering transition at 69 °K.[19] From Fig. 1, which has a bilogarithmic scale, it is clear that between 2 and 65 °K the specific heat is varying almost as T^3. Above 65 °K the specific heat rises less rapidly, as expected, while there is a deviation from T^3 behavior at temperatures below 2 °K.

The ground state of the Eu^{3+} ion in EuGaG is $^7F_0$, while the first excited state is $^7F_1$. Studies of the optical-absorption spectra of the Eu^{3+} ion in yttrium gallium garnet (YGaG) verify these level assignments for Eu^{3+} in diamagnetic garnets, and determine their energies as 442, 497, and 559 °K.[6] The susceptibility of EuGaG can be satisfactorily explained with the same level assignment.[2] Because of the magnitudes of the splittings

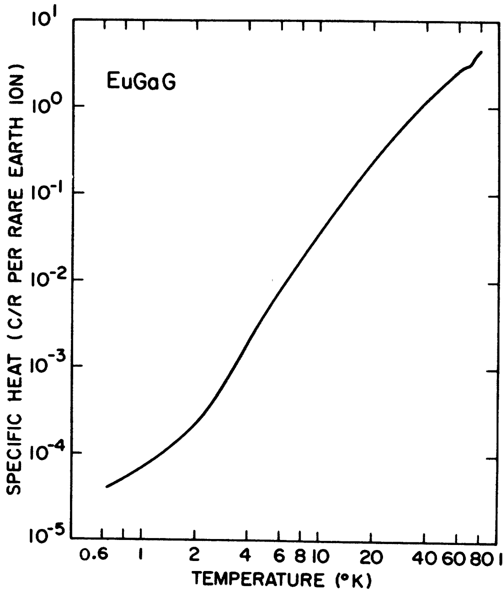

FIG. 1. Total specific heat of EuGaG in smoothed form as a function of temperature.

TABLE I. Specific heat of garnets.

	C_p (C/R per rare-earth ion)				C_p(C/R per rare-earth ion)		
T(°K)	EuGaG	PrGaG	DyGaG	T(°K)	EuGaG	PrGaG	DyGaG
0.5	0.000 021	0.000 35	0.200	5.0	0.0042	0.168	0.101
0.6	0.000 026	0.000 35	0.192	6.0	0.0077	0.247	0.165
0.7	0.000 032	0.000 36	0.192	7.0	0.0130	0.321	0.228
0.75	0.000 036	0.000 38	0.191	8.0	0.0196	0.365	0.289
0.8	0.000 039	0.000 39	0.190	9.0	0.0232	0.393	0.349
0.85	0.000 044	0.000 41	0.186	10.0	0.0367	0.415	0.396
0.9	0.000 048	0.000 43	0.185	15.0	0.116	0.436	0.516
0.95	0.000 053	0.000 45	0.181	20.0	0.241	0.531	0.636
1.0	0.000 058	0.000 47	0.170	30.0	0.731	0.938	1.14
1.5	0.000 120	0.001 02	0.130	40.0	1.40	1.65	1.93
2.0	0.000 23	0.0030	0.093	50.0	2.10	2.35	2.87
2.5	0.000 41	0.0110	0.071	60.0	2.85	3.06	3.75
3.0	0.000 75	0.0267	0.058	70.0	3.69	3.77	4.41
3.5	0.001 24	0.053	0.054	80.0	4.61	4.61	5.21
4.0	0.001 90	0.092	0.061	90.0	5.57	4.86	5.75

the contribution of the excited levels to the specific heat in our temperature range is small. We estimate it to be 5% at 80 °K and less than 1% at 50 °K. This contribution is not large enough, compared with the lattice specific heat, to enable us to analyze, unambiguously, our results in terms of the separate lattice and electronic contributions above 65 °K.

Below 65 °K the specific-heat variation can be explained in terms of the lattice contribution, except at the very lowest temperatures. The resulting variation of the effective Debye temperature Θ_D is shown in Fig. 2, which also illustrates the density of original data in this work. In previous work on the specific heat of garnets,[1] lack of data on the lattice specific-heat contribution generally led to the assumption of a T^3 dependence over the temperature range of interest with a constant Θ_D obtained from a variety of sources. A variation of the effective Θ_D through the rare-earth sequence was assumed to depend upon the mass variation of the rare-earth ions since the specific heat of yttrium gallium garnet (YGaG) gave a Θ_D of 490 °K, while the rare-earth garnets, of much greater mass number, have values about 100 °K lower. In particular, the analysis of the specific heat of NdGaG in the temperature region below 4.2 °K into T^3 and T^{-2} contributions gives a Θ_D of 385 ± 5 °K.[1] This value compares well with the values for EuGaG between 2 and 5 °K shown in Fig. 2, suggesting that although neodymium and europium have considerably different mass numbers (144.3 and 152.0, respectively), Θ_D has much less variation across the garnet sequence than comparison with the value for YGaG would indicate. The garnet Θ_D seems to depend on the total garnet formula-unit mass rather than the rare-earth ion mass above as previously concluded.[20] In practice most rare-earth garnets have specific-heat contributions from other sources that exceed the lattice contributions below 20 °K making determination of the lattice contribution difficult, but at the same time reducing the effect of any uncertainty in its value on the analysis of other contributions to the specific heat.

Below about 2 °K the specific heat for EuGaG can no longer be explained by a lattice term of the T^3 form, for any reasonable values of Θ_D. In Fig. 3 we show the smoothed data for the specific heat of our sample, compared with the lattice specific heat extrapolated below 2.5 °K, assuming $\Theta_D = 396$ °K. The measured specific heat exceeds the extrapolated lattice term by a factor of two at 1 °K and the discrepancy increases at lower temperatures. The excess specific heat (C_{ex}) is also shown in Fig. 3, and is seen to have a peak at about

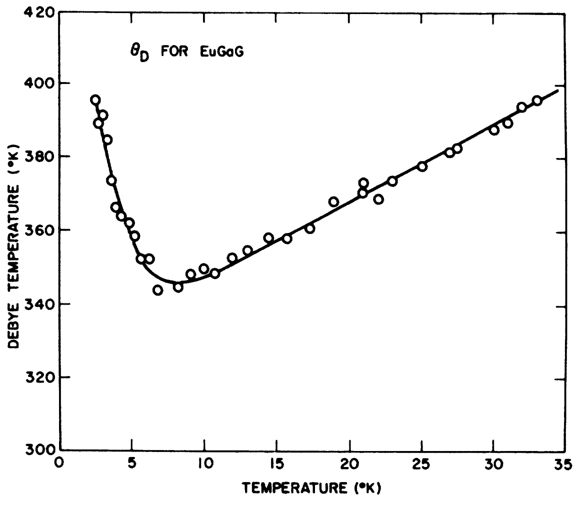

FIG. 2. Variation of Debye temperature Θ_D for EuGaG.

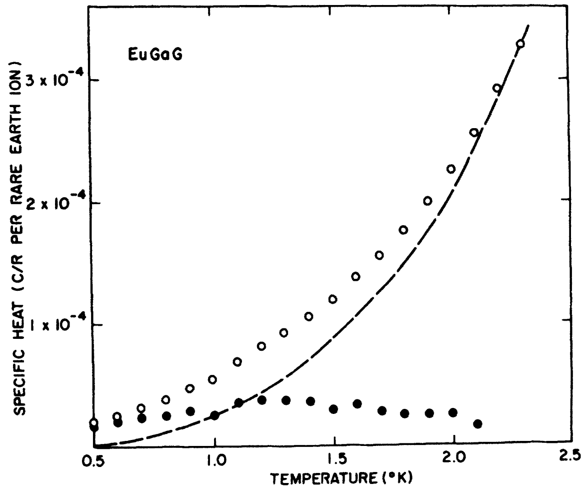

FIG. 3. Specific heat of EuGaG as a function of temperature. The open circles indicate the total specific heat C. The dashed line represents the lattice specific heat C_L for Θ_D of 396 °K. The solid circles are the excess specific heat C_{ex}.

1.5 °K. Although europium does have two naturally occurring isotopes (^{151}Eu, $I=\frac{5}{2}$, 47.8% and ^{153}Eu, $I=\frac{5}{2}$, 52.2%) C_{ex} does not vary as $1/T^2$ as would be expected for a nuclear contribution. Two other possible explanations depend on the presence of small amounts of rare-earth impurities. Several rare-earth gallium garnets undergo magnetic ordering at temperatures below 1 °K and traces as small as 0.01% could explain the excess specific heat observed. A more likely explanation, however, is that a trace of gadolinium is present, since gadolinium is next to europium in the periodic table, and separation of adjacent rare earths to high purity is very difficult. The specific heat of GdGaG shows an anomaly which has a rounded form very similar in shape and position to our excess specific heat, and again an amount as small as 0.005% is sufficient. We conclude therefore that the excess specific heat is probably due to impurities, and that below 2 °K the specific heat of pure EuGaG can be described by a T^3 lattice term with $\Theta_D = 396 \pm 5$ °K. We use this lattice specific heat as a basis for analysis of the other samples below.

Praseodymium gallium garnet

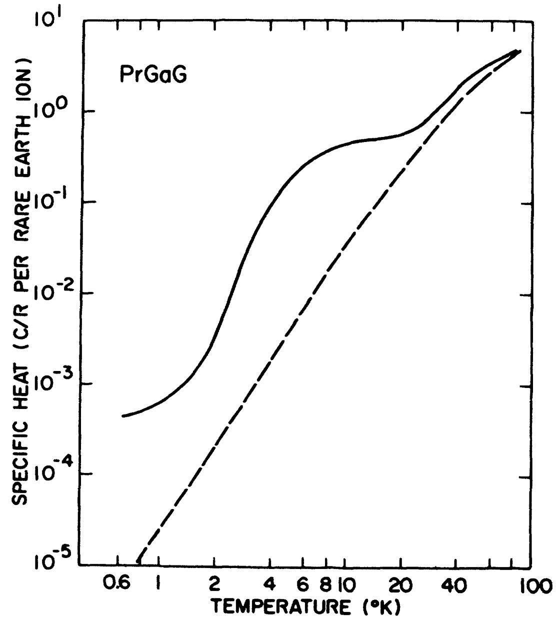

FIG. 4. Total specific heat of PrGaG in smoothed form as a function of temperature.

The sample measured was a cylindrical sintered block, with a mass of 39.23 g. The sample thermal capacity was at least six times greater than that of the addenda at all temperatures, resulting in a precision of ±3% at all temperatures. The specific heat in smoothed form is shown in Fig. 4, and is tabulated in Table I. For comparison, the lattice specific heat of EuGaG is also shown. For PrGaG there are three regions of excess specific heat, the most dominant being the large Schottky-type anomaly with a peak at 10 °K. In addition there is an anomalous behavior below 1 °K, and increasing excess specific heat at temperatures above 30 °K.

The ground state of the Pr^{3+} ion in the garnet is $^3H_4$ verified for Pr^{3+} in yttrium aluminum garnet (YAlG) by Wong *et al.*[7] Pr^{3+} is a non-Kramers ion. Studies of Pr^{3+} in yttrium gallium garnet (YGaG) and YAlG by Hooge[5] indicate that the lowest levels of the $^3H_4$ state are the Γ_5 triplet and the Γ_1 singlet, with the former as the ground state. This is in agreement with the level assignments of Lea, Leask, and Wolf for pure cubic crystalline fields for $J=4$.[21] However, the crystalline field in the garnets is not purely cubic, resulting in separation of the ground-state triplet as was observed in optical absorption measurements by Hooge.[5] He found that the Γ_5 triplet was split into three levels at 0, 32 (22 cm^{-1}), and 72 °K (50 cm^{-1}) for Pr^{3+} in YAlG, and 0, 32 (23 cm^{-1}), 55 °K (39 cm^{-1}) for Pr^{3+} in YGaG. He estimated the level of the Γ_1 singlet to be 774 °K (538 cm^{-1}), which is well above our own temperature range. Paramagnetic resonance measurements for Pr^{3+} by Belorizky and Ayant[4] give the levels of the Γ_5 triplet as 0, 20.7, and 68.7 °K.

The double Schottky-type anomaly we observe, with a main peak at 10 °K, and a secondary rise above 30 °K we attribute to the splitting of this Γ_5

triplet. By subtracting the lattice specific heat, assumed to be the same as EuGaG, we obtained the excess specific heat as a function of temperature, and attempted to fit the experimental values to calculations for the split triplet Γ_5 state. The best fit was obtained with level splittings of 22 and 130 °K, but the peak calculated value was $0.44C/R$ per rare earth at 10 °K, compared with the experimental value of $0.38C/R$ per rare earth at the same temperature. Furthermore, on the critical low-temperature side of the anomaly, the calculations were high by 20% at 5 °K and low by 60% at 2 °K. Similar behavior has been observed before in[1] HoGaG, in praseodymium ethylsulphate,[12] and is also observed in our own sample of DyGaG described below.

A much better fit to both the peak and the low-temperature side of the anomaly was made based upon the explanation of Baker and Bleaney[11] for linewidths in EPR experiments, and used by Meyer[12] for praseodymium ethylsulphate, that is the energy levels are not sharply defined and are best described by a Gaussian distributions, of the form

$$P(\Delta) = \frac{1}{(2\pi)^{3/2}\sigma} \exp\left[-\frac{1}{2}\left(\frac{T-\Delta}{\sigma}\right)^2\right], \tag{4}$$

where Δ is the mean splitting of the level and σ is the standard deviation. The specific heat is then given by

$$C(\Delta, T) = \int_0^\infty C(\Delta', T)P(\Delta')\, d\Delta' . \tag{5}$$

The effect of the Gaussian level distribution is to lower the peak value of the specific heat, decrease the slope of the low-temperature side of the anomaly, but not to affect the total entropy associated with the anomaly. Using this approach we obtain a value of $\Delta = 26$ °K with $\sigma = 5$ °K. The calculation and data then agree, well within experimental scatter, through almost three decades in the magnitude of the specific heat. Because of the large background lattice specific heat, which makes C_E above 40 °K increasingly uncertain, we retain the value of 130 °K for the highest level. A summary of the energy-level determinations for Pr^{3+} in dilute samples and normal samples is given in Table II.

Below 2 °K the specific heat of PrGaG exceeds the lattice specific heat. The excess specific heat C_{ex} is a maximum at about 1.8 °K and decreases a factor of 2 by 0.5 °K. At 1 °K it is about 20 times the lattice specific heat. The temperature dependence of C_{ex} does not indicate either a nuclear contribution to the specific heat, nor the onset of ordering. Capel[22] has predicted that ordering will not occur if the energy splitting between the ground and excited states exceed 7 °K (5 cm^{-1}). C_{ex} may again be due to trace amounts of other garnet impurities which order in this region, pointing out the importance of making measurements on extremely pure samples of PrGaG and EuGaG.

Dysprosium gallium garnet

The sample measured was a single crystal with a mass of 2.14 g. Although comparable in mass to the EuGaG, the thermal capacity is so much greater than for that material at low temperatures that we were able to determine the specific heat of DyGaG to ±2% at 1 °K though only to ±10% at 80 °K. The smoothed specific heat for DyGaG is shown in Fig. 5 and is tabulated in Table I. In addition to a Schottky-type anomaly with a peak at about 14.5 °K accompanied by a higher-temperature anomaly similar to that in PrGaG we observed excess specific heat below 3 °K much larger than

TABLE II. Summary of splittings.

Ion	Host	Value (°K)	Method	Ref.
Pr^{3+}	YAlG	32, 72	Optical absorption	5
	YGaG	32, 55	Optical absorption	5
	PrGaG	20.7, 68.7	Paramagnetic resonance	4
	PrGaG	22, 130	Specific heat	This work
	PrGaG	26	Specific heat with Gaussian distribution $\sigma = 5$ °K	This work
Dy^{3+}	YAlG	76	Paramagnetic relaxation	10
	YGaG	22	Paramagnetic relaxation	10
	DyGaG	30	Raman spectroscopy	9
	DyGaG	34	Specific heat	This work
	DyGaG	33	Specific heat with Gaussian distribution $\sigma = 7$ °K	This work

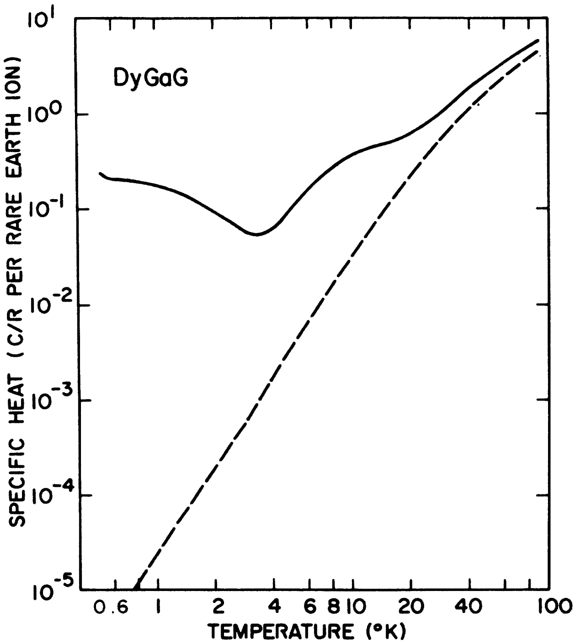

FIG. 5. Total specific heat of DyGaG in smoothed form as a function of temperature.

that in EuGaG or PrGaG. A similar anomaly has been observed before in a polycrystalline sample.[1]

The ground state of the Dy^{3+} ion in DyGaG is $^6H_{15/2}$, and has been verified for the ion in DyGaG by Raman spectroscopy by Wadsack *et al.*[9] In a pure cubic field the crystalline-field calculations of Lea, Leask, and Wolf predict that the $^6H_{15/2}$ manifold splits into a ground-state doublet Γ_7, an excited doublet Γ_6, and three higher excited Γ_8 quartets. Since Dy^{3+} is a Kramers ion the doublets will not be split by the crystalline field. Wadsack *et al.*[9] report the excited level to be at 30 °K, while specific-heat measurements, limited to the temperature range up to 4.2 °K, predict the excited level to be at 34 °K. Paramagnetic relaxation measurements for Dy^{3+} in YAlG and YGaG show excited levels at 76 and 22 °K respectively.[10]

Our measurements, which have been carried out over a wider temperature range than any before, suggest that the Schottky-type anomaly at 14.5 °K is due to the excited doublet, while the excess specific heat at temperatures above 60 °K is due to the effects of the higher-energy Γ_8 quartets. Again we subtract the lattice specific heat of EuGaG to determine the excess specific heat for DyGaG. In fitting the Schottky anomaly to the proposed energy levels we encountered difficulties similar to those described above for PrGaG. The best fit using single valued energy levels was with the doublet at 34 °K ± 1 °K and indicates the first quartet levels to be about 200 °K ± 25 °K. The latter assignment is difficult due to the large lattice specific-heat term. A much better fit was obtained to the peak and the low-temperature side of the anomaly using a Gaussian distribution of levels, and gave $\Delta = 33$ °K and $\sigma = 7$ °K, in Eqs. (4) and (5).

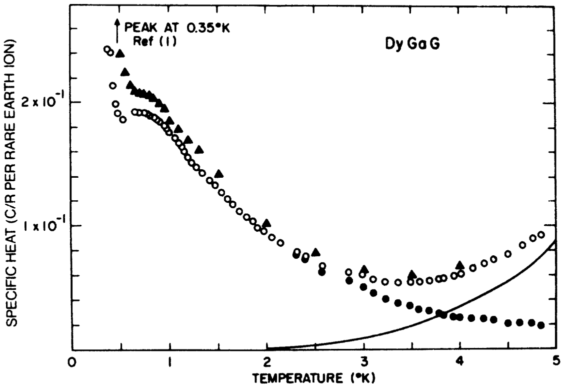

FIG. 6. Specific heat of DyGaG vs temperature. The open circles represent the total specific heat. The solid circles represent the excess specific heat in the region of 2 °K. The solid line represents the Schottky specific heat calculated for the Gaussian energy distribution of $\Delta = 33$ °K and $\sigma = 7$ °K. The solid triangles show the data of Onn *et al.* (Ref. 1).

The specific heat of this single-crystal sample of DyGaG below 5 °K, is shown in Fig. 6, where it is compared with the sintered sample of Onn *et al.*[1] A previous single-crystal measurement by Henderson and Meyer[23] had revealed only a broad peak at 1 °K. The present sample shows a behavior very similar to the sintered sample, though the hope that the single crystal might order at a higher temperature than the sintered sample was not realized. In the new crystal the broad peak at 0.75 °K and the rapid rise below 0.5 °K are separated by a definite minimum though no maximum is observed on the low-temperature peak before 0.36 °K, our lowest attainable temperature. The behavior of the specific heat is still not clearly explained. Cooke *et al.*[3] in studies of the magnetic susceptibility of DyGaG observed no approach to ordered behavior down to 0.6 °K though Capel[22] had predicted ordering in the vicinity of 1 °K. We note that the excess specific heat does vary as $1/T^2$ at a temperature down to 2 °K. The anomalies are far too large, and agree too well between samples of differing origin, to be explained by impurities. DyAlG is known to order antiferromagnetically at 2.5 °K[24] due to a combination of dipole-dipole and exchange interactions, and is a very good approximation to the Ising model due to the anisotropic g factors. For Dy^{3+} in the aluminum garnet, the g factors are $g_x = 0.73$, $g_y = 0.4$, and $g_z = 18.2$, while in the gallium garnet they are $g_x = 11.07$, $g_y = 1.07$, and $g_z = 7.85$.[3] The behavior of the specific heat below 0.5 °K can probably be ascribed to the onset of ordering initiated by dipole-dipole interactions at temperatures above 1 °K, but dominated by exchange interactions below 0.5 °K. We have calculated the entropy associated with the low-temperature anomaly observed in our sample and that of Ref. 1 for the temperature range 0.35–15 °K. Since C_{ex} varies as $1/T^2$ between 2 and 5 °K we extrapolated the $1/T^2$ dependence to higher temperatures for the entropy determination. The values obtained were $0.34R$ (single crystal) and $0.45R$ (polycrystalline) which represents about 50 and 65%, respectively, of the value $0.693R$ associated with a separated doublet or an ordering transition. Entropy contributions below 0.37 °K cannot at present be determined.

Possible explanations of the double anomaly include the possibility that the level assignments of Wadsack *et al.* are not definite. We note that (i) they do not observe the transitions to the Γ_8 quartets predicted to be at 232 °K (166 cm^{-1}) and 637 °K (455 cm^{-1}) and above and (ii) the intensities calculated for the level assignments do not agree with their observed intensities.[9] An alternative energy-level assignment consists of doublets at 0 and 1.3 °K (Γ_7 and Γ_6, respectively) and a quartet (Γ_8) at 34 °K with the higher level quartets above 200 °K. The specific-heat anomaly at 14 °K can still be described in position and magnitude by this energy level scheme. In addition the peak at 0.6 °K can be explained by a splitting of the Γ_7 and Γ_6 levels of about 1.3 °K (obtained for the $1/T^2$ high-temperature tail). The rise in specific heat below 0.5 °K arises from the onset of magnetic ordering. These level schemes are still consistent with the observed Raman spectrum. Measurements to lower temperatures of both the specific heat and magnetic susceptibility are planned.

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