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# Magnetic Properties of Neodymium–Small Rare Earth Gallium Garnets with the Rare Earth Ions on Two Crystallographic Sites*

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Garnets of the type $\{Nd_{3-y}R_y\}[R_xGa_{2-x}](Ga_3)O_{12}$, in which R is Yb, Tm, Er, Ho, or Dy, and $x$ is as high as 2, have been subjected to magnetic measurements. All preparations have been studied over the temperature range 78–300°K and some also at 4.2°K and/or over the range 1.6–300°K. The materials are paramagnetic with Curie–Weiss behavior, but in some the slopes of $1/\chi_M$ vs. $T$ plots change at very low temperature. Comparisons are made between experimental Curie constants and those calculated from theoretical values and from values obtained with garnets containing the same rare earth ions on only one or the other of the two crystallographic sites. Over the temperature ranges in which the various materials were studied, no evidence has been found for long-range ordering which results in ferrimagnetism, ferromagnetism, or antiferromagnetism.

## Introduction

Garnets with rare earths or yttrium on the dodecahedral sites and $Fe^{3+}$ on the octahedral and tetrahedral sites have been almost exhaustively studied (*1*). An example is $\{Y_3^{3+}\}[Fe_2^{3+}](Fe_3^{3+})O_{12}$ (YIG), in which the curly brackets indicate eightfold dodecahedral coordination (a distorted cube), the square brackets sixfold octahedral coordination, and the parentheses fourfold tetrahedral coordination. In this compound, there is a ferrimagnetic superexchange interaction between the ferric ions on the octahedral and tetrahedral sites so that there is a net moment of five Bohr magnetons per formula unit which results from the antiparallel magnetic alignment of the ferric ions in the two sublattices.

The theoretical ferrimagnetic moment of rare earth ions is $gJ$, where $J$ is $L$–$S$ for those with less-than-half-filled $f$-shells and $L+S$ for those with half- or more-than-half-filled $f$-shells. $gJ$ is $L+2S$ for the latter group and a little less than $L$–$2S$ for many, but not all, of the ions of the former group.

In the compound $\{Gd_3^{3+}\}[Fe_2^{3+}](Fe_3^{3+})O_{12}$ (GdIG), the $Gd^{3+}$ ions partake in the superexchange interaction along with the ferric ions. $Gd^{3+}$ has a spin quantum number ($S$) of 7/2 and an orbital angular momentum quantum number ($L$) of zero. Since the net moment of each $Gd^{3+}$ ion is $gJ = L + 2S$, the three $Gd^{3+}$ ions have a total moment of 21 Bohr magnetons. At 0°K the net ferrimagnetic moment observed for GdIG is 16 Bohr magnetons per formula unit; this indicates that the spin moment of the dodecahedral sublattice is parallel to the moment of the octahedral sublattice.

Substitution of some $Nd^{3+}$ for $Y^{3+}$ in YIG (it is not possible to prepare $Nd_3Fe_5O_{12}$ itself because of size restrictions) results in an increase in the net ferrimagnetic moment because $L = 6$ and $S = 3/2$ so that the moment due to the orbital angular momentum is greater than and opposite in direction to that due to the spin; there is, as a result, a net additional moment parallel to the tetrahedral sublattice, which is the one which already predominates in YIG (*2*, *3*).

Although gadolinium iron garnet exhibits a ferrimagnetic moment in precise agreement with this simple model, the moments are found to be lower than predicted on this basis for the analogous compounds of other rare earths. Also, it is found that the magnetic moment due to the rare earth ions falls off fairly rapidly above 0°K.

Gilleo and Geller (*4*) observed ferrimagnetism in $\{Gd_3^{3+}\}[Mn_2^{2+}](GaGe_2)O_{12}$; this shows that a

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dodecahedral–octahedral superexchange interaction is possible between a rare earth ion and a transition metal ion even in the absence of magnetic ions on the tetrahedral sites. There have, however, been no reports of rare earth–rare earth ferrimagnetic interaction.

Suchow, Kokta, and Flynn (*5*) reported new garnet compounds with trivalent rare earth ions on both dodecahedral and octahedral sites of the type $\{Nd_{3-y}R_y\}[R_xGa_{2-x}](Ga_3)O_{12}$, in which R is Lu, Yb, Tm, Er, Ho, or Dy. In the case of R = Lu, it is possible to obtain $x = 2$ with $y = 0$, but when R is Yb or Tm, $x = 2$ was obtained only with values of $y$ above certain minima. For R = Er, Ho, or Dy, it was found that the maximum possible $x$-values are less than 2.

The magnetic properties of these preparations and some additional ones have now been measured and the results are the subject of the present paper.

## Lattice Constants

In our earlier work (*5*), we reported experimental lattice constants of a number of preparations and also calculated lattice constants based on a formula which we developed. In those cases where the preparations were single-phase, the observed and calculated values checked each other quite well. At that time, we employed Ahrens (*6*) ionic radii in our formula. Since then, however, the Shannon–Prewitt (*7*) 'IR' radii have become available and they appear to be more suitable for our purpose because separate values are given for coordination numbers 6 and 8 for the rare earths, whereas the Ahrens radii aref or coordination number 6 only. Because of this and because we plan to employ Shannon–Prewitt radii in related forthcoming publications, the lattice constants have been recalculated using these radii and the modified formula

$$\begin{aligned} a_{\text{calc}} &= (\text{average } r_{\text{dod}} - r_{Nd^{3+}})(2.15) \\ &\quad + (\text{average } r_{\text{oct}} - r_{Ga^{3+}})(1.56) \\ &\quad + a_{Nd_3Ga_5O_{12}} \\ &= (\text{average } r_{\text{dod}} - 1.12)(2.15) \\ &\quad + (\text{average } r_{\text{oct}} - 0.620)(1.56) + 12.504, \end{aligned}$$

where $r_{\text{dod}}$ and $r_{\text{oct}}$ represent radii of ions on the dodecahedral and octahedral sites, respectively.

This also affords an opportunity to correct a small numerical error in our earlier paper (*5*). The factor Å $\Delta a$/Å $\Delta r_{\text{dod}}$ should have been 1.67 (rather than 1.72). Using this correct value, we have recalculated the lattice constants with Ahrens radii. The newly calculated lattice constants using both Ahrens radii (with the corrected formula) and Shannon–Prewitt 'IR' radii are given in Table I. Both sets of calculated values are fully consistent with the conclusions drawn earlier (*5*). Observed and calculated lattice constants (using Shannon–Prewitt 'IR' radii) of the single-phase preparations with which the present paper deals are given in Tables II and IV.

## Experimental Methods of Magnetic Measurement

All preparations described herein were subjected to measurement at temperatures from 78 to 300°K with the Faraday apparatus previously described (*8*) (at a field strength of about 6 kG). Five were also measured at 4.2°K with a vibrating sample magnetometer (field strength about 7.8 kG) in the laboratory of Professor Aaron Wold at Brown University, and two samples were checked at temperatures down to 1.6°K with a pendulum magnetometer (field strength 15.2 kG) in the laboratory of R. C. Sherwood of Bell Telephone Laboratories. The data were put into the form of $1/\chi_M$ vs. $T$ plots, and Curie constants determined from the slopes of the resulting straight line portions in the temperature range 78–300°K (see Ref. *8*).

## Results and Discussion

Before making measurements on the preparations with which this paper deals, garnet compounds or solid solutions containing pertinent rare earth ions only on octahedral sites (in germanates) and only on dodecahedral sites (in gallates) were prepared and their magnetic susceptibilities measured. The magnetic properties of the compounds (but not the solid solutions) have been reported earlier in the literature (by Belov, Mill, Sokolov, and Than (*9*), for instance), but it was thought necessary to repeat the work with the same apparatus and under the same conditions (especially the temperature range) employed for the measurements on our new materials. The data are plotted in Figs. 1 and 2, in which the compounds and solid solutions are grouped, for the sake of minimizing the number of figures required, according to their magnetic susceptibilities rather than their compositions. The materials are all paramagnetic and obey the Curie–Weiss law, at least over the range

TABLE I

OBSERVED AND RECALCULATED LATTICE CONSTANTS

| Compound or Solid Solution | Lattice Constant, $a$(Å) | | |
|---|---|---|---|
| | Observed | Corrected calculated values using Ahrens (6) radii | Calculated using Shannon–Prewitt (7) 'IR' radii |
| $\{Nd_3\}[Ga_2](Ga_3)O_{12}$ | $12.50_4$ | [a] | [a] |
| $\{Yb_3\}[Ga_2](Ga_3)O_{12}$ | $12.20_3$ | [a] | [a] |
| $\{Nd_3\}[Lu_2](Ga_3)O_{12}$ | $12.88_1$ | [a] | [a] |
| $\{Nd_3\}[Yb_2](Ga_3)O_{12}$ | $12.89_0$[b] | 12.90 | 12.89 |
| $\{Nd_3\}[Tm_2](Ga_3)O_{12}$ | $12.88_2$[b] | 12.91 | 12.91 |
| $\{Nd_3\}[Er_2](Ga_3)O_{12}$ | $12.83_1$[b] | 12.95 | 12.93 |
| $\{Nd_3\}[Ho_2](Ga_3)O_{12}$ | $12.65_2$[b] | 12.98 | 12.94 |
| $\{Nd_3\}[Dy_2](Ga_3)O_{12}$ | $12.51_0$[b] | 13.00 | 12.96 |
| $\{Nd_{2.8}Lu_{0.2}\}[Lu_2](Ga_3)O_{12}$ | $12.86_6$ | 12.86 | 12.86 |
| $\{Nd_{2.7}Yb_{0.3}\}[Yb_2](Ga_3)O_{12}$ | $12.86_4$ | 12.87 | 12.86 |
| $\{Nd_{2.5}Yb_{0.5}\}[Yb_2](Ga_3)O_{12}$[c] | $12.85_5$ | 12.85 | 12.84 |
| $\{Nd_{2.4}Tm_{0.6}\}[Tm_2](Ga_3)O_{12}$ | $12.85_4$ | 12.86 | 12.85 |
| $\{Nd_{1.9}Er_{1.1}\}[Er_2](Ga_3)O_{12}$ | $12.81_3$[b] | 12.86 | 12.83 |
| $\{Nd_{1.35}Ho_{1.65}\}[Ho_2](Ga_3)O_{12}$[d] | — | 12.86 | 12.82 |
| $\{Nd_{1.1}Dy_{1.9}\}[Dy_2](Ga_3)O_{12}$[d] | — | 12.87 | 12.84 |

[a] Calculations based on these.

[b] From nominal compositions.

[c] Note that this preparation contains more Yb ($y = 0.5$) on the dodecahedral site than the minimum ($y = 0.3$) required to obtain a single-phase garnet.

[d] Hypothetical compositions with $y$ values obtained upon extrapolation of curve in Fig. 5(b) in Ref. 5.

TABLE II

EXPERIMENTAL AND CALCULATED LATTICE CONSTANTS AND MOLAR CURIE CONSTANTS ($C_M$) OF GARNETS WITH TRIVALENT RARE EARTH IONS ON EITHER DODECAHEDRAL OR OCTAHEDRAL SITES

| Compound | Lattice Constant, $a$(Å) | | Experimental $C_M$ | $C_M$ calculated from theoretical values (in Column 3 of Table III) |
|---|---|---|---|---|
| | Observed | Calculated (using Shannon–Prewitt (7) 'IR' radii) | | |
| $\{Sr_3\}[Yb_2](Ge_3)O_{12}$ | $13.02_8$ | — | 4.92 | 5.12 |
| $\{Sr_3\}[Tm_2](Ge_3)O_{12}$ | $13.05_0$ | — | 12.64 | 14.18 |
| $\{Sr_3\}[Er_2](Ge_3)O_{12}$ | $13.07_3$ | — | 19.24 | 22.76 |
| $\{Yb_3\}[Ga_2](Ga_3)O_{12}$ | $12.20_3$ | [a] | 6.03 | 7.68 |
| $\{Tm_3\}[Ga_2](Ga_3)O_{12}$ | $12.22_9$ | 12.22 | 19.74 | 21.27 |
| $\{Er_3\}[Ga_2](Ga_3)O_{12}$ | $12.25_5$ | 12.25 | 29.41 | 34.14 |
| $\{Ho_3\}[Ga_2](Ga_3)O_{12}$ | $12.28_2$ | 12.29 | 36.53 | 41.82 |
| $\{Dy_3\}[Ga_2](Ga_3)O_{12}$ | $12.31_4$ | 12.31 | 37.91 | 42.18 |
| $\{Nd_3\}[Ga_2](Ga_3)O_{12}$ | $12.50_4$ | [a] | 3.74 | 4.86 |

[a] Calculations based on these.

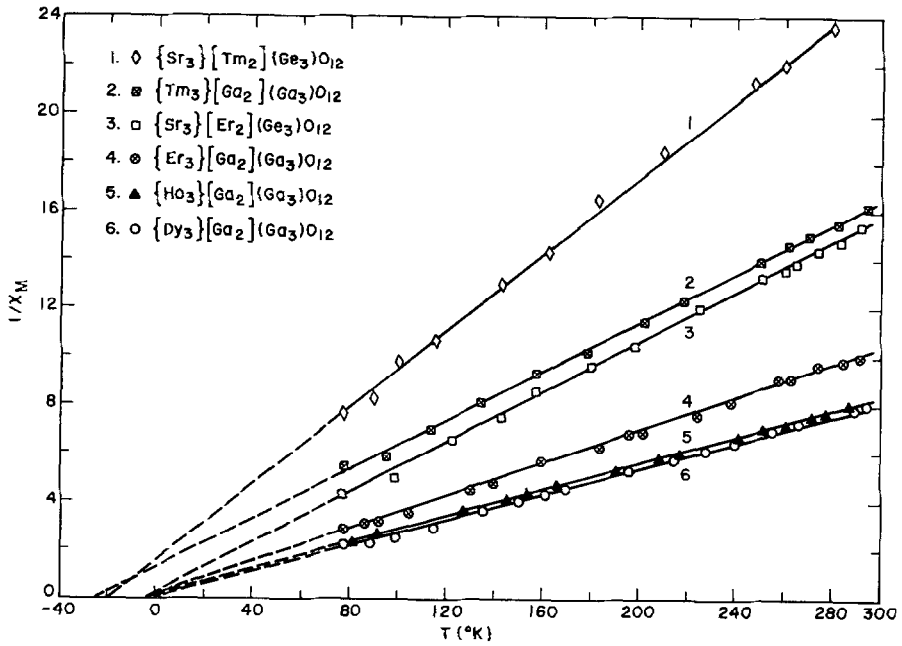


FIG. 1. Reciprocal molar susceptibility versus absolute temperature for garnet compounds with trivalent rare earth ions on either dodecahedral or octahedral sites.

78–300°K. The dashed-line portions are extrapolations to $1/\chi_M = 0$ in order to indicate the magnitudes of the Weiss constants.

The molar Curie constants ($C_M$) obtained from the 78–300°K portions of the plots are given in Table II along with those calculated from theoretical values. ($C_M$ values for the solid solutions of Figs. 1 and 2 will be given in Table IV). Table III gives the individual gram-atom Curie constants ($C_{M(\text{ind})}$) for the pertinent rare earth ions as calculated from our experimental values in Table II and from the theoretical magnetic moments given by Kern and Raccah (*10*). Some of the Curie constants in Tables II and III

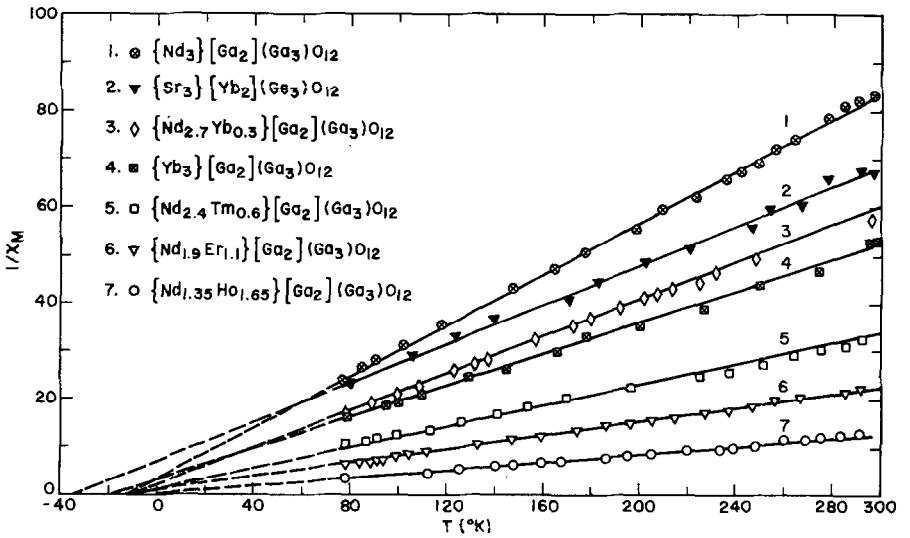


FIG. 2. Reciprocal molar susceptibility versus absolute temperature for garnet compounds and solid solutions with trivalent rare earth ions on either dodecahedral or octahedral sites.

TABLE III

INDIVIDUAL GRAM-ATOM CURIE CONSTANTS ($C_{M(ind)}$)

| (1) Ion | (2) From experimental $C_M$ values in Table II | | (3) Calculated from theoretical magnetic moments in Ref. *10* |
|---|---|---|---|
| | Dodecahedral Site | Octahedral Site | |
| $Yb^{3+}$ | 2.01 | 2.46 | 2.56 |
| $Tm^{3+}$ | 6.58 | 6.32 | 7.09 |
| $Er^{3+}$ | 9.80 | 9.62 | 11.38 |
| $Ho^{3+}$ | 12.18 | —[a] | 13.94 |
| $Dy^{3+}$ | 12.64 | —[a] | 14.06 |
| $Nd^{3+}$ | 1.25 | —[b] | 1.62 |

[a] We were unable to prepare single-phase Sr or Ca germanate garnets with these rare earths on octahedral sites by solid state reaction of the oxides at 1350°C.

[b] $Nd^{3+}$ does not enter octahedral sites.

contain more figures than are justified for final data. These values are, however, intermediate for our purpose, and the extra figures will be dropped in the final results given in Table IV.

The low experimental values found in this temperature range for $C_M$ (Table II) and $C_{M(ind)}$ (Table III) were not unexpected. Such low values were reported not only by Belov *et al.* (*9*) but also by Aléonard and Pauthenet (*11*) who measured the magnetic susceptibilities of rare earth gallium garnets with the rare earth only on the dodecahedral sites. The lower than theoretical values are attributed to partial quenching of the magnetic moment (*11*, *12*). Our experimental values are therefore consistent with the values in the literature. The data indicate little or no dependence on site in the cases of $Tm^{3+}$ and $Er^{3+}$, but the difference appears to be significant for $Yb^{3+}$.

The new materials whose magnetic properties are reported in this paper are listed in Table IV. These are all single-phase garnets, most of which were reported in our earlier publication (*5*) but several of which were not. Those reported herein for the first time are the preparations containing $Ho^{3+}$ and $Dy^{3+}$. To prepare these, $y$-values (indicating the amount of small rare

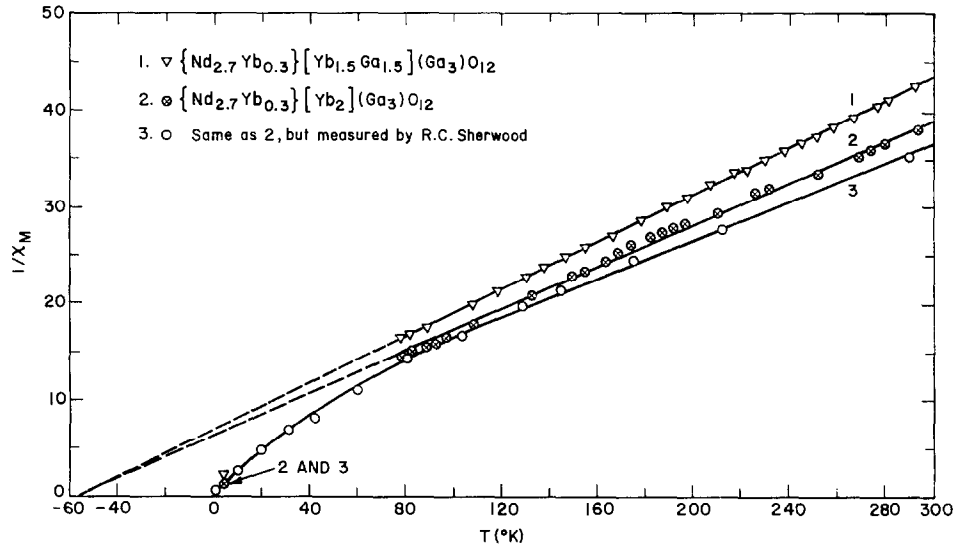


FIG. 3. Reciprocal molar susceptibility versus absolute temperature for garnets with trivalent rare earth ions on both dodecahedral and octahedral sites ($R$ = Yb).

TABLE IV

EXPERIMENTAL AND CALCULATED LATTICE CONSTANTS AND MOLAR CURIE CONSTANTS ($C_M$) OF GARNETS WITH TWO RARE EARTH IONS ON DODECAHEDRAL SITES AND $Ga^{3+}$ AND/OR RARE EARTH IONS ON OCTAHEDRAL SITES

| Composition | Lattice Constant, $a$(Å) | | $C_M$ | | |
|---|---|---|---|---|---|
| | Observed | Calculated (using Shannon–Prewitt (7) 'IR' radii) | Experimental | Calculated from theoretical values (in Column 3 of Table III) | Calculated from experimental values for ions on dodecahedral and octahedral sites (in Column 2 of Table III for most[a]) |
| $\{Nd_{2.7}Yb_{0.3}\}[Ga_2](Ga_3)O_{12}$ | $12.48_6$ | 12.47 | 5.18 | 5.14 | 3.98 |
| $\{Nd_{2.7}Yb_{0.3}\}[Yb_{1.5}Ga_{0.5}[(Ga_3)O_{12}$ | $12.76_7$ | 12.76 | 8.19 | 8.98 | 7.67 |
| $\{Nd_{2.7}Yb_{0.3}\}[Yb_2](Ga_3)O_{12}$ | $12.86_4$ | 12.86 | 9.33 (10.0[b]) | 10.3 | 8.90 |
| $\{Nd_{2.4}Tm_{0.6}\}[Ga_2](Ga_3)O_{12}$ | $12.45_4$ | 12.45 | 8.69 | 8.14 | 6.95 |
| $\{Nd_{2.4}Tm_{0.6}\}[Tm_{1.6}Ga_{0.4}](Ga_3)O_{12}$ | $12.78_4$ | 12.77 | 18.2 | 19.5 | 17.1 |
| $\{Nd_{2.4}Tm_{0.6}\}[Tm_2](Ga_3)O_{12}$ | $12.85_4$ | 12.85 | 21.2 (22.2[b]) | 22.3 | 19.6 |
| $\{Nd_{1.9}Er_{1.1}\}[Ga_2](Ga_3)O_{12}$ | $12.41_4$ | 12.41 | 14.1 | 15.6 | 13.2 |
| $\{Nd_{1.9}Er_{1.1}\}[Er_{1.5}Ga_{0.5}](Ga_3)O_{12}$ | $12.75_1$ | 12.73 | 26.9 | 32.7 | 27.6 |
| $\{Nd_{1.35}Ho_{1.65}\}[Ga_2](Ga_3)O_{12}$ | $12.40_0$ | 12.39 | 23.4 | 25.2 | 21.8 |
| $\{Nd_{1.35}Ho_{1.65}\}[Ho_{0.5}Ga_{1.5}](Ga_3)O_{12}$ | $12.52_3$ | 12.50 | 28.1 | 32.2 | 28.0 |
| $\{Nd_{1.35}Ho_{1.65}\}[HoGa](Ga_3)O_{12}$ | $12.63_3$ | 12.61 | 35.0 | 39.1 | 34.2 |
| $\{Nd_{1.1}Dy_{1.9}\}[Ga_2](Ga_3)O_{12}$ | $12.38_5$ | 12.38 | 25.0 | 28.5 | 25.4 |
| $\{Nd_{1.1}Dy_{1.9}\}[Dy_{0.5}Ga_{1.5}](Ga_3)O_{12}$ | $12.50_1$ | 12.50 | 30.6 | 35.5 | 31.6 |
| $\{Nd_{1.1}Dy_{1.9}\}[DyGa](Ga_3)O_{52}$ | $12.52_2$ | 12.53 | 36.0 | 42.6 | 37.9 |

[a] Because we did not have our own data for $Dy^{3+}$ and $Ho^{3+}$ on octahedral sites (see Table III), values taken from the higher temperature data (about 40–80°K) in the publication of Belov *et al.* (9) were used for them. These $C_{M(\text{ind})}$ values, 12.4 for $Dy^{3+}$ and 12.1 for $Ho^{3+}$, appear reasonable.

[b] Value of R. C. Sherwood.

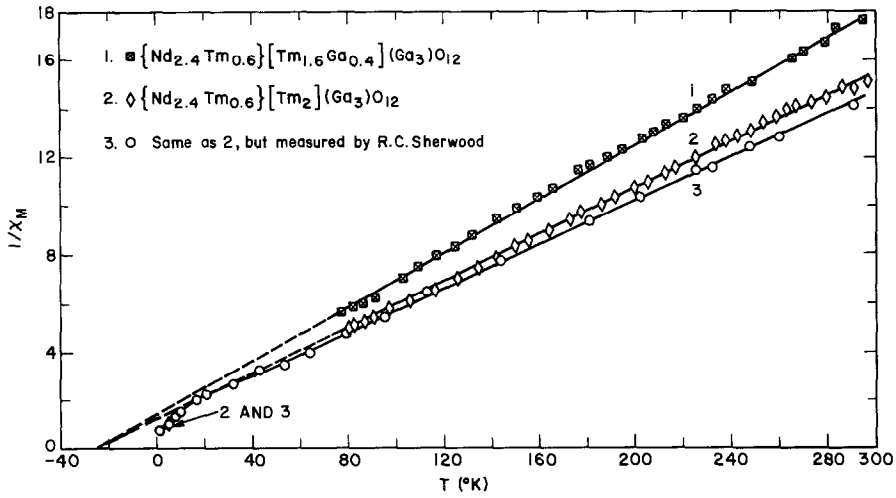


FIG. 4. Reciprocal molar susceptibility versus absolute temperature for garnets with trivalent rare earth ions on both dodecahedral and octahedral sites ($R$ = Tm).

earth on the dodecahedral sites) were taken by the extrapolation procedure discussed earlier (*5*). As in our earlier work with $Er^{3+}$ in garnets, it was found that it is not possible to fill the octahedral sites entirely with $Ho^{3+}$ and $Dy^{3+}$. The magnetic data for all of the preparations listed in Table IV are given in Figs. 3–5. Once again the Curie–Weiss law is seen to be obeyed, at least over the 78–300°K range, and the dashed-line portions are extrapolations to indicate the magnitudes of the Weiss constants.

In some cases, the 4.2°K points fall on these extrapolations, but in other cases, as the graphs show, a change of slope at low temperature is indicated. This change, wherever it occurs, is to a higher value of $\Delta(1/\chi_M)/\Delta T$, which means

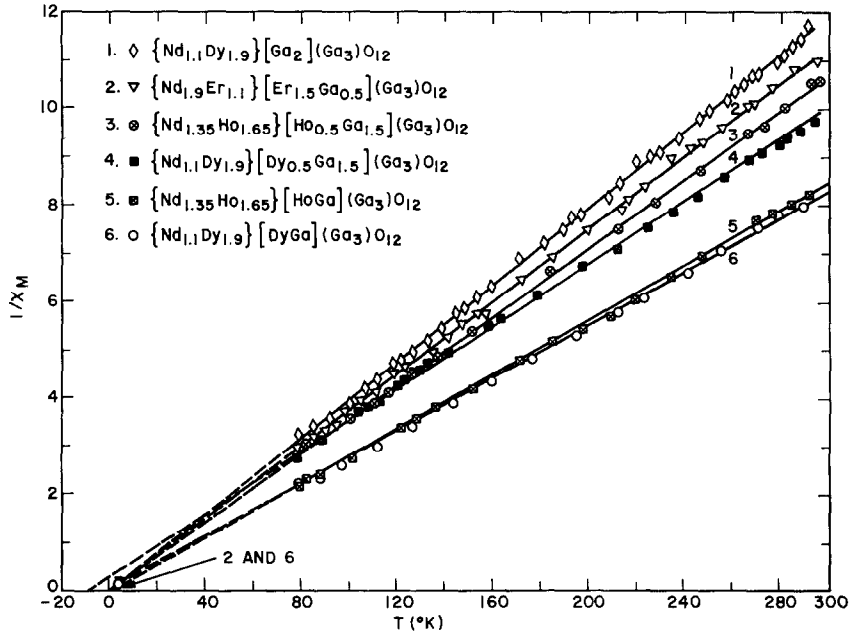


FIG. 5. Reciprocal molar susceptibility versus absolute temperature for garnets with trivalent rare earth ions on both dodecahedral and octahedral sites ($R$ = Er, Ho, Dy).

that the $1/\chi_M$ vs. $T$ plot curves downward toward the $T$ axis. The experimental $C_M$ values, those calculated from theoretical values, and those calculated primarily from our experimental values for ions on dodecahedral and octahedral sites are given in Table IV.

There appears to be a trend in the paramagnetic data given in Table IV, though it is difficult to be certain that it is real because our Curie constant measurements are reliable probably only to about 5%. The presence of the heavier small rare earths along with Nd does, however, seem to remove some or all of the quenching. This tendency decreases as the small rare earth becomes lighter and in the case of the lightest used, Dy, there is even a bit more quenching than is expected from the calculation from experimental values.

In no case is there any evidence from the graphs containing data at 4.2°K and from 78–300°K of ferromagnetic, ferrimagnetic, or antiferromagnetic ordering. Ferromagnetism can probably be ruled out on the basis of the absence of positive Weiss constants; antiferromagnetism would cause the $1/\chi_M$ vs. $T$ curve to change direction upward so this can also be eliminated as a possibility. However, ferrimagnetism cannot be entirely ruled out on the basis of these measurements because the $1/\chi_M$ value at 4.2°K is not necessarily very different from that which would obtained if ferrimagnetism were present. For this reason, two samples ($\{Nd_{2.4}Tm_{0.6}\}[Tm_2](Ga_3)O_{12}$ and $\{Nd_{2.7}Yb_{0.3}\}[Yb_2](Ga_3)O_{12}$) were studied over the range 1.6–300°K; the results are included in Figs. 3 and 4. Although changes in slope were observed, there was no indication in either one of the presence of a Curie point. Measurements were made, in addition, of the magnetic behavior of several samples at 4.2°K as a function of decreasing field (over the range 7.8 to 0 kG) and no evidence was found of any magnetic remanence which one might expect if ferrimagnetism were present. Neither did the two samples measured at 1.6°K show any hysteresis in decreasing field over the range 15.2 to 0 kG.

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