

Garnets with Dodecahedral Rare Earths and Scandium, Octahedral Scandium, and Tetrahedral Iron. II. Magnetic Studies

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Garnets with magnetic trivalent rare earth ions (Nd, Sm, Eu, Gd, Tb, Dy) filling all or nearly all dodecahedral sites while nonmagnetic Sc^{3+} ions fill all octahedral sites and magnetic Fe^{3+} ions fill all or nearly all tetrahedral sites have recently been reported by this laboratory. They afford an opportunity to seek magnetic interaction between dodecahedral rare earth ions and tetrahedral ferric ions in the absence of the additional interaction with octahedral iron which occurs in more conventional rare earth iron garnets such as $\{\text{Gd}_3\}[\text{Fe}_2](\text{Fe}_3)\text{O}_{12}$. For each composition, dependence of magnetization on temperature was measured between room temperature and that of liquid helium. Measurements were also made at liquid helium temperature of the dependence of magnetization on applied field with values up to 60.7 kOe. Low temperature results are in most cases ascribed to ferrimagnetic ordering but with canting of ion moments to explain why magnetic saturation has not been attained even with the maximum field applied. As is usually the case, the magnetic behavior of the Sm compound is quite different from that of the others and the possibilities of antiferromagnetism, paramagnetism, and metastable ferrimagnetism are discussed.

Introduction

The background for this paper may be found in an earlier publication from this laboratory (1) which dealt with the preparation of garnets with magnetic trivalent rare earth ions filling all or nearly all dodecahedral sites while nonmagnetic Sc^{3+} ions fill all octahedral sites and magnetic Fe^{3+} ions fill all or nearly all tetrahedral sites. Such materials afford an opportunity to study any possible dodecahedral-tetrahedral magnetic interactions which might occur in the absence of the strong superexchange interactions found when Fe^{3+} ions occupy both octahedral and tetrahedral sites. Of the many compositions reported in our earlier paper, those with maximum concentrations of magnetic ions have been chosen for measurement of magnetic properties.

Experimental

Compositions of the preparations subjected to measurement of magnetic properties are

given throughout this paper, with a complete list occurring in Table II; all were single phase and polycrystalline. The possibility of Lu^{3+} - Sc^{3+} site switching in the Nd-Lu-Sc-Fe garnets was discussed in Ref. (1), but it was pointed out there that this would have no effect on magnetic properties because both of these ions are nonmagnetic.

Magnetization of all samples was measured as a function of temperature in a field (H) of 15.3 kOe with the pendulum magnetometer described in Ref. (2). This apparatus was also employed to measure magnetization as a function of magnetic field with values of up to 15.3 kOe at 1.5°K. For these latter measurements, with the exception of one Sm compound run which will be noted, samples were first cooled to the temperature of liquid helium prior to the application of maximum field. Magnetization was then measured with decreasing field and subsequently, for checking, with increasing field. This method does not permit measurement at zero field. The magnetization of one sample (the Gd compound)

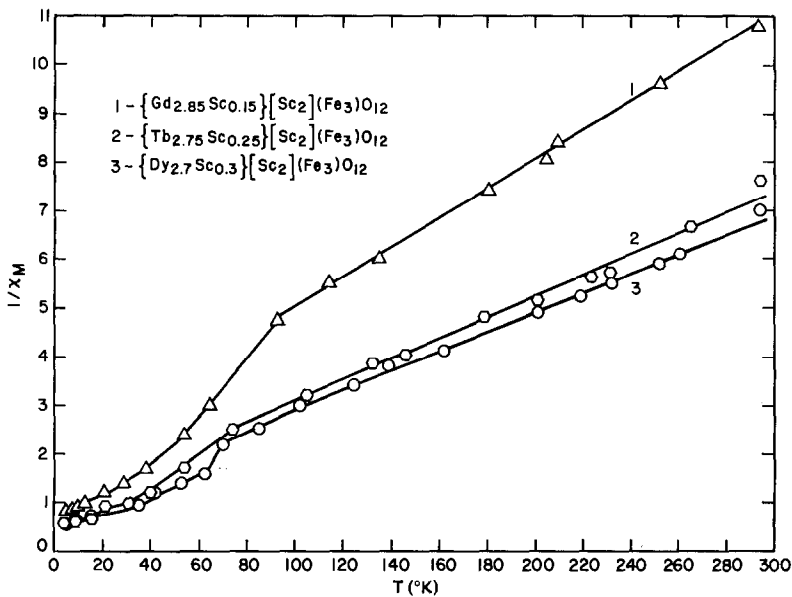


FIG. 1. Reciprocal molar magnetic susceptibility versus absolute temperature for $\{RE_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$, with $RE = Gd, Tb, \text{ and } Dy$.

was also measured as a function of field with values of up to 60.7 kOe at 4.2 $^{\circ}\text{K}$, using the method of extraction of the specimen from one of two oppositely wound coils in the field of a superconducting magnet and measuring the

voltage produced. In this case cooling to liquid helium temperature was followed by measurement of magnetization starting at zero field and increasing to the maximum value attainable.

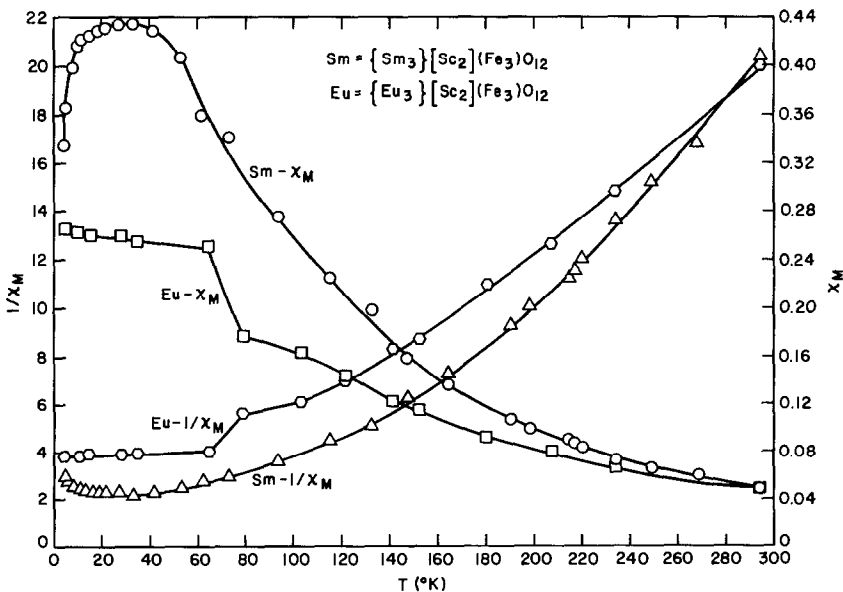


FIG. 2. Molar magnetic susceptibility and reciprocal molar magnetic susceptibility versus absolute temperature for $\{RE_3\}[Sc_2](Fe_3)O_{12}$, with $RE = Sm$ and Eu .

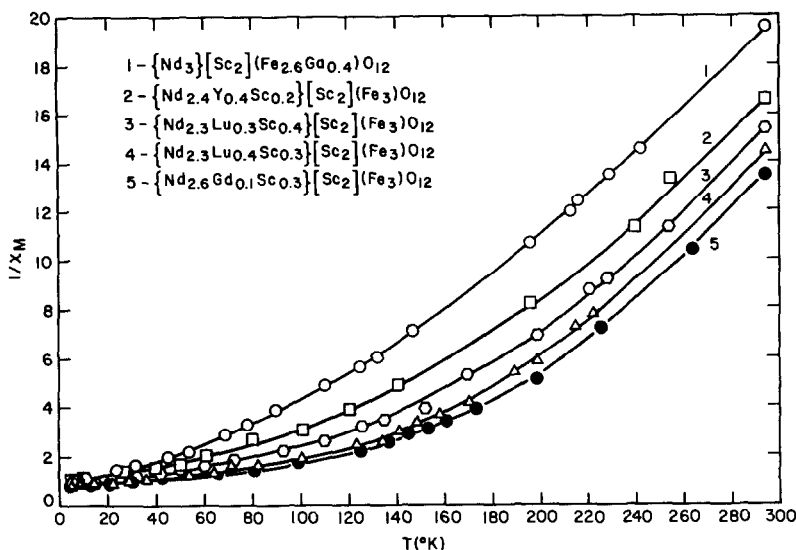


FIG. 3. Reciprocal molar magnetic susceptibility versus absolute temperature for Nd-Sc-Fe garnets.

Results and Discussion

Values of magnetization per gram (σ_g) obtained with the pendulum magnetometer were

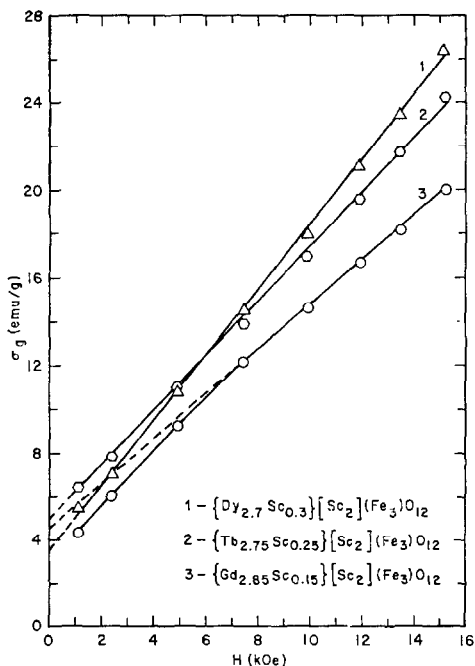


FIG. 4. Magnetization versus magnetic field for $\{RE_{3-y}Sc_y\}[Sc_2](Fe_3)O_{12}$, with RE = Gd, Tb, and Dy.

¹ In Gd^{3+} , L = 0 so that J = S.

converted to molar magnetic susceptibility (χ_M) by the relationship $\chi_M = (\sigma_g/H)$ (Formula Weight). Figures 1, 2, and 3 contain plots of $1/\chi_M$ vs absolute temperature for the 10 compositions studied. Figure 2, which presents the data for the Sm and Eu compounds, also contains plots of χ_M vs absolute temperature

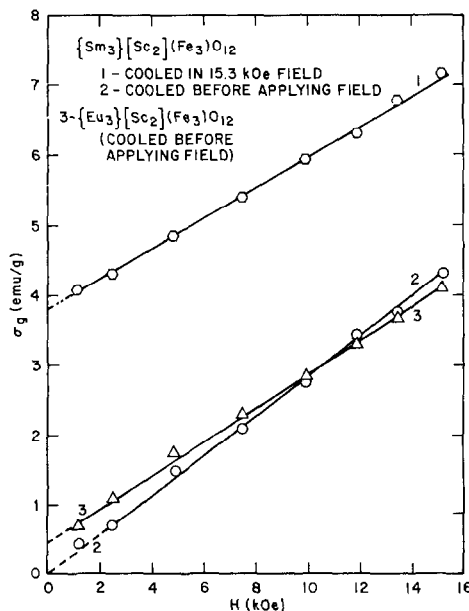


FIG. 5. Magnetization versus magnetic field for $\{RE_3\}[Sc_2](Fe_3)O_{12}$, with RE = Sm and Eu.

because these curves add clarity in these cases.

Figures 4, 5, and 6 give the magnetization per gram (σ_g) vs field relationships. Figure 5 contains two types of data for $\{\text{Sm}_3\}[\text{Sc}_2](\text{Fe}_3)\text{O}_{12}$: the normal kind (that is, with the sample cooled before the field was applied) and another in which the sample was cooled in the maximum field. Figure 7 contains plots of magnetization vs field data for $\{\text{Gd}_{2.85}\text{Sc}_{0.15}\}[\text{Sc}_2](\text{Fe}_3)\text{O}_{12}$ in two different runs with maximum fields of 15.3 and 60.7 kOe.

In all cases where the trivalent rare earth ion was of the $J = L + S$ type (i.e., Gd³⁺, Tb, and Dy; see Fig. 1), essentially straight-line relationships (Curie-Weiss behavior) were observed between $1/\chi_M$ and T at higher temperatures but changes in slope occurred in all three at about 60–90°K. (The exact temperatures of these slope changes are not necessarily known because our measurements do not in

all cases include a sufficient number of points in the vicinity of the change.) These slope changes are very much like that found by Geller *et al.* (3) for $\{\text{GdCa}_2\}[\text{Zr}_2](\text{Fe}_3)\text{O}_{12}$. Molar Curie constants calculated from the slopes of the straight line portions of the curves are given in Table I along with the constants calculated by summing the individual molar Curie constants of the paramagnetic ions present in the compound. (For a more complete discussion of this, see Ref. (5)). As seen, agreement is quite good. The data in Fig. 4 show that saturation was not reached in any of these materials at 15.3 kOe, nor was it attained in the Gd preparation even at 60.7 kOe (see Fig. 7). However, Figs. 4 and 7 both show the presence of spontaneous magnetization. Values of spontaneous magnetization (σ_0) were obtained by extrapolation of straight line portions of the curves to zero field. The

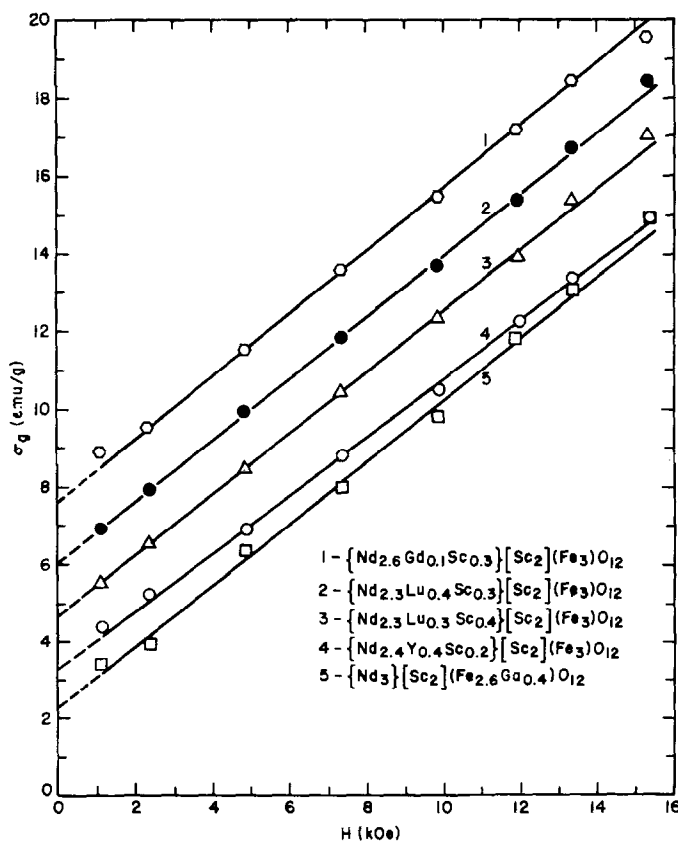


FIG. 6. Magnetization versus magnetic field for Nd-Sc-Fe garnets.

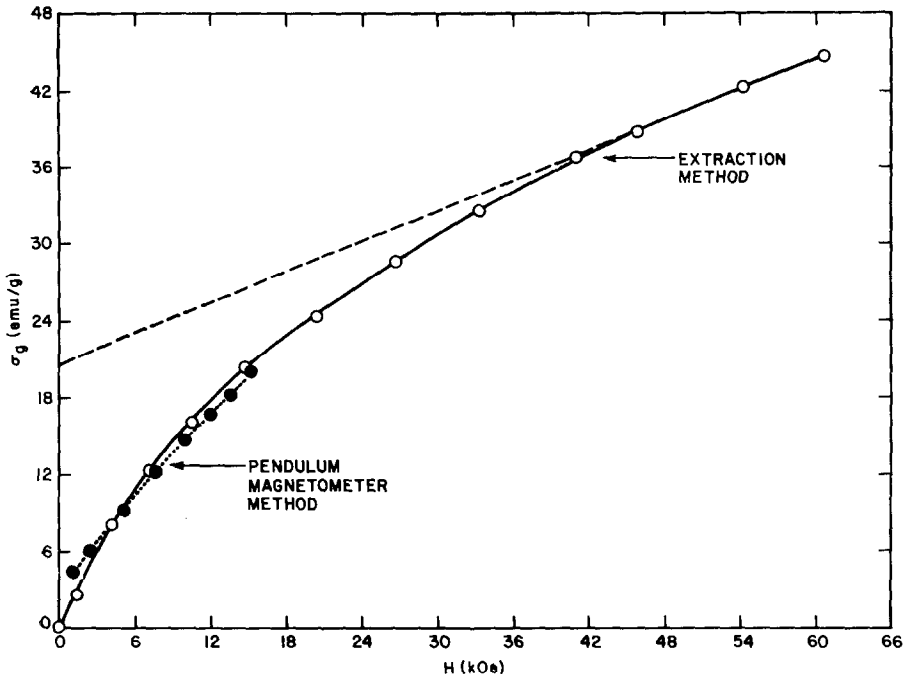


FIG. 7. Magnetization versus magnetic field (maximum values 15.3 and 60.7 kOe) for $\{Gd_{2.85}Sc_{0.15}\}[Sc_2](Fe_3)O_{12}$.

Bohr magneton values given in Table II were then calculated from

$$n_B = \frac{(\sigma_g) (\text{Formula weight})}{N\mu_B}$$

where N = Avogadro's number and $\mu_B = 9.27 \times 10^{-24}$ A m², the value of the Bohr

magneton. ($N\mu_B$ is therefore 5585.) Except to give an idea of relative magnitudes, these values are not very useful because it is the saturation magnetization values which would permit unequivocal interpretation of the data. In addition, comparison of the data for the Gd composition with the different maximum

TABLE I
EXPERIMENTAL AND CALCULATED MOLAR CURIE CONSTANTS (C_M)

| Composition | Experimental C_M | C_M Calculated from theoretical values of $C_{M(\text{ind})}^a$ |
|--|--------------------|---|
| $\{Gd_{2.85}Sc_{0.15}\}[Sc_2](Fe_3)O_{12}$ | 33.0 | 35.3 |
| $\{Tb_{2.75}Sc_{0.25}\}[Sc_2](Fe_3)O_{12}$ | 47.0 | 45.2 |
| $\{Dy_{2.7}Sc_{0.3}\}[Sc_2](Fe_3)O_{12}$ | 51.0 | 51.0 |
| $\{Nd_{2.6}Gd_{0.1}Sc_{0.3}\}[Sc_2](Fe_3)O_{12}$ | 9.7 | 18.0 |
| $\{Nd_{2.3}Lu_{0.4}Sc_{0.3}\}[Sc_2](Fe_3)O_{12}$ | 9.2 | 16.8 |
| $\{Nd_{2.3}Lu_{0.3}Sc_{0.4}\}[Sc_2](Fe_3)O_{12}$ | 9.8 | 16.8 |
| $\{Nd_{2.4}Y_{0.4}Sc_{0.2}\}[Sc_2](Fe_3)O_{12}$ | 10.5 | 16.9 |
| $\{Nd_3\}[Sc_2](Fe_{2.6}Ga_{0.4})O_{12}$ | 10.5 | 16.2 |

^a Theoretical trivalent rare earth $C_{M(\text{ind})}$ values calculated from the theoretical magnetic moments given by Kern and Raccach (4). Fe^{3+} value calculated from magnetic moment based on spin-only behavior.

TABLE II
SPONTANEOUS MAGNETIZATION VALUES OBSERVED

| Composition | $\sigma_{0(g)}$ | n_B |
|---|-----------------|------------------|
| {Gd _{2.85} Sc _{0.15} }[Sc ₂](Fe ₃)O ₁₂ | | |
| At max. H = 15.3 kOe | 4.55 | 0.7 |
| At max. H = 60.7 kOe | 20.70 | 3.4 ^a |
| {Tb _{2.75} Sc _{0.25} }[Sc ₂](Fe ₃)O ₁₂ | 5.00 | 0.8 |
| {Dy _{2.7} Sc _{0.3} }[Sc ₂](Fe ₃)O ₁₂ | 3.55 | 0.6 |
| {Sm ₃ }[Sc ₂](Fe ₃)O ₁₂ | | |
| Cooled in field | 3.79 | 0.6 |
| Cooled before field applied | 0.00 | 0 |
| {Eu ₃ }[Sc ₂](Fe ₃)O ₁₂ | 0.48 | 0.1 |
| {Nd _{2.6} Gd _{0.1} Sc _{0.3} }[Sc ₂](Fe ₃)O ₁₂ | 7.63 | 1.2 |
| {Nd _{2.3} Lu _{0.4} Sc _{0.3} }[Sc ₂](Fe ₃)O ₁₂ | 6.04 | 0.9 |
| {Nd _{2.3} Lu _{0.3} Sc _{0.4} }[Sc ₂](Fe ₃)O ₁₂ | 4.70 | 0.7 |
| {Nd _{2.4} Y _{0.4} Sc _{0.2} }[Sc ₂](Fe ₃)O ₁₂ | 3.33 | 0.5 |
| {Nd ₃ }[Sc ₂](Fe _{2.6} Ga _{0.4})O ₁₂ | 2.29 | 0.4 |

^a 4.95 is the theoretical value for ferrimagnetism at saturation.

fields indicates that several nearly straight line segments with decreasing slopes can be found at various points along the curve; this would presumably continue until true saturation was attained. The gradually decreasing slope indicates that we are not here dealing with Dzyaloshinsky-type (δ) "weak" or "parasitic" ferromagnetism superimposed on antiferromagnetism since this would result in the straight-line relationship, $\sigma = \sigma_0 + \chi H$. The existence of spontaneous magnetization does show, however, that these compounds are ferromagnetic or ferrimagnetic at low temperatures, and the absence of a positive Weiss constant indicates that the ordering is ferrimagnetic, presumably by superexchange between dodecahedral and tetrahedral sublattices, but with canting of ion moments. We assume that the slope changes signal the onset of ordering. The divergence of the two curves near zero field in Fig. 7 is due to the difference in the manner in which the field was applied (as described under Experimental).

Sm and Eu do not behave magnetically like most of the other rare earths because their multiplet intervals are comparable to kT . The $1/\chi_M$ vs T curves in Fig. 2 do not, therefore, show Curie-Weiss behavior. At about 80°K,

the Eu preparation shows a change in slope, presumably due to the onset of ordering, similar to that seen in the Gd, Tb, and Dy materials. As the temperature is further decreased, this is followed by a near leveling off of χ_M (and of $1/\chi_M$). The Eu data in Fig. 5 and Table II indicate spontaneous magnetization which we again take to be due to ferrimagnetism even though saturation could not be attained, presumably because of canting. Leveling off of magnetic susceptibility at low temperatures is typical of Eu³⁺ behavior observed in other compounds where ferrimagnetic superexchange does not occur. Therefore, when {Eu₃}[Sc₂](Fe₃)O₁₂ orders at low temperature, the magnetization of the Eu³⁺ sublattice should be approximately independent of temperature, as should also be that of the Fe³⁺ sublattice. One would expect, as a result, that the net ferrimagnetic magnetization would be nearly temperature independent, and this is what we observe.

The Sm preparation curves in Fig. 2 do not have sharp slope changes like those of the Gd, Tb, Dy, and Eu materials. One does, however, observe a gradually changing slope in the same low temperature region, but the magnetization passes through a peak at 33°K. Such peaking is found in antiferromagnetic materials, which should show no spontaneous magnetization. Curve 2 of Fig. 5, which was obtained by cooling to liquid He temperature before applying the field, does indeed not show any. On the other hand, Curve 1, obtained by cooling while the 15.3 kOe field was applied, does show spontaneous magnetization (see also Table II) although, as before, saturation is not reached. This could mean that the material is ferrimagnetic at about 33°K but that exact antiferromagnetic compensation occurs at a lower temperature although the ferrimagnetic interaction can be frozen in by the applied field as the temperature is decreased.

There is still another possibility, however, which appears quite likely. One usually observes a reversal in the magnetic susceptibility of Sm³⁺ compounds at low temperatures. One Sm compound could even have a peak at a temperature at which another exhibits a trough. In our case (see Fig. 2), there is a

maximum in χ_M at 33°K. Rather similar results have been reported for the intermetallic compounds SmIn_3 (7) and SmZn_2 (8). Buschow *et al.* (9) and Malik *et al.* (10) have been able to explain such apparently erratic behavior of Sm^{3+} on the basis of the variation in the crystal field (superimposed on the exchange and applied fields) which is presented to the ion in different compounds. Because of the closeness of the multiplet spacings in Sm^{3+} , the various fields bring about mixing of the higher multiplet levels (especially $J = \frac{7}{2}$) into the ground state level ($J = \frac{5}{2}$). As a result, the population of electrons in the various levels (and therefore the magnetic moment of the ion) depends on these fields, and there is a crossover temperature, whose value is especially sensitive to the crystal field, at which J goes from $L - S$ to $L + S$ behavior. We can therefore offer the following alternate explanation for the observed behavior of our Sm preparation: The Sm^{3+} has a very low moment near absolute zero, too small to permit any superexchange interaction between the dodecahedral Sm^{3+} sublattice and the tetrahedral Fe^{3+} sublattice, and therefore paramagnetism results. However, at temperatures closer to 33°K, the Sm^{3+} moment is sufficiently higher so that ferrimagnetic interaction with the Fe^{3+} spins of the tetrahedral sublattice can occur. The data would still require that the field freeze in the ferrimagnetic interaction metastably on subsequent cooling.

All the $1/\chi_M$ vs T data for the Nd preparations are plotted in Fig. 3. None of these shows any sharp change in slope at low temperature, but the magnetization vs field data in Fig. 6 all show spontaneous magnetization (although not magnetic saturation), thereby once more indicating ferrimagnetism at liquid helium temperature. The spontaneous magnetization values in Bohr magnetons are given in Table II. The curves in Fig. 3 do not appear to result from the Curie-Weiss law. Although approximately straight line behavior can be inferred in the region approaching room temperature, the molar Curie constants obtained from these lines (see Table I) are 35–46% lower than values calculated for these compositions. In the case of the Nd preparations, then, one sees what is presumably ferrimagnetism at liquid

helium temperature, but there are no sharp transition temperatures, ordering fades out gradually as the temperature is increased, and there is finally even quenching below the paramagnetic value.

As stated above, results would be more easily analyzed if magnetic saturation could be attained. The difficulty in reaching saturation is probably due to strong or sharp canting of the moments of the rare earth and ferric ions on the dodecahedral and tetrahedral sublattices in the absence of magnetic ions on the octahedral sites. What we have called ferrimagnetism is not, therefore, the simple type with exactly antiparallel alignment of the moments. That situation and saturation could presumably be brought about with fields in excess of 100 kOe. This figure is based on extrapolation of the high-field curve in Fig. 7, but it is likely that all the magnetization vs field curves would similarly exhibit gradually reduced slopes at higher fields.

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