Magnetic Study of the Lighter Rare-Earth Ions in the Iron Garnets

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The magnetic behavior of the trivalent ions of La, Pr, Sm, and Eu in the iron garnets in the range 0 to 298°K has been determined, that of the Nd^{3+} ion having been reported earlier. The diamagnetic ion La^{3+} behaves similarly to Y^{3+}. An applied field of about 70 kOe appears to produce magnetic saturation of $\{Y_2Pr\}Fe_2Fe_3O_{12}$ at 4.2°K, the contribution of the Pr^{3+} ion being 1.6 μ_B at this temperature. The Sm^{3+} ion introduces large anisotropy but spherical crystals of samarium iron garnet allowed to move freely in the applied field lead to saturation at relatively low fields. The Sm^{3+} ion contributes a moment of 0.14 μ_B at 0°K to the net magnetization and behaves similarly to the Pr^{3+} and Nd^{3+} ions at temperatures below 298°K in that its moment adds to that of the resultant of the iron sublattice moments. Results of measurements of a single-crystal sphere of europium iron garnet are in agreement with those made on a polycrystalline specimen by Villers *et al.*

INTRODUCTION

THERE have now been several studies of the lanthanum- and praseodymium-substituted yttrium iron garnets (YIG) and of samarium and europium iron garnets. Because of the increasing importance of the magnetic garnets, our refined technique of preparation of polycrystalline garnets, and increased purity of the oxides, it appeared worthwhile to reexamine these garnets. Also, measurements on sound single crystals have given some further insight into the magnetic behavior of samarium iron garnet.

EXPERIMENTAL

Polycrystalline materials were prepared as described elsewhere.[1,2] The specimens used were those analyzed crystallographically in Ref. 2. The single crystals used in this study were crystallized from a PbO-B_2O_3 flux; details of these preparations are to be published separately.[3]

Magnetic measurements were made over the temperature range 1.4 to 298°K with a pendulum magnetometer[4] to fields of 15 300 Oe. High-field measurements, to 80 000 Oe, were made using the Bitter-type magnet and an extraction method for the determination of the moment. Calibration was carried out with spectroscopically pure nickel.

LANTHANUM IN YTTRIUM IRON GARNET

Henry[5] has reported the results of high-field measurements on several lanthanum-substituted yttrium iron garnets at liquid helium temperature. In no case did he obtain a value of 5.0 μ_B per formula unit which is the expected value. Loriers and Villers[6] have reported results of measurements at about 20 kOe (temperature not given) on the same system. Aharoni and Schieber[7] have made magnetic measurements in the temperature range 100 to 700°K on a specimen alleged to be $\{La_{0.5}Y_{2.5}\}Fe_2Fe_3O_{12}$; no applied field magnitudes were given.

It has been shown[2,6,8] that the maximum amount of La which may replace Y in YIG is 0.45, i.e., as indicated by $\{La_{0.45}Y_{2.55}\}Fe_2Fe_3O_{12}$. Our measurements were made on a specimen of formula $\{La_{0.40}Y_{2.60}\}Fe_2Fe_3O_{12}$; the results are shown in Fig. 1. The magnetic behavior in the temperature range studied is not significantly different from that of YIG in the same range (see also Fig. 4).

PRASEODYMIUM IN YTTRIUM IRON GARNET

Henry, Villers, and Loriers have reported[9] the results of high-field measurements on Pr-substituted yttrium iron garnets. The magnetization per formula unit $\{Y_{3-x}Pr_x\}Fe_2Fe_3O_{12}$, at 4.2°K, was found to be $(4.8+1.88x)\mu_B$.[10] Results of measurements in the temperature range 100 to 600°K on $\{Y_{2.5}Pr_{0.5}\}Fe_2Fe_3O_{12}$ and $\{Y_2Pr\}Fe_2Fe_3O_{12}$ have been reported by Aharoni and Schieber[7]; no field magnitudes were given. Loriers and Villers[6] have reported results of measurements at 20 kOe (temperature not given) on the system $\{Y_{3-x}Pr_x\}Fe_2Fe_3O_{12}$. The maximum amount of Pr per formula unit that may be substituted for yttrium was found by Loriers and Villers[6] to be ~1.4 and, more precisely,[2] 1.33 by one of us[2] (G.P.E.).

[1] S. Geller, H. J. Williams, R. C. Sherwood, and G. P. Espinosa, J. Phys. Chem. Solids **23**, 1525 (1962).
[2] G. P. Espinosa, J. Chem. Phys. **37**, 2344 (1962).
[3] J. P. Remeika (to be published).
[4] R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956).
[5] W. E. Henry, J. Phys. Soc. Japan **17**, Suppl. BI, 361 (1962).
[6] J. Loriers and G. Villers, Compt. Rend. **252**, 1590 (1961).
[7] A. Aharoni and M. Schieber, J. Phys. Chem. Solids **19**, 304 (1961).
[8] In the paper by S. Geller, Suppl. J. Appl. Phys. **31**, 30S (1960), the preparation of a garnet $\{La_{1.5}Y_{1.5}\}[Fe_2](Fe_3)O_{12}$ was credited to unpublished work by M. A. Gilleo. Unfortunately, an error in the formula, which should have been $\{La_{0.5}Y_{2.5}\}[Fe_2](Fe_3)O_{12}$, escaped detection until after publication. The maximum amount of La that can be substituted for Y is, however, now found to be 0.45 per formula unit.
[9] W. E. Henry, G. Villers, and J. Loriers, Seventh Conference on Magnetism and Magnetic Materials, Phoenix, Arizona, Paper No. 94, 1961 (unpublished).
[10] The value 4.8 μ_B is presumably that attributed to YIG itself. Some years ago, M. A. Gilleo and S. Geller [Phys. Rev. **110**, 73 (1958)] obtained a value of 4.96 μ_B per YIG formula unit. More recently, the value 5.01 μ_B was obtained (Ref. 1). See also Fig. 4.

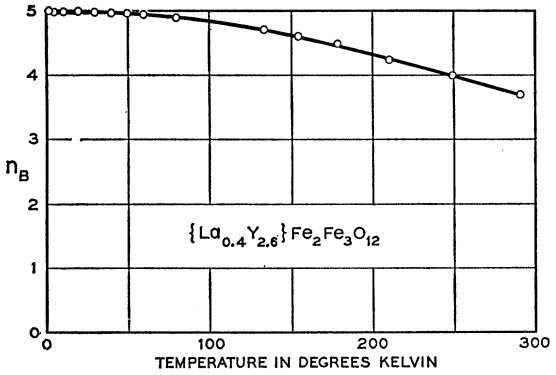

FIG. 1. n_B versus T for $\{La_{0.40}Y_{2.60}\}Fe_2Fe_3O_{12}$. Applied fields of 9.6 and 14.24 kOe give the same n_B values at a given temperature over the whole range investigated.

Our measurements were made on a polycrystalline specimen $\{PrY_2\}Fe_2Fe_3O_{12}$. The results on a sintered specimen at a field of 14.24 kOe are shown in Fig. 2. However, magnetic saturation was not attained at this field. Measurements on a powdered specimen at 4.2°K and fields to 80 kOe indicated saturation at about 70 kOe. The moment of the specimen at this field is 6.6 μ_B per formula unit. This value is actually in good agreement with that, 6.7 μ_B, obtained by Henry *et al.* The contribution from a Pr^{3+} ion, however, is not 1.9 μ_B but 1.6 μ_B.

SAMARIUM IRON GARNET

Pauthenet[11] has reported magnetization versus temperature data on polycrystalline samarium iron garnet. He found a moment per formula unit of 4.66 μ_B at 4.2°K and a maximum of 4.72 μ_B at 66.5°K. Aharoni and Schieber[7] reported no observable difference in the magnetization versus temperature behavior in the range 100 to about 600°K for samarium and yttrium iron garnets and for various solid solutions of samarium in yttrium iron garnet. Loriers and Villers[6] and Cunningham and Anderson[12] have also reported data on this system. None of these results are in detailed agreement with ours.

Shown in Fig. 3 are magnetization versus temperature data on polycrystalline samarium iron garnet at fields of 4.8, 9.6, and 14.24 kOe. It is apparent that below about 140°K, saturation is not attained at the highest applied field. The minimum at about 35°K results from the large anisotropy[13] caused by the Sm^{3+} ion. This was further ascertained from measurements on a single crystal not aligned exactly along the easy direction.

Two single-crystal spheres (total wt=0.0875 g) were placed in a capsule in such a manner that they could move freely in the applied magnetic field. Saturation appeared to be attained at a field of 4.9 kOe, the lowest field at which measurements were made, over the whole temperature range 1.4 to 298°K. The spontaneous magnetization versus temperature obtained is shown in Fig. 4. Also shown are the results recently obtained on a polycrystalline specimen of yttrium iron garnet.

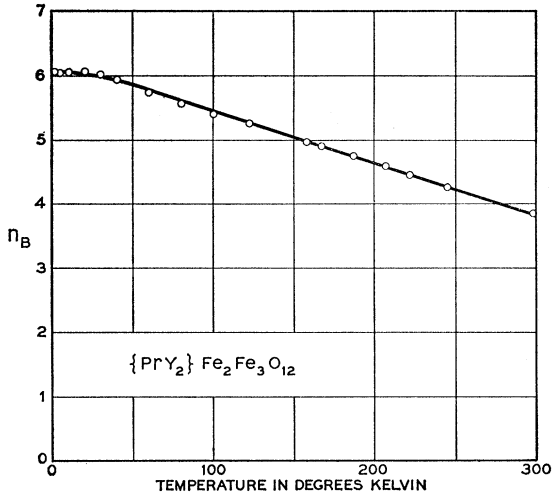

FIG. 2. n_B versus T for $\{PrY_2\}Fe_2Fe_3O_{12}$ at an applied field of 14.24 kOe (not saturating).

At 0°K, the moment of samarium iron garnet is 5.43 μ_B, implying a contribution of 0.14 μ_B per Sm^{3+} ion to the total moment. In the temperature range 0 to 298°K, the moment of samarium iron garnet is everywhere larger than that of YIG. Near 300°K, the slope $|dn_B/dT|$ for the samarium iron garnet is greater than that of YIG so that it appears that the two curves will cross each other at some temperature above 300°K. Extension of the curves indicates that this might occur at about 330°K.

The results indicate that the Sm^{3+} ion behaves similarly to the Pr^{3+} and Nd^{3+} ions in the garnets; that is, because J is oppositely directed to[14] S, the moments of

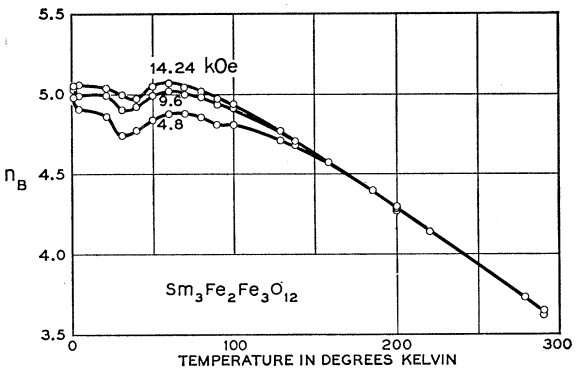

FIG. 3. n_B versus T at three fields for polycrystalline samarium iron garnet.

[11] R. Pauthenet, Ann. Phys. (N.Y.) **3**, 424 (1958).
[12] J. R. Cunningham, Jr., and E. E. Anderson, Suppl. J. Appl. Phys. **31**, 45S (1960).
[13] J. F. Dillon, Jr., and J. W. Nielson, Phys. Rev. **120**, 105 (1960); R. F. Pearson and R. W. Cooper, J. Phys. Soc. Japan **17**, Suppl. BI, 369 (1962); R. F. Pearson, J. Appl. Phys. **33**, 1236 (1962).
[14] L. Néel, Compt. Rend. **206**, 49 (1938).

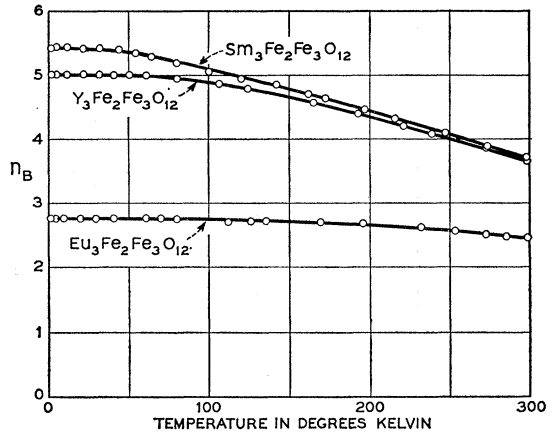

FIG. 4. n_B versus T for spherical crystals of samarium iron garnet and of europium iron garnet allowed to rotate freely in the applied field. Shown also is the curve for polycrystalline yttrium iron garnet. All specimens were saturated at field of 4.9 kOe or lower.

the Sm^{3+} ion add to the resultant moment of the iron sublattices at low temperatures. The orbital contribution, however, decreases faster with temperature than does that of the spin and so, at some higher temperature, the curves for the samarium and yttrium iron garnets cross; and beyond this temperature, the spin contribution is dominant and therefore the moments of the Sm^{3+} ions subtract from the resultant moment of the iron sublattices.[15]

EUROPIUM IRON GARNET

Pauthenet[11] has reported magnetic data for europium iron garnet. More recently, Villers, Loriers, and Clerc[16] have reported results on the yttrium-europium iron garnet system. Our results obtained on a spherical crystal (wt, 0.1415 g) of europium iron garnet allowed to move freely in the field are shown in Fig. 4. Saturation was attained at 4.8 kOe over the whole temperature range investigated. The results appear to agree well with those of Villers *et al.*[14] for EuIG, their measurements having been made on polycrystalline specimens. Because these measurements were probably made at moderate fields, it is probable that the Eu^{3+} ion does not introduce the high anisotropy observed for the other lighter magnetic rare-earth ions.

The magnetic behavior of EuIG has been treated theoretically by Wolf and Van Vleck[17] who used Pauthenet's[11] data on YIG empirically corrected to n_B (at 0°K) equal to 5.0 μ_B and Pauthenet's actual experimental values on EuIG to compute the exchange field acting on a Eu^{3+} ion at 0°K. On the assumptions that the back-effect of the Eu^{3+} ions on the Fe^{3+} ion moment alignment and Eu^{3+}–Eu^{3+} ion moment interactions are negligible and that the crystallographically different Fe^{3+} ion magnetizations are the same,[18] the exchange field H_{ex} was considered to be equal to aM_{Fe}. With the moment 0.81 μ_B for the Eu^{3+} ion at $T=0$°K derived from Pauthenet's data, aM_{Fe}/k was found from the theory to be 24°K. The constant a and the results for YIG were used to determine the magnetization versus temperature curve for EuIG. Agreement with Pauthenet's data is excellent.

Our results on EuIG differ somewhat from those of Pauthenet. The moment of a Eu^{3+} ion at 0°K is found to be 0.74 μ_B leading to, at 0°K, $aM_{Fe}/k=22$°K. The empirically corrected curve for YIG does not agree with our measurements. However, using our data, agreement given by the Wolf-Van Vleck treatment is still excellent.

SUMMARY

As a result of the work herein reported we may conclude that: (1) The La^{3+} ion behaves as expected when substituted for Y^{3+} ion in YIG; namely, it does not have a significant effect on the magnetic behavior. (2) The Sm^{3+} ion behaves similarly to the Pr^{3+} and Nd^{3+} ions in that its moment in at least the temperature range 0 to 298°K adds to the resultant moment of the iron sublattices. (3) The moments at 0°K of Pr^{3+}, and of Sm^{3+} ions are 1.6 and 0.14 μ_B, respectively. The value for the Nd^{3+} ion, 1.2—1.3 μ_B, has been reported earlier.[19] (4) The spontaneous magnetization versus temperature data for a spherical crystal of EuIG are in good agreement with those on polycrystalline material,[14] the Eu^{3+} ion moment at 0°K being 0.74 μ_B.

ACKNOWLEDGMENTS

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[15] J. A. White and J. H. Van Vleck, Phys. Rev. Letters **6**, 412 (1961).

[16] G. Villers, J. Loriers, and F. Clerc, Compt. Rend. **255**, 1196 (1962).

[17] W. P. Wolf and J. H. Van Vleck, Phys. Rev. **118**, 1490 (1960).

[18] The authors recognize, of course, that this may not be correct but indicate that existing experimental data do not permit taking this refinement into account. Indications from neutron diffraction studies on polycrystalline specimens [E. Prince, Acta Cryst. **10**, 787 (1957); F. Bertaut, F. Forrat, A. Herpin, and P. Mériel, Compt. Rend. **243**, 898 (1956); U. S. Kuzminov, I. I. Yamzin, and N. V. Belov, Kristallografiya **7**, 946 (1962)] are that the moments are different at temperatures above 0°K. However, there are some other indications (to be published) that the moments are not appreciably different.

[19] S. Geller, H. J. Williams, and R. C. Sherwood, Phys. Rev. **123**, 1692 (1961).