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Magnetic and Crystallographic Study of Neodymium-Substituted Yttrium and Gadolinium Iron Garnets

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A study of the garnet systems $\{R_{3-x}Nd_x\}Fe_2Fe_3O_{12}$, $R \equiv Y$ or Gd, indicates, as expected, that the moment contributed by the Nd^{3+} ion adds to that of the resultant contributed by the iron sublattices, similar to the results of earlier work by others on intermetallic systems involving rare earths and also on Nd- and Pr-substituted yttrium iron garnets. This has been explained on the basis that in the $L-S$ ions Nd and Pr, $\mathbf{J}$ is generally directed oppositely to $\mathbf{S}$. It has been found that the anisotropy introduced by the Nd^{3+} ion prevents saturation at applied fields up to 14 000 oe, and at first a null method involving the garnet system $\{Gd_{2-x}Y_xNd\}Fe_2Fe_3O_{12}$ was used to find the moment contributed by the Nd^{3+} ion at 0°K; the moment obtained by this method is 1.2 μ_B. Subsequently, measurements made to fields of 80 000 oe at 4.2°K on the garnets $\{Y_2Nd\}Fe_2Fe_3O_{12}$ and $\{Gd_2Nd\}Fe_2Fe_3O_{12}$ proved that the extrapolation of n_B vs $1/H_a$ to $1/H_a=0$ from the lower field values did not give the proper moments for these compounds. The specimens appeared to be saturated at fields above 70 000 and 60 000 oe, respectively, and gave moments of 6.2 μ_B and 7.7 μ_B, respectively, per formula unit. These values indicate moments for the Nd^{3+} ion of 1.2 μ_B and 1.3 μ_B, respectively. These values corroborate that found by the aforementioned compensation point method. The low value contrasted with the ground-state gJ value of 3.27 μ_B indicates a considerable crystal field effect on the Nd^{3+} ion in the garnets. Maxima have been found for amounts of Nd substitution in Y, Gd, and Sm iron garnets. These data in turn lead to prediction regarding maximum substitution of Nd in other rare-earth iron garnets and also predict a maximum lattice constant close to 12.538 A for any iron garnet, indicating that Pm iron garnet would not exist. Data are given also on some other garnets used to strengthen our conclusions. The garnet $Gd_{1.5}Nd_{1.5}Ga_2Ga_3O_{12}$ may be antiferromagnetic but with a Néel temperature below 1.4°K. Magnetic and crystallographic data are also given on the garnets $\{Gd_{1.5}Er_{1.5}\}Fe_2Fe_3O_{12}$ and $\{Y_{1.5}Er_{1.5}\}Fe_2Fe_3O_{12}$, both of which lead to 5.4 μ_B for the Er^{3+} ion contribution at 0°K, in good agreement with the value deduced from Pauthenet's measurements on erbium iron garnet.

INTRODUCTION

IN recent work[1] in these Laboratories on compounds Co_5R ($R \equiv$ rare earth) having the Cu_5Ca-type structure, Nd and Pr behaved as though their moments were adding to those of the cobalt atoms, whereas those of Gd, Tb, Dy, Ho, Er, and Tm were behaving oppositely. To be sure, the antiferromagnetic interactions in the intermetallic compounds do not have the same origin as in the garnets. Yet it appeared that the end results could be similar. We therefore decided to determine the effects of Nd substitution for Gd in gadolinium iron garnet. Further, to obtain an independent idea of the behavior of the magnetization vs temperature of the Nd^{3+} ion, we decided later to do some work on the Nd-substituted yttrium iron garnet.

As will be shown subsequently, seemingly anomalous results were at first obtained for the apparent behavior of the Nd^{3+} ion magnetization and for comparison we therefore prepared and studied $\{Gd_{1.5}Nd_{1.5}\}Ga_2Ga_3O_{12}$, $\{Er_{1.5}R_{1.5}\}Fe_2Fe_3O_{12}$, $R \equiv Y$, Gd. Also as we came to understand the results, another interesting series of experiments for determination of the 0°K magnetization of the Nd^{3+} ion was suggested to us by A. M. Clogston (see Discussion) and we therefore studied part of the system $\{Y_{2-x}Gd_xNd\}Fe_2Fe_3O_{12}$.

In the metal structures mentioned above, it was apparent that the total moment of an $L+S$ rare-earth ion followed the vector $\mathbf{S}$ in such a manner that its direction was generally the same as that of $\mathbf{S}$, the maximum moment attainable from such an atom, being $gJ=L+2S$. An $L-S$ ion, on the other hand, has its net moment in a direction generally opposite to that of $\mathbf{S}$. Thus if, as one would expect, the important antiferromagnetic interaction occurs through the spin-spin interaction, then the net sublattice moments of Nd and Pr should be directed positively with respect to the net Co sublattice of the compounds and this is what is observed. Similarly in the garnets, the Nd^{3+} and Pr^{3+} ion moment contributions should be parallel to those of the net Fe^{3+} ion sublattice moments.[2,3]

The results already obtained at room temperature by Goldring, Schieber, and Vager[4] confirm this explanation.[5] These authors, however, had claimed that the results should be considered as unexpected.

The seemingly anomalous result we obtained was the apparent difference in the Nd^{3+} ion contribution to the spontaneous magnetization when it was substituted for Gd^{3+} from when it was substituted for Y^{3+}. It appears that this comes about from the anisotropy introduced by the Nd^{3+} ion. This has been established not only by deduction from experiments mentioned earlier but has been corroborated by high-field (up to 80 000 oe) measurements on $\{Gd_2Nd\}Fe_2Fe_3O_{12}$ and on $\{Y_2Nd\}Fe_2Fe_3O_{12}$.

Included in this report is a crystallographic study

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[1] E. A. Nesbitt, H. J. Williams, J. H. Wernick, and R. C. Sherwood, J. Appl. Phys. **32**, 342S (1961).

[2] We wish to thank J. A. White for an elucidating discussion of the magnetic behavior of the rare-earth ions.

[3] Since the completion of the manuscript of this paper, two publications containing an explanation for this behavior of the Nd^{3+} ion in the garnets have appeared: one by the present authors, a brief abstract of the present paper to be presented at the Washington, D. C. meeting of the American Physical Society [Bull. Am. Phys. Soc. **6**, 230 (1961)]; the other by W. P. Wolf [J. Appl. Phys. **32**, 742 (1961)].

[4] G. Goldring, M. Schieber, and Z. Vager, J. Appl. Phys. **31**, 2057 (1960).

[5] In a preprint of a paper sent to us by Aharoni, Frei, and Schieber, the authors have also obtained results (to temperatures down to liquid nitrogen) which confirm this explanation. In their paper, the authors credit Dr. R. L. White with the explanation of their results. This paper, we are informed, is to be published in the Journal of the Physics and Chemistry of Solids.

also of the $\{Sm_{3-x}Nd_x\}Fe_2Fe_3O_{12}$ system which, together with the analogous Gd and Y systems, has led to a prediction of the maximum lattice constants and amounts of Nd substitution in most of the rare-earth iron garnets.

EXPERIMENTAL

Preparation of Compounds

Appropriate quantities of oxides to make 0.001 mole of product were mixed and ground in an agate mortar. Each mix was pressed into a pill of half-inch diameter using a pressure of approximately 4 tons/sq. in. Each pill was then fired at temperatures shown in Tables I–IV in either oxygen or air atmosphere for various periods. X-ray powder diffraction photographs were taken of each specimen using 114.6-mm diameter Straumanis-type Norelco cameras and Cr K radiation. If any trace of an extraneous phase or broad lines in the back reflection region were found, the pill was crushed and the specimen reground, made into a pill again, and refired. Photographs were taken again to check for extraneous phases or broad back-reflection lines. This process was repeated until we were assured of single phase material at least as ascertained by x-ray photography. In the case that after several repetitions, the specimen looked unsatisfactory, a new specimen was prepared.

In some cases, very faint traces of extraneous phase remained. However, magnetic measurements were not made on these samples, which were used mainly to establish crystallographic relationships as will be shown subsequently.

There may be several causes for the occurrence of "unsatisfactory" specimens when prepared in the fashion described above. Small disproportionate losses of constituents in the initial preparation process could cause this. Also, because the solid-state reaction is diffusion dependent, it would seem that constituents which do not react to form the garnet could become separated or form products which become separated to such an extent that reaction becomes improbable. The regrinding and refiring procedure aids in bringing these unreacted constituents together. But this attempt at obtaining single-phase material might also prove inadequate in some cases as for example, if the temperature range for stability of a given composition is very narrow.

Magnetic Measurements

Measurements of magnetic moment were made in the temperature range 1.4–298°K usually at three different applied fields H_a, namely, 5, 9.6, and 14 koe, by means of a pendulum magnetometer of the type already described elsewhere.[6] Details of determination of spontaneous magnetizations will be given in the course of the discussion of the various systems.

Measurements at high fields (to 80 000 oe) were made on $\{Gd_2Nd\}Fe_2Fe_3O_{12}$ and on $\{Y_2Nd\}Fe_2Fe_3O_{12}$ using the Bitter-type magnet and an extraction method for determination of the moment. Galvanometer deflections were transformed into μ_B units by comparison of measurements made at fields $\leq 14\,000$ oe with results obtained from the pendulum magnetometer.

CRYSTALLOGRAPHIC DATA

The lattice constants of the various specimens $\{R_{3-x}Nd_x\}Fe_2Fe_3O_{12}$ are listed in three tables: (I) $R \equiv Gd$; (II) $R \equiv Y$; (III) $R = Sm$. The lattice constants of miscellaneous other specimens used in this work are listed in Table IV.

Table I. Lattice constants and preparation information for garnets $\{Gd_{3-x}Nd_x\}Fe_2Fe_3O_{12}$.

x	a (A)	Firing procedure Temp., °C (hr)
0.00	12.472±0.003[a]	b
0.25	12.482	1425 (1), (2)
0.50	12.493	1425 (1), (2)
0.75	12.503	1500 (3), 1420 (18)
1.00	12.514	1500 (3), 1400 (2)
1.25	(12.524)[c]	1425 (1), (2), 1450 (18)
1.30	(12.525)[c]	1250 (21), 1410 (26)
1.40	(12.529)[c]	1415 (2), (65)
1.50	(12.530)[c]	1230 (20), 1415 (17)

[a] This is an improved value over that, 12.474 A, reported earlier [S. Geller and D. W. Mitchell, Acta Cryst. 12, 936 (1959)].
[b] Prepared by D. W. Mitchell using a coprecipitation technique followed by drying, calcining, and firing as described by M. A. Gilleo and S. Geller, Phys. Rev. 110, 73 (1958).
[c] Not single-phase material. For $x=1.50$, lattice constant definitely indicates lower value of x, i.e., 1.40 (see text).

Table II. Lattice constants and preparation information for the garnets $\{Y_{3-x}Nd_x\}[Fe_2](Fe_3)O_{12}$.

x	a (A)	Firing procedure Temp., °C (hr)
0.00	12.376±0.004[a]	
1.00	12.449±0.003	1450 (2), (2), (2), 1300 (2)
1.50	12.485	1400 (3), 1350 (2), 1300 (2)
1.80	(12.504)[b]	1350 (6), 1270 (96), 1400 (23)
1.90	(12.511)[b]	1350 (18), 1400 (96)
2.00	(12.512)[b]	1350 (18), 1410 (20)
2.50	(12.513)[b]	1415 (1½), (18)

[a] From S. Geller and M. A. Gilleo, J. Phys. Chem. Solids 3, 30 (1957).
[b] These are not single-phase materials and the lattice constants (see Fig. 1) represent lower amounts of Nd than those given by the values of x (see text).

Table III. Lattice constants and preparation information for garnets $\{Sm_{3-x}Nd_x\}Fe_2Fe_3O_{12}$.

x	a (A)	Firing procedure Temp., °C (hr)
0.00	12.530±0.003[a]	b
0.10	12.533	1415 (65)
0.25	12.535	1415 (1), (22)
0.375	(12.537)[c]	1415 (1½), (18)

[a] See Table I, footnote a.
[b] See Table I, footnote b.
[c] Not single-phase material.

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[6] R. M. Bozorth, H. J. Williams, and D. E. Walsh, Phys. Rev. **103**, 572 (1956).

TABLE IV. Lattice constants and preparation information for other garnets investigated.

Compound	a (A) Observed	Calculated	Firing procedure Temp., °C (hr)
$\{Gd_{1.5}Nd_{1.5}\}Ga_2Ga_3O_{12}$	12.437±0.004	12.445	1475 (3), 1400 (18), (19), 1500 (1)
$\{Y_{1.07}Gd_{0.93}Nd\}Fe_2Fe_3O_{12}$	12.477±0.003	12.479	1400 (18), 1300 (65), 1410 (26)[a]
$\{Y_{1.10}Gd_{0.90}Nd\}Fe_2Fe_3O_{12}$	12.477	12.478	1300 (21), 1375 (17)[b]
$\{Y_{1.12}Gd_{0.88}Nd\}Fe_2Fe_3O_{12}$	12.476	12.477	1350 (70), (22), 1415 (18)[a]
$Er_3Fe_2Fe_3O_{12}$	12.347		1415 (2), (21)
$\{Gd_{1.5}Er_{1.5}\}Fe_2Fe_3O_{12}$	12.411	12.410	1400 (18), (22)
$\{Y_{1.5}Er_{1.5}\}Fe_2Fe_3O_{12}$	12.361	12.362	1400 (18), (22)
$\{Er_{1.5}Nd_{1.5}\}Fe_2Fe_3O_{12}$	12.470	12.472	1400 (18)

[a] Magnetic measurements made after second and third firings.
[b] Magnetic measurements made after first and second firings.

The data of Tables I and II are plotted in Fig. 1. Note that as one would expect, the lattice constant vs composition behavior is linear. Also important is the fact that extrapolation to $x=3$ yields very nearly the same value, 12.596(±0.001) A in the two cases, indicating the self-consistency of all of the data and giving us confidence in the quality of our specimens.

In the $\{Gd_{3-x}Nd_x\}Fe_2Fe_3O_{12}$ system, single-phase specimens were produced with x as high as 1.00. The specimens with $x=1.25$, 1.30, and 1.40 had faint traces of extraneous phase and the central values of the lattice constants of the last two were slightly lower (Table I) than the expected values, 12.526 and 12.530 A, for the respective compositions. The specimen with $x=1.50$ was not single phase and the sharply defined garnet phase present had a lattice constant, 12.530 A, indicating a composition corresponding to $x=1.40$, which appears to be the maximum attainable in this system.

In the $\{Y_{3-x}Nd_x\}Fe_2Fe_3O_{12}$ system, values of x to 1.50 gave single-phase garnets according to the x-ray diffraction photographs. For $x=1.8$, 1.9, 2.0, and 2.5 our experiments did not yield strictly single-phase specimens although for $x=1.8$ and 1.9 the final specimens gave photographs which indicated only very small amounts of extraneous phase. The lattice constants of the garnet phases indicated compositions with $x=1.76$ and 1.86, respectively. The photograph of the finally fired $x=2$ specimen indicated the presence of a substantial amount of the perovskite-like phase, but gave a sharply defined garnet phase with lattice constant 12.512 A, indicating a value of $x=1.87$. The specimen with initial reactant composition given by $x=2.5$ gave a powder photograph which indicated a garnet phase with $a=12.513$ A. This is equivalent to $x=1.88$ which may be taken as the maximum for a stoichiometric garnet phase in this system.

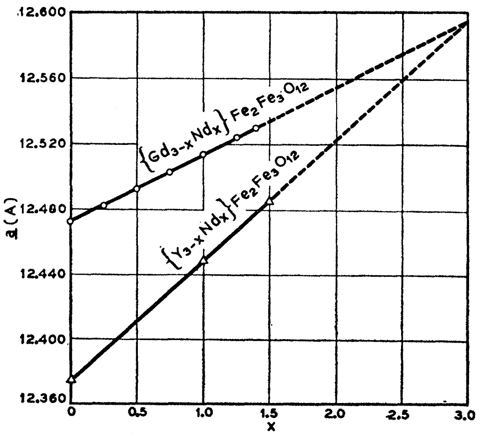

FIG. 1. Lattice constant vs x for neodymium-substituted gadolinium and yttrium iron garnets.

From a few observations of the kind described above, it seemed that one could predict the limits of substitution of Nd for any of the other rare-earth ions in the iron garnets. (In fact similar experiments could be carried out for Pr and La and for other octahedral and tetrahedral ions.) We noticed that the maximum lattice constant attainable appeared to be associated with the difference in the effective sizes of the atoms involved, that is, the larger the difference, the lower the maximum lattice constant attainable.

Now in a first approximation, one might expect that the iron-oxygen arrangement would determine the maximum allowable size of the rare-earth ion in the dodecahedral site. This is so because the Fe–O distances in the particular polyhedra tend to remain the same even though the size of the dodecahedral ion may be changed. For example, compare the refined structures of yttrium iron garnet[7] and gadolinium iron garnet.[8] Examination of the structure shows how the oxygen ions move to accommodate the rare-earth ion while sustaining the expected Fe–O distances. Obviously there will be a limit to the allowable distortion.

In the second approximation a mixed rare-earth iron garnet will have local disorder introduced by ions of different size in crystallographically equivalent sites. This disorder probably prevents the attainment of a single maximum lattice constant for *all* rare-earth iron garnets in which Nd is substituted for the particular rare earth.

To make these arguments more definitive we attempted substitutions of Nd for Sm in samarium iron

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[7] S. Geller and M. A. Gilleo, J. Phys. Chem. Solids **3**, 30 (1957).
[8] J. E. Weidenborner, Acta Cryst. (to be published).

garnet. We found, as expected, that not much Nd can be substituted for Sm and the largest lattice constant attainable was 12.537 A for the garnet phase of a specimen with intended $x=0.375$. The lattice constants for the specimens made are given in Table III. From these one deduces that the actual value of x for the garnet phase with lattice constant 12.537 A is 0.35. Two specimens with intended $x=0.50$ gave powder photographs which indicated the presence of considerably more perovskite-like than garnet phase. An accurate measurement of lattice constant was not feasible, but it is unlikely that it is greater than 12.537 A.

In Fig. 2, we plot the three maximum lattice constants of the Nd-substituted systems against the lattice constants of the pure end-members. We propose that the line passing through these points represents the line of maximum lattice constant for Nd substitution in (end member) garnets which have lattice constants plotted as abscissa. Also in Fig. 2 we plot the values of maximum x in $\{R_{3-x}Nd_x\}Fe_2Fe_3O_{12}$ vs lattice constant of pure end-member garnets. These curves also indicate that the maximum possible value of a lattice constant for pure end-member *iron* garnet is close to 12.538 A and therefore that PmIG most likely would not exist.[9] The value 12.538 A is also undoubtedly close to the maximum value for any *mixed* rare-earth *iron* garnet.

As expected there was no difficulty in obtaining the garnets $\{Gd_{1.5}Er_{1.5}\}Fe_2Fe_3O_{12}$, $\{Y_{1.5}Er_{1.5}\}Fe_2Fe_3O_{12}$, and $\{Gd_{1.5}Nd_{1.5}\}Ga_2Ga_3O_{12}$; in these cases all end members exist. Also as expected, lattice constants of these garnets are equal (within experimental error) to the arithmetic averages of the end-member garnets. The lattice constants of the garnets

$$\{Y_{3-x-y}Gd_xNd_y\}[Fe_2](Fe_3)O_{12}$$

are, as expected, equal to the weighted arithmetic means of the values of the end-member garnets, taking the lattice constant of a *hypothetical* $Nd_3Fe_2Fe_3O_{12}$ to be 12.596 A, of $Er_3Fe_2Fe_3O_{12}$, 12.347 A, of $Gd_3Fe_2Fe_3O_{12}$, 12.472 A. The values reported by Bertaut and Forrat[10] for GdGaG and NdGaG are, respectively, 12.39 and 12.50 A. These would give an average of 12.445 A, which, considering the probable error of at least 0.01 A in the Bertaut-Forrat values, is in good agreement (see Table IV) with the observed value for

$$\{Gd_{1.5}Nd_{1.5}\}Ga_2Ga_3O_{12}.$$

TABLE V. n_B at $H=\infty$, $T=0°K$ based on measurements made at $H_a \leq 14\,000$ oe for systems $\{R_{3-x}Nd_x\}Fe_2Fe_3O_{12}$, $R\equiv Gd$, Y.

x		$n_B(\infty,0)$
	$R\equiv Gd$	
0.00		16.0
0.25		13.8
0.50		11.4
0.75		9.5
1.00		7.2
	$R\equiv Y$	
0.00		5.0
1.00		5.95
1.50		6.4

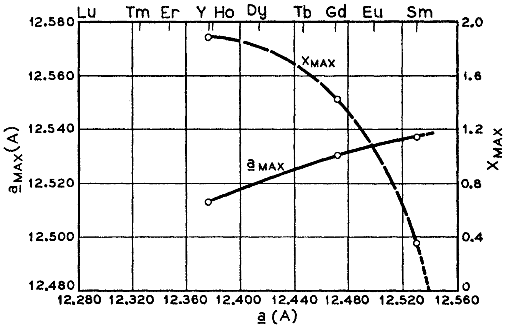

FIG. 2. Maximum lattice constant and maximum x in $\{R_{3-x}Nd_x\}Fe_2Fe_3O_{12}$, where R is a rare-earth or yttrium ion, vs lattice constant of end-member rare-earth or yttrium iron garnet. (Lattice constants of Tm, Ho, Dy, and Tb iron garnets from Bertaut and Forrat.[9])

MAGNETIC DATA

Curves in terms of n_B vs temperature for the systems $\{Gd_{3-x}Nd_x\}Fe_2Fe_3O_{12}$ and $\{Y_{3-x}Nd_x\}Fe_2Fe_3O_{12}$ at an applied field of 14 000 oe are shown in Fig. 3. The values of n_B extrapolated to "infinite" field (from data obtained at $\leq 14\,000$ oe) and 0°K for the various specimens are listed in Table V and plotted in Fig. 4. Curves

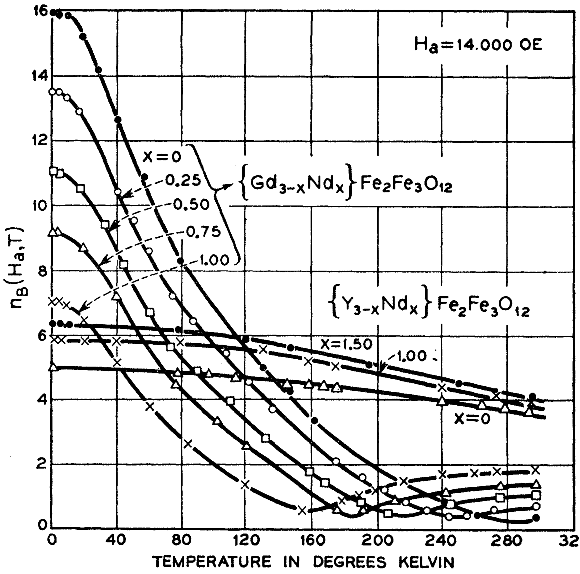

FIG. 3. n_B vs T for Nd-substituted gadolinium and yttrium iron garnets. [Data for pure $Y_3Fe_2Fe_3O_{12}$ are at $H_a=13\,000$ oe and from Gilleo and Geller (Table I, reference b).]

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[9] If we plot the lattice constants given here for Er, Gd, Sm, and Nd (hypothetical) iron garnets and of EuIG from the reference in Table I, footnote a, against atomic number, the five points lie on a line which indicates a lattice constant of 12.561 A for PmIG. F. Bertaut and F. Forrat [Compt. rend. **244**, 96 (1957)], predicted a value of 12.57 A for PmIG.

[10] F. Bertaut and F. Forrat, Compt. rend. **243**, 1219 (1956).

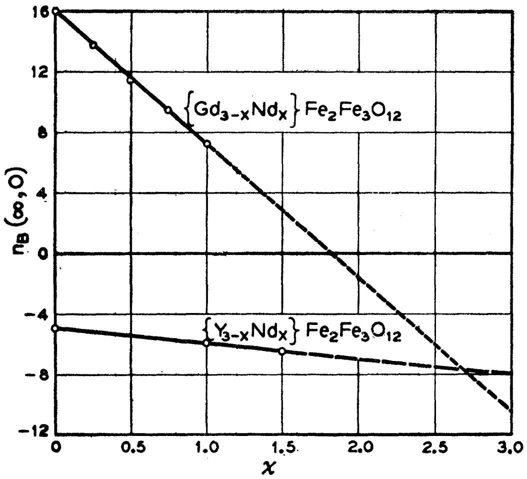

FIG. 4. Spontaneous magnetizations, extrapolated to "infinite" field and 0°K, vs x of garnets $\{R_{3-x}Nd_x\}Fe_2Fe_3O_{12}$, $R\equiv$Gd or Y.

of n_B vs T for $\{Y_{1.5}Er_{1.5}\}Fe_2Fe_3O_{12}$ and

$$\{Gd_{1.5}Er_{1.5}\}Fe_2Fe_3O_{12}$$

at $H_a = 14\,000$ oe are shown in Fig. 5.

In Fig. 6, $1/\chi_n$ vs T is plotted for

$$\{Gd_{1.5}Nd_{1.5}\}Ga_2Ga_3O_{12}.$$

The linear extrapolation intersects the $1/\chi_n = 0$ at about -0.5°K. Also the curve of χ_n vs T at $H_a = 14\,000$ oe seems still to be rising at 1.4°K (Fig. 6) indicating that if this specimen is antiferromagnetic, the Néel temperature is below 1.4°K. Measurements at 1300 oe also showed susceptibility vs T behavior similar to that at 14 000 oe; in particular, no susceptibility peak was observed above 1.4°K. Thus interaction, if any, between the rare-earth ions must be extremely weak.

Curves for the system $\{Y_{2-x}Gd_xNd\}Fe_2Fe_3O_{12}$ are shown in Fig. 7. These experiments were carried out to determine more exactly the moment contributed by the Nd^{3+} ion.

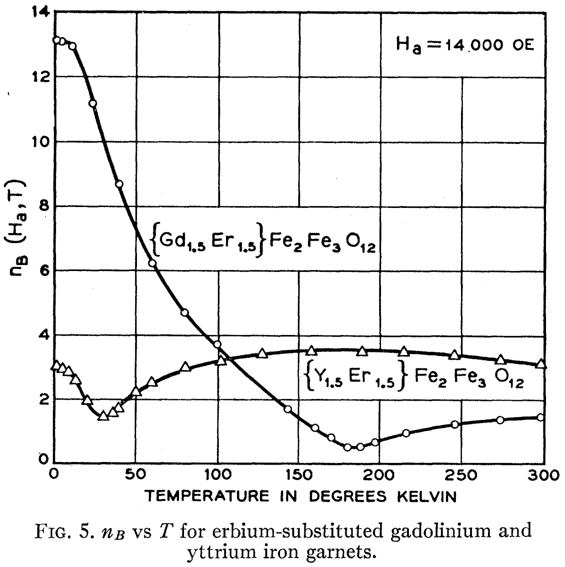

FIG. 5. n_B vs T for erbium-substituted gadolinium and yttrium iron garnets.

DISCUSSION

General

The main purpose of this work was to determine the magnetic behavior of the Nd^{3+} ion in the garnets. Extrapolation of moments to "infinite" field and 0°K gave the results shown in Fig. 4. (Individual values are listed in Table V.) These results *imply* that when Nd^{3+} is substituted for Gd^{3+}, it contributes at 0°K a moment of $(1.8\pm0.2)\mu_B$, but when substituted for Y^{3+}, it contributes $(0.9\pm0.1)\mu_B$. Such results would on first consideration hardly be expected. There does not seem to be any reason why the Nd^{3+} ion should behave so differently magnetically when substituted for two different ions. Almost certainly the difference in crystal field effects would not be large. Further, one would expect that (as for example in the case of the lattice constants) the extrapolation to a *possible* $Nd_3Fe_2Fe_3O_{12}$ would give the same results for the two cases. On the contrary, it appears that the contribution of the Nd^{3+} ion in *each* of the systems is quite constant for the various values of x.

One of the first thoughts which occurred to us was the possibility of interaction with the Gd^{3+} ions in the one case and no interaction with Y^{3+} ions in the other. If the former were strong enough, the different behavior of the Nd^{3+} ions might thereby be explained. However, this did not seem like a very probable explanation because of the known weak or nonexistent interaction between the dodecahedrally situated ions[11–14] and also because of the structural evidence.[7,8] Nevertheless, we decided to check this by measurements of the $\{Gd_{1.5}Nd_{1.5}\}[Ga_2](Ga_3)O_{12}$ garnet. As shown above,

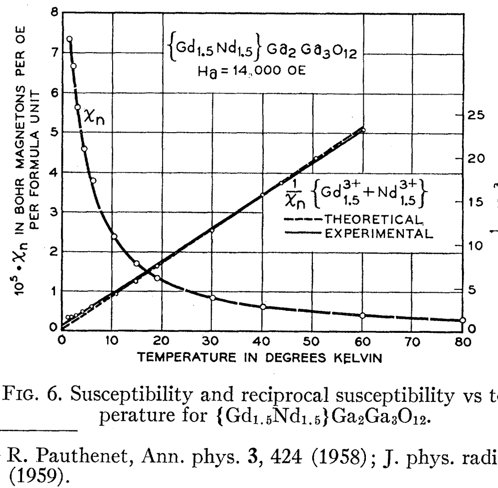

FIG. 6. Susceptibility and reciprocal susceptibility vs temperature for $\{Gd_{1.5}Nd_{1.5}\}Ga_2Ga_3O_{12}$.

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[11] R. Pauthenet, Ann. phys. 3, 424 (1958); J. phys. radium 20, 388 (1959).

[12] M. A. Gilleo and S. Geller, J. Phys. Chem. Solids 10, 187 (1959).

[13] R. M. Bozorth and S. Geller, J. Phys. Chem. Solids 11, 263 (1959).

[14] M. Ball, G. Garton, M. J. M. Leask, D. Ryan, and W. P. Wolf, J. Appl. Phys. 32, 267S (1961).

this experiment indicated extremely weak or no interaction.

Now, it has recently been shown[14] that the garnet $\mathrm{Dy_3Al_2Al_3O_{12}}$ has a Néel temperature of 2.55°K whereas $\mathrm{Dy_3Ga_2Ga_3O_{12}}$ remains paramagnetic down to lower temperatures than this. In this case, a change in geometry (see also references 12, 15) resulting from the difference in sizes of the $\mathrm{Ga^{3+}}$ and $\mathrm{Al^{3+}}$ ions apparently has a measurable effect on the strength of the interactions. But this happens only when the potential interaction is at most very weak. Therefore one would suspect that with $\mathrm{Fe^{3+}}$ ions filling the octahedral and tetrahedral sites, the strength of magnetic interaction between $\mathrm{Gd^{3+}}$ and $\mathrm{Nd^{3+}}$ ions would not be significantly different from that in the $\mathrm{Ga^{3+}}$ compound.

We decided to determine the effect of substituting the $L+S$ ion $\mathrm{Er^{3+}}$ for $\mathrm{Gd^{3+}}$ and $\mathrm{Y^{3+}}$ in iron garnets. In these two cases the spontaneous magnetizations of $\{\mathrm{Gd_{1.5}Er_{1.5}}\}\mathrm{Fe_2Fe_3O_{12}}$ and $\{\mathrm{Y_{1.5}Er_{1.5}}\}\mathrm{Fe_2Fe_3O_{12}}$ at 1.4°K extrapolated to infinite field were 13.8 μ_B and 3.2 μ_B, respectively. Assuming a net amount of 5.0 μ_B for the iron sublattices and 7.0 μ_B for each $\mathrm{Gd^{3+}}$ ion, the Er contribution was computed to be 5.4 μ_B in both cases. This value checks well with that, 5.3 μ_B, deduced from the results of Pauthenet[11] on $\mathrm{Er_3Fe_2Fe_3O_{12}}$.

The answer to the apparent anomaly could now only be in the anisotropy introduced by the $\mathrm{Nd^{3+}}$ ion. Dillon and Nielsen[16] showed that minute amounts of $\mathrm{Nd^{3+}}$ ion doping of yttrium iron garnet introduced high anisotropy in the field for resonance surface.

Now suppose that in the Gd–Nd garnets, saturation is not attained at the fields applied. In all the compounds studied the total $\mathrm{Gd^{3+}}$ ion moments at 0°K are greater than the sum of the $\mathrm{Nd^{3+}}$ ion and iron sublattice moments. Thus, the $\mathrm{Gd^{3+}}$ magnetizations will be more nearly polarized with the applied field and therefore data obtained from specimens which were not saturated, cause us to assign too high a moment to $\mathrm{Nd^{3+}}$ if we assign the usual 7.0 μ_B to each $\mathrm{Gd^{3+}}$ ion and 5.0 μ_B to the net iron sublattice moment at 0°K. Conversely, a low measured 0°K moment for the Y–Nd compounds leads to too low a value for the $\mathrm{Nd^{3+}}$ ion contribution if 5.0 μ_B is taken as the net moment of the iron sublattices. Obviously, if all of the particles are not well aligned with the field, it is improper to assign the saturation moments to $\mathrm{Gd^{3+}}$ and $\mathrm{Fe^{3+}}$ ions. It would appear then that the moment contributed by the $\mathrm{Nd^{3+}}$ ion when substituted in the garnets is between that given when substituted for $\mathrm{Y^{3+}}$ and when substituted for $\mathrm{Gd^{3+}}$ ion, that is, between 0.95 μ_B and 1.8 μ_B.

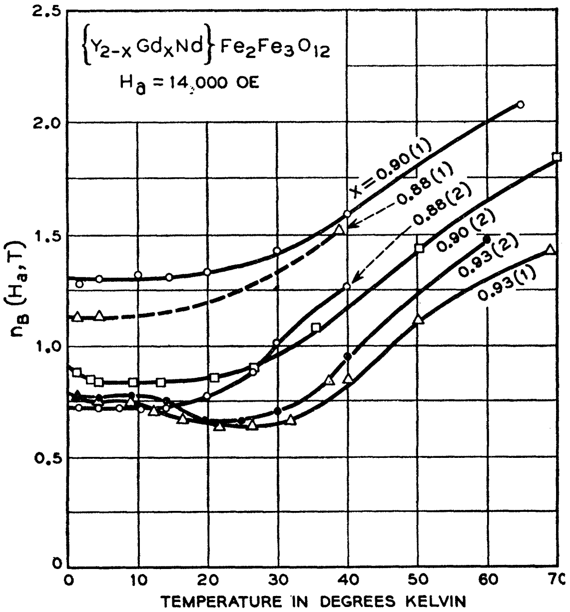

FIG. 7. n_B vs T for system $\{\mathrm{Y_{2-x}Gd_xNd}\}\mathrm{Fe_2Fe_3O_{12}}$.

Since the Nd-substituted garnets could not be saturated with the maximum field, 14 000 oe, of the electromagnet associated with the pendulum magnetometer, we could not obtain the $n_B(H=0)$ vs T curve for the Nd sublattice as in the case of Gd.[17,18] However, it should be possible to obtain a better value than $(1.4\pm0.5)\mu_B$ for the 0°K moment of the Nd ion. One way to do this is to use the compensation points of the $\{\mathrm{Gd_{3-x}Nd_x}\}\mathrm{Fe_2Fe_3O_{12}}$ and make a long extrapolation of these points vs x. The value of x at 0°K would give a measure of the Nd moment. However, it should be kept in mind that the behavior of compensation point vs composition might not be linear over the whole range ≥ 0.[18] Nevertheless the linear extrapolation (Fig. 8) gives a value of 2.0 for x at $\theta_c=0$°K. That is, this extrapolation predicts that if it were possible to prepare the garnet $\{\mathrm{GdNd_2}\}\mathrm{Fe_2Fe_3O_{12}}$ it would have a compensation point at 0°K. Again, assuming 7 μ_B for Gd and 5 μ_B for the net Fe sublattice moment, the Nd contribution, would be 1.0 μ_B. However, if the point for

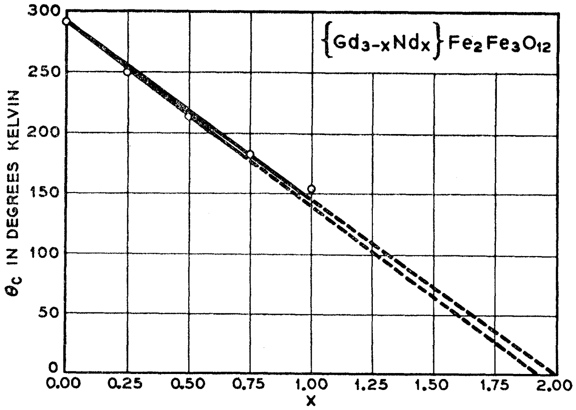

FIG. 8. Compensation point vs x in $\{\mathrm{Gd_{3-x}Nd_x}\}\mathrm{Fe_2Fe_3O_{12}}$. The lower line ignores the point for $x=1.00$.

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[15] S. Geller, J. Appl. Phys. **31**, 30S (1960).

[16] J. F. Dillon, Jr., and J. W. Nielsen, Phys. Rev. **120**, 105 (1960).

[17] G. Villers, J. Loriers and C. Claudel, Compt. rend. **247**, 710 (1958).

[18] S. Geller, J. Phys. Chem. Solids **16**, 21 (1960).

$\{Gd_2Nd\}$ is assumed to be somewhat erratic, the extrapolation yields $x=1.90$ which in turn leads to a moment of 1.4 μ_B for Nd. Thus since there is some doubt associated with this extrapolation, it does not lead to a much better result than that obtained from the average of the apparent moments deduced from the

$$\{Gd_{3-x}Nd_x\}Fe_2Fe_3O_{12}$$

and $\{Y_{3-x}Nd_x\}Fe_2Fe_3O_{12}$ systems.

The ideal system to study for our purposes appeared to be $\{Y_{2-x}Gd_xNd\}Fe_2Fe_3O_{12}$. Assuming the Nd^{3+} ion to have a 0°K effective moment of 1.5 μ_B, the garnet having a 0°K compensation point is

$$\{Y_{1.07}Gd_{0.93}Nd\}Fe_2Fe_2O_{12}.$$

This actually gave a compensation point at 26°K. The composition $\{Y_{1.10}Gd_{0.90}Nd\}Fe_2Fe_3O_{12}$ gives Nd an effective moment of 1.3 μ_B; this garnet however gave a compensation point of 10°K. An extrapolation indicated an effective moment of 1.2 μ_B for Nd and the composition $\{Y_{1.12}Gd_{0.88}Nd\}Fe_2Fe_3O_{12}$ would then have a 0°K compensation point, which was found to be the case.

Our conclusion that extrapolation based on measurements made at fields $\leq 14\,000$ oe was not giving correct moments for compounds, appeared to evoke some skepticism. Through arrangement with Bozorth we were able to make some measurements at higher fields on the Bitter-type magnet.

In Fig. 9, we plot moment vs applied field for $\{Gd_2Nd\}Fe_2Fe_3O_{12}$ and $\{Y_2Nd\}Fe_2Fe_3O_{12}$. The former appears to be saturated at 60, the latter at 70 koe, the moments being 7.7 μ_B and 6.2 μ_B, respectively. These in turn lead to Nd^{3+} ion contributions of 1.3 μ_B and 1.2 μ_B, respectively (assuming that 4.2°K is near enough to 0°K to assume that the Gd^{3+} ion contributes 7.0 μ_B and the resultant Fe^{3+} ion sublattice contribution is 5.0 μ_B). These values are in good agreement with that obtained from the compensation point study of the $\{Y_{2-x}Gd_xNd\}Fe_2Fe_3O_{12}$ system.

Compensation Points

A well-prepared polycrystalline specimen of GdIG appears to have a true ($n_B \equiv 0$ at θ_c) compensation point. However, polycrystalline mixed rare-earth iron garnet specimens do not appear to have compensation points at which $n_B \equiv 0$. Although it appears possible in some cases to obtain a θ_c with $n_B(0,T)$ very close to zero there appears to be some residual spontaneous magnetization where the compensation points should be.

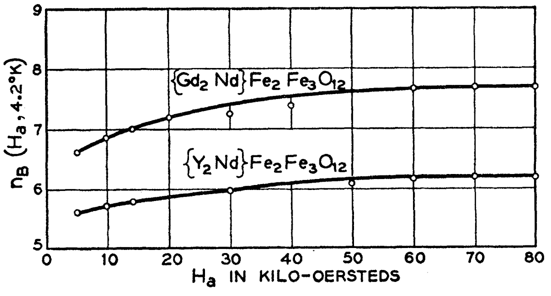

FIG. 9. n_B vs H_a for $\{Gd_2Nd\}Fe_2Fe_3O_{12}$ and $\{Y_2Nd\}Fe_2Fe_3O_{12}$.

It is possible that at least part of this deviation from zero may result from a range of composition[19] in the specimen which may not be easily detected in the x-ray data. In some cases it may happen that too great a range of composition is required to give sizable residual moments and only extremely careful x-ray diffraction analysis could possibly lead to the quantitative determination of the distribution of composition.

On the basis of existing data, it is simplest to discuss the case of a specimen in the $\{Gd_{3-x}Y_x\}Fe_2Fe_3O_{12}$ system. When $x=1$, a good single crystal with random distribution of Gd^{3+} and Y^{3+} ions over the dodecahedral sites should have a compensation point at 173°K.[17,18] The lattice constants of Y and Gd iron garnets are 12.376 and 12.472 A, respectively, and justifiably assuming a linear relation with composition, the garnet $\{Gd_2Y\}[Fe_2](Fe_3)O_{12}$ should have the lattice constant 12.440 A. Now the limits of error we put on our lattice constants, usually 0.003 A, may be conservative. But suppose that 12.440 A is absolutely correct for this garnet (i.e., with $x=1.00$), and that there were some garnet present in the polycrystalline specimen with lattice constant 12.437 A. This would then have the formula $\{Gd_{1.91}Y_{1.09}\}Fe_2Fe_3O_{12}$. At 173°K, this garnet has a calculated spontaneous magnetization[18] ($H=0$) of 0.2 μ_B per formula unit. The garnet with lattice constant 12.443 A would be $\{Gd_{2.09}Y_{0.91}\}Fe_2Fe_3O_{12}$ also with 0.2 μ_B per formula unit. These crystallites would contribute to the residual moment. However, if we assume a Gaussian distribution of composition, i.e., following the function $1/\sigma(2\pi)^{\frac{1}{2}}\exp(-x^2/2\sigma^2)$, and no greater difference in composition than that given by the ± 0.003 A limits, the *maximum* possible residual moment will be less than 0.2 μ_B for this case; in fact, if we assume that 0.2 μ_B is 3σ, the average or residual moment should be 0.03 μ_B. Thus if the only cause of residual moment at the nominal compensation point of a polycrystalline specimen in the $\{Gd_{3-x}Y_x\}Fe_2Fe_3O_{12}$ system is a Gaussian-type range of composition, the residual moments should be very low in this system for well sintered specimens that give sharp x-ray diffraction patterns.

Now it is also possible that the distribution in composition may be skewed. Such a situation would lead not only to a residual moment but also to a shift in the compensation point. In recent work by Anderson *et al.*[20] on the $\{Gd_{3-x}Y_x\}Fe_2Fe_3O_{12}$ system lattice

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[19] We are informed that J. F. Dillon, Jr., also has had this idea for some time. Furthermore, he points out and we believe, correctly, that because any mixed-ion garnet will be strained to some extent, it is possible that for some particles the strain will cause a shift in compensation point. Thus if the nominal compensation point is in the proper place for a certain solid solution, the polycrystalline specimen will have some residual moment as a result of this strain.

[20] E. E. Anderson, J. R. Cunningham, and G. E. McDuffie, Phys. Rev. **116**, 624 (1959).

constants and nominal compensation points are shown. Large *apparent* residual moments, greater than 1 μ_B, at the compensation points are indicated. At least part of these may be attributed to a paramagnetic contribution from Gd. But we note that their lattice constant for GdIG is 12.463, 0.01 A smaller than the well authenticated one reported here. This indicates the presence of a smaller ion impurity or perhaps incorrect stoichiometry. Nevertheless the compensation point appears to be in the correct place. However, the nominal compensation point of their $\{Gd_2Y\}Fe_2Fe_3O_{12}$ appears to be about 25°K too high,[17,18] although that of their $\{Gd_{1.5}Y_{1.5}\}Fe_2Fe_3O_{12}$ also appears to be at the correct value. It is possible that the nature of the specimen compositions would be important in explaining some of these results.

If the data reported here are examined it is found that under the applied field of 14 000 oe the largest *apparent* residual moment is 0.5 μ_B for any of the specimens in the $\{Gd_{3-x}Nd_x\}Fe_2Fe_3O_{12}$ system. In all these cases at least part of these are due to the paramagnetic contributions of the Gd^{3+} and Nd^{3+} ions. In the case of $\{Gd_2Nd\}Fe_2Fe_3O_{12}$, at least 0.2 μ_B may be subtracted for this reason. Again a normal distribution of composition in the crystallites would not seem to account for the remaining moment, but a skewed one favoring more particles with less Nd is indicated not only because this would give a higher residual moment, but also in this case the compensation point is almost 10°K too high according to the plot of θ_c vs composition (Fig. 8).

In the experiments with the $\{Y_{2-x}Gd_xNd\}Fe_2Fe_3O_{12}$ system, there was further indication that at least part of the residual moment at the compensation point could be caused by inhomogeneity in composition. In the case of $\{Y_{1.07}Gd_{0.93}Nd\}Fe_2Fe_3O_{12}$, initially a nominal compensation point of 26°K was obtained. At this point the residual ferromagnetic moment was approximately 0.4 μ_B. The 0°K saturation magnetization extrapolated to $H_a=0$ appeared to be approximately 0.6 μ_B. If the net moment contributed by the Nd^{3+} ion is 1.2 μ_B, the moment of

$$\{Y_{1.07}Gd_{0.93}Nd\}Fe_2Fe_3O_{12}$$

at 0°K should be 0.3 μ_B; thus the moment at 0°K is approximately 0.3 μ_B too high.

Because we wished to obtain a compound containing Nd^{3+} with an exactly 0°K compensation point, we next made $\{Y_{1.10}Gd_{0.90}Nd\}Fe_2Fe_3O_{12}$. We expected, at the least, that the moment at 0°K of this material would be lower than that for $x=0.93$. However, this turned out not to be the case. The 0°K spontaneous moment extrapolated to $H_a=0$, 1.2 μ_B, was apparently twice that of the $x=0.93$ specimen. The specimen was therefore reground and refired (see Table IV). Magnetic measurement of this specimen gave $\mu_B(0,0)=0.7$ μ_B, or about 60% of the first value. With a contribution of 1.2 μ_B from the Nd^{3+} ion, the spontaneous moment of this specimen at 0°K should be 0.1 μ_B. Thus there appears to be a discrepancy of 0.6 μ_B for this specimen. The specimen with $x=0.88$, presumably having a 0°K compensation point first had a residual moment of 0.85 μ_B, but after refiring, this was reduced to 0.55 μ_B. Regrinding and refiring of the specimen with $x=0.93$ did not change the residual moment significantly.

We note (Table IV) that there is no significant difference in the lattice constants of the three specimens tested in this system. Thus the existence of a composition range in these specimens would not be easily detectable by the x-ray powder diffraction technique.

It is difficult to see how the discrepancies could be so large if they arise from composition range and/or strain. It is perhaps possible that even after the several firings, homogeneity was not attained and strain was not reduced to a minimum. It is also difficult to see any other cause for an extra spontaneous moment. Any distortion of spin arrangement as for example as described by Geschwind and Walker[21] or resulting from particles constrained to lie skew to the applied field would very likely give a contribution linear with H_a and would appear as a paramagnetic contribution.

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[21] S. Geschwind and L. R. Walker, J. Appl. Phys. **30**, 163S (1959).