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The Absolute Saturation Magnetization and Remanence of Substituted Yttrium Iron Garnets-$5Fe_2O_3xLa_2O_3(3-x)Y_2O_3$ and $5Fe_2O_3xNd_2O_3(3-x)Y_2O$

WARREN E. HENRY*

U.S. Naval Research Laboratory, Washington D.C., U.S.A.

A low temperature investigation, in magnetic fields up to 106,000 gauss and in zero fields has been carried out on yttrium iron garnets in which substitutions for up to 66 percent of the yttrium were made by neodymium and up to 16 percent by lanthanum. The concentration affects the saturation magnetization and the remanence. The saturation magnetization is of the order of 10 Bohr magnetons per formula for the lanthanum substituted garnets but show a slight systematic trend. The remanence is small. For the neodymium substituted garnets, the saturation magnetization increased rapidly with concentration (3.2 Bohr magnetons per mole per formula), reaching 14 Bohr magnetons per formula at $x=1.5$. At higher concentrations there is an apparent reversal. The remanence is a rapid function of concentration and reaches 12.4 Bohr magnetons per formula (90 per cent of the saturation magnetization) at $x=1.5$; there is an apparent reversal in the remanence at the higher concentrations coming down to less than 9 Bohr magnetons per formula at $x=2.0$. The characters of the dependences of magnetization on concentration of substituted ions raise the question as to the nature of distribution of ions in the octahedral, tetrahedral and dodecahedral sites. A sample displacement method was used and calibration was with nickel.

The discovery by Bertaut of the ferromagnetic garnets brought to light a magnetic system in which magnetic ions occupy three types of sites in contrast to the ferrites, discovered by Professor Takei in which there are two sites for magnetic ions: tetrahedral and octahedral. In the ferrites, as shown by Néel, the net saturation is the result of opposing magnetic polarizations. An insight into the preferential distribution of magnetic ions in the spinel lattice can be had from the saturation magnetization of γ-Fe_2O_3 in which preference is shown for the octahedral sites.

In the garnet case, a dodecahedral site is added. A study of the site preferences by ions in garnets is of interest. This investigation is an attempt at understanding these preferences. It is possible to get insight from a knowledge of the general lattice configuration[1] of the magnetic garnet, the general magnetic structure,[2] including defects, the saturation magnetization of the unsubstituted yttrium iron garnet[3] and through measurements of the absolute saturation magnetization of substituted yttrium iron garnets in which the ion sizes are different for the displaced and displacing ions—here the stoichiometric replacements are lanthanum and neodymium respectively for yttrium.

The samples consist of substituted yttrium iron garnets $5Fe_2O_3xLa_2O_3(3-x)Y_2O_3$ and $5Fe_2O_3xNd_2O_3(3-x)Y_2O_3$ in which x has the values 0.05, 0.15, 0.25 and 0.50 for La_2O_3 and 0.50, 1.00, 1.50 and 2.00 for Nd_2O_3. These substituted garnets were prepared with a purity of 99.9 percent with respect to the rare earth components by a method previously employed[4] and kindly furnished by M. Gerard Villers and M. J. Loriers, Laboratoire de Bellevue, Centre National de la Recherche Scientifique, Meudon, France.

The magnetic measurements were made by a sample displacement method[5] in which the sample is moved between centers of coils wound in series opposition and in series with a ballistic galvanometer. The deflection of the galvanometer is proportional to the magnetic moment of the sample. The moment measuring system is calibrated with pure iron or nickel as a standard. Liquid helium temperatures were maintained with a metal

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* Now at Lockheed Research Laboratory, Palo Alto, Calif.

dewar[6].

Figure 1 shows curves in which magnetization is plotted against magnetic field at a temperature (4.2°K) at which the high field magnetization is temperature independent. It is seen that over most of the high field range, the lanthanum substituted garnets show a field independence (saturation) at 4.2°K. On the other hand, the neodymium substituted garnets show less ease in saturating. At the highest neodymium concentration, saturation is not quite reached at 100,000 gauss. At $x=1.5$ there is a constant small slope of 4×10^{-6} Bohr magneton per formula per gauss in the high field range.

Figure 2 shows a plot of magnetization vs. concentration for a temperature of 4.2°K and for 100,000 gauss (representing saturation for most of the samples) and for zero magnetic field.

It is seen that the extrapolated values of the magnetization per formula at $x=0$ accords well with the experimental values previously obtained[3]. For the lanthanum substituted garnets there is initially a slope in the curve of saturation magnetization vs. concentration per molecule of La_2O_3 added. Between $x=0.25$ and $x=0.50$, there is a change in the sign of the slope. Since lanthanum has no *f* electrons, the addition of lanthanum cannot change the total number of magnetic atoms in the lattice because lanthanum is replacing yttrium, another non-magnetic atom. It can affect the net magnetization by changing the distribution of the magnetic ions. Lanthanum could have the effect of shifting Fe^{+++} away from octahedral sites thus reducing the opposition to tetrahedral Fe^{+++}. After a maximum is reached in the net magnetization, the result of addition of more lanthanum ions might force Fe^{+++} out of tetrahedral sites, thus tending to reduce the net magnetization. It is seen that for the lanthanum substituted garnets the remanence has the small value of 0.2 Bohr magneton per formula at $x=0.05$. There is only a slight change in zero field magnetization with lanthanum concentration, initially. However, between $x=0.25$ and $x=0.50$, there is a suggested abrupt change in the slope of the remanence curve.

The neodymium substituted garnets exhibit a spectacular increase in saturation magne-

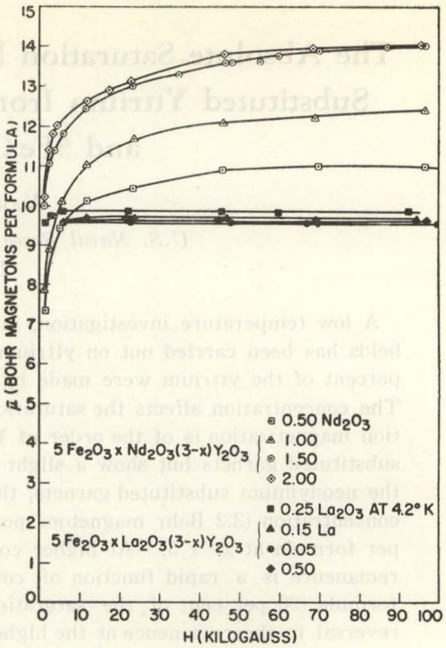

Fig. 1. Plots of magnetization vs. magnetic field at 4.2°K of substituted yttrium iron garnets.

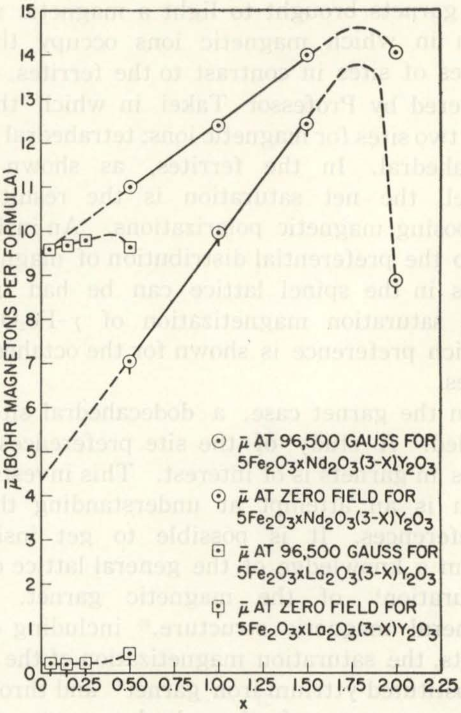

Fig. 2. Plots of saturation magnetization and remanence vs. concentration of substituted yttrium iron garnets.

tization with increase in neodymium concentration. A 50 per cent increase in the net saturation magnetization is seen for $x=1.50$ and for $x=2.00$. A peak probably comes between $x=1.50$ and $x=2.00$. In the case of neodymium substitution for yttrium there is a magnetic moment to be added to or subtracted from the net magnetization attributed to balance between Fe^{+++} ions on tetrahedral and octahedral sites.

Neodymium is reluctant to go into dodecahedral sites and may prefer another site, if possible, octahedral, then tetrahedral sites as opposed to dodecahedral sites, although compounds of direct substitution of large ions in the dodecahedral site is known[7]. The net magnetization measured is given by

$$\bar{\mu}_F=\mu_B(9.5+3.2x) \qquad (1)$$

up to $x=1.50$. This would be the case if the neodymium ion should do the magnetic equivalent of the following: select octahedral sites and line up antiparallel to the iron ions in the octahedral site, and if the moment of neodymium is taken as 1.6 Bohr magnetons per atom of neodymium as was experimentally determined in neodymium oxide[8] and in neodymium metal. Beyond $x=1.5$ the tetrahedral sites, on the above picture or its equivalent, may then be preferred leading to a reduction of the saturation magnetization.

Alternate explanations are also possible, perhaps likely, in which the neodymium and lanthanum would be "well behaved" and enter the dodecahedral sites in which case the initial increase in the magnetization with increasing concentration must be explained in a non-traditional way. In the case of the lanthanum substitution it is difficult but can be explained by ignoring the small increase in the magnetization with concentration of lanthanum. In the neodymium substitutions case, there would be such an increase due to an overpowering of the neodymium ions by the molecular field[9] arising from a garnet sublattice. A positive slope in the magnetization curve can also be qualitatively explained by an anomalous orbital effect[10] in which the *j-j* coupling and non-diagonal matrix elements connecting lower to upper states play a role.

It is seen that the remanence is high at 4.2°K and a strong function of the neodymium concentration, reaching 12.4 Bohr magnetons per formula (about 90 percent of the saturation magnetization) at $x=1.50$ in the neodymium substituted garnet. At $x=2.0$, the remanence is lowered, indicating a corresponding lowering of the anisotropy. There is also a temperature dependence of the remanence. For example, at 77.4°K the saturation magnetization for neodymium substituted garnet ($x=1.50$) is 13.1 Bohr magnetons per formula, but the remanence is only 0.88 Bohr magneton per formula. For $x=2.00$, the saturation magnetization is 13.0 Bohr magnetons per formula and the remanence is 3.05 Bohr magnetons per formula at 77.4°K.

The investigation of the lanthanum and neodymium substituted yttrium iron garnets has demonstrated initial increases in saturation magnetization with increase in concentration of rare earth ions, thus inducing speculation as to the effect of ion size and nature on the magnetic structure of the three site garnets and the interaction of the rare earth ions with exchange and crystalline electric fields. Also, the results point up the temperature dependence of the magnetic anisotropy.

We wish to thank Monsieur Gerard Villers and Monsieur Jean Loriers for supplying the samples of the lanthanum and neodymium substituted yttrium iron garnets used in this investigation.

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DISCUSSION

J. H. Van Vleck: It would be very interesting and informative if Dr. Henry could make some of his saturation measurements on SmIG. This material appears to be rather unusual in having a large exchange splitting of the ground Kramers doublet, but existing experiments have not revealed any corresponding magnetic moment. It would be desirable to see how closely the spin and orbital contributions to the magnetic moment really cancel each other.

W. E. Henry: I shall be happy to make saturation magnetization measurements on the samarium iron garnets.

L. R. Bickford: It seems surprising that the neodymium ion would prefer the octahedral to the dodecahedral sites.

W. E. Henry: It would be surprising to have the neodymium ions go into the non-dodecahedral sites except that the non-existence of cerium, lanthanum, praseodymium and neodymium garnets indicates difficulty in entering the dodecahedral sites. Also, the addition of neodymium increases the moment, while for the rare earth garnet substitution of other ions which do for sure replace yttrium in the dodecahedral sites, there is an initial decrease in the moment with increase in concentration.

E. W. Gorter: (1) I think it is extremely unlikely that La^{3+} and Nd^{3+} which are larger than the ions Sm^{3+} to Lu^{3+}, which occupy dodecahedral C sites, will occupy the smaller octahedral A sites, this would also mean that Fe^{3+} ions should occupy C sites; so far such small ions have not been found to occupy C sites.

(2) I remember well, Bertaut has made (La, Y) and (Nd, Y) garnets and found La and Nd enter C sites.

(3) Do you really need your assumption (Nd on A sites) to explain your results?

W. E. Henry: (1) Since the lanthanum and neodymium garnets do not exist, one assumes that it is difficult to replace yttrium by these ions. I am not sure where the iron ions would go, unless there is a defect type transference of the iron ions.

(2) You will notice that I referred to the work of Bertaut in preprint. This was cited as an exception and even here, the substitution was not complete. The magnetic properties also seem to be different from those in the present investigation.

(3) My explanation is not given as the only explanation not even the most likely, but only as a possible explanation in view of the positive slope in the magnetization vs. concentration curve. For example, the small *g*-value treatment given by Prof. Van Vleck in a preceding paper could explain positive slope for neodymium substitutions even with entrance into the dodecahedral site.