# NEW MAGNETIC MATERIALS—GARNET FERRITES

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WITHIN the last year and a half or two years, great interest has developed in the study of a new class of ferrites that have the so-called garnet structure. This interest is caused by the fact that the garnet ferrites display properties favorable for their use in microwave applications. Their main advantage, as compared with ferrites with spinel structure, is an extremely narrow ferromagnetic resonance-absorption line. Crystals of some garnet ferrites give an absorption line-width of a few oersteds,[1,2] whereas crystals of spinel ferrites have a width of several tens of oersteds.

Apart from the practical aspect, the study of garnet ferrites is of great interest for the theory of magnetism and crystal chemistry, because their structure is quite different from the familiar structure of the spinel ferrites. Knowledge of their ferromagnetic properties gives additional information about the nature of spontaneous magnetization and its relation to the structure of the material.

The ferromagnetic properties of the garnet ferrites were discovered quite recently, in 1956, by the French scientists Bertaut and Forrat[3] and Pauthenet,[4] and independently a little later, in 1957, by the Americans Geller and Gilleo. Garnet ferrites have the formula

$$3\,Me_2O_3 \cdot 5\,Fe_2O_3 \text{ (or } Me_3Fe_2Fe_3O_{12}),$$
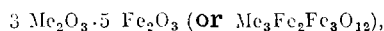
where Me is one of the rare-earth elements or yttrium.

The preparation of such a type of compound is carried out in accordance with usual ceramic practice, from iron oxides and oxides of rare-earth elements. Crystals are grown from the melt by slow cooling from 1325°C to about 900°C, with lead oxide as solvent.[6] The crystal lattice of a garnet ferrite is cubic; it contains a very large number of ions located at different crystallographic sites. Because of the complexity of the distribution of anions and cations within it, it is almost impossible to depict. The $Fe^{3+}$ and $Me^{3+}$ cations occupy spaces between the oxygen ions. These can be fourfold, the 24 d sites (tetrahedral spaces); sixfold, the 16 a sites (octahedral spaces); or eightfold, the 24 c sites. The $Fe^{3+}$ ions are distributed over the d and a sites, the $Me^{3+}$ ions over the c sites.

To explain the magnetic properties of the garnet ferrites, Néel[7] proposed to regard the lattice of these substances as composed of three sublattices (in contrast to the spinels, in which, of course, two sublattices are considered, with more octahedral than tetrahedral sites). The $Fe^{3+}$ ions are distributed over two of these (the a and the d), with more tetrahedral than octahedral sites. The $Me^{3+}$ ions are distributed over the third sublattice (the c). According to Néel, there is a strong negative interaction between the first two sublattices, a and d; as a result, there occurs a resultant spontaneous magnetization J (on account of the excess of "tetrahedral" magnetic "moments"). The $Me^{3+}$ ions are magnetized by the weak field of sublattices d and a, and in consequence the moments of the c sites are directed opposite to the magnetization of sublattice d. The distribution of sublattice magnetizations can be pictured schematically as follows:

$$\underset{Me^{3+}}{\overset{c}{\longrightarrow}}\ \underset{Fe^{3+}}{\overset{d}{\longleftarrow}}\ \underset{Fe^{3+}}{\overset{a}{\longrightarrow}}.$$
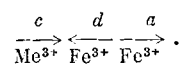
This scheme provides a possibility of calculating the magnetic moments (per mole) of the garnet ferrites at 0°K. Thus for the case of gadolinium garnet, $3Gd_2O_3 \cdot 5Fe_2O_3$, we have (noticing that $M_c = 7\mu_B$ and $M_d = M_a = 5\mu_B$):

$$6M_c - (6M_d - 4M_a) = 6 \times 7\mu_B - (6 \times 5\mu_B - 4 \times 5\mu_B) = 32\mu_B.$$

Experiment gives $30\mu_B$. In the case of yttrium garnet, since Y is nonmagnetic, we have $6M_d - 4M_a = 10\mu_B$, which also agrees with experiment. Thus analysis of the magnitudes of the magnetic moments in garnet ferrites corroborates Néel's "three-sublattice" hypothesis. Recently this hypothesis has been corroborated by neutron diffraction experiments.[8]

Thus in the case of the garnet ferrites we encounter a new form of uncompensated antiferromagnetism, caused by the nonequivalence of three magnetic sublattices. At the present time the following data are known on the magnetic properties of garnet ferrites. The temperature dependence of the spontaneous magnetization has been studied in the range 2.2 to 750°K, by the method of removal from the field, for the following garnet ferrites:

$3Me_2O_3 \cdot 5Fe_2O_3$, where $Me = Gd$, Tb, Dy, Ho, Er, Tu, Yb, Lu, Sm, Eu, or Y. For the majority of the ferrites, the dependence of magnetization on field satisfies the following relation:

$$\sigma_H = \sigma_s + \chi H,$$

where $\sigma_S$ is the spontaneous magnetization, and $\chi$ is the susceptibility in strong fields and is independent of the field. The spontaneous magnetization $\sigma_S$ was found by extrapolation to zero field of the straight part of the curve in strong fields.
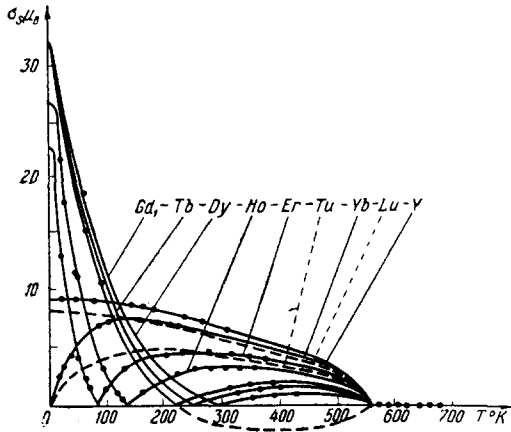


FIG. 1. Temperature dependence of the spontaneous magnetization $\sigma_s$ (in $\mu_B$ per mol) for garnet ferrites.

In Figs. 1 and 2 are shown curves of the temperature dependence of the spontaneous·magnetization (in $\mu_B$ per mol) for all the garnet ferrites investigated. In these figures there are two characteristic peculiarities that should be noted:

1. In the majority of the garnet ferrites (with the exception of the ferrites of Y, Lu, Sm, and Eu), there are observed compensation points, at which the magnetizations of the sublattices compensate each other.

2. It is a surprising and interesting fact that all these substances have about the same Curie point (in contrast to this, the molar magnetic moments at 0°K vary over a relatively wide range). The coincidence of the Curie points must be attributed to
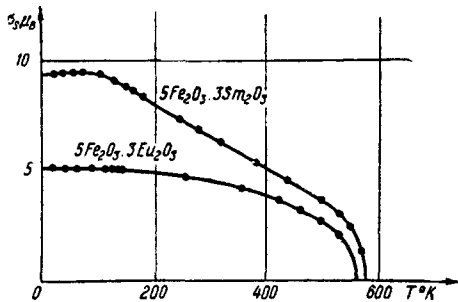


FIG. 2. Temperature dependence of the spontaneous magnetization $\sigma_s$ (in $\mu_B$ per mol) for garnet ferrites of samarium and europium.
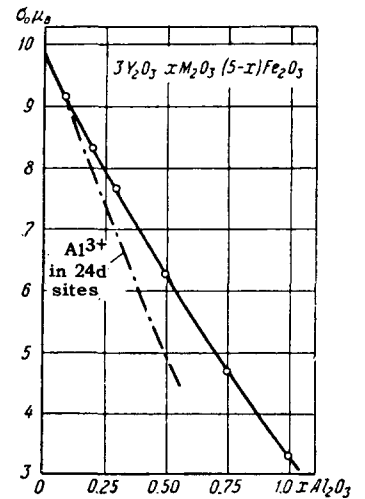


FIG. 3. Dependence of the spontaneous magnetization $\sigma_0$ (in $\mu_B$ per mol) on content of substitutional $Al^{3+}$ ions.

the fact that the $Me^{3+}$ ions take little part in the ferromagnetism; the interaction of the c lattice with the d and a is small, therefore here the magnitude of the Curie point is determined essentially by the strength of the interaction between the iron ions (the number of which remains approximately the same in all the garnet ferrites).

In the foreign literature there have recently[9-11] appeared numerous papers on the investigation of
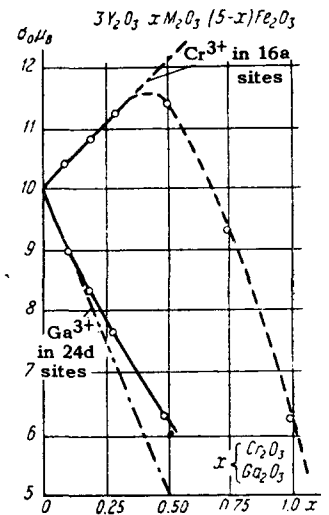


FIG. 4. Dependence of the spontaneous magnetization $\sigma_0$ (in $\mu_B$ per mol) on content of substitutional $Cr^{3+}$ and $Ga^{3+}$ ions.

the replacement of iron ions by other ions in the stoichiometric garnet ferrite $3Me_2O_3 \cdot 5Fe_2O_3$.

Substitutions of this type are directed at two goals: (1) investigation of garnet ferrites with new magnetic properties; (2) elucidation of the role of the sublattices in ferromagnetism; this can be accomplished by changing the number of magnetic ions in the lattices by introducing nonmagnetic or magnetic ions into them.

It should be noted also that experiments of this type are of interest for crystal chemistry. If ions with a different electron configuration and atomic radius are introduced into the sublattices, these

Magnetic moment $n\mu_B$ and
Curie temperature $\theta$ for
$3Y_2O_3 \cdot xMe_2O_3 (5 - x) Fe_2O_3$

| $x\,Me_2O_3$ | $n\mu_B$ observed | $\theta,\ °K$ observed |
|---|---|---|
| 0 | 9.92 | 545 |
| 0.25 $Ga_2O_3$ | 7.95 | 519 |
| 0.75 $Ga_2O_3$ | 4.35 | 460 |
| 0.34 $Al_2O_3$ | 7.00 | 497 |
| 1.00 $Al_2O_3$ | 5.25 | 415 |
| 0.25 $Sc_2O_3$ | 11.97 | 500 |
| 0.75 $Sc_2O_3$ | 14.4 | 365 |
| 0.50 $In_2O_3$ | 13.8 | 444 |
| 0.25 $Cr_2O_3$ | 10.95 | 515 |

ions will prefer fourfold, sixfold, or eightfold sites, and consequently it is possible thus to change the distribution of atoms in the garnet structure and to study their role in magnetization. Most of the experiments have been done by replacement of the iron in yttrium garnet ferrite by the ions: $Al^{3+}$, $Ga^{3+}$, $Cr^{3+}$, $Sc^{3+}$, $In^{3+}$. Introduction of $Al^{3+}$ and $Ga^{3+}$ ions decreases the magnetic moments of the garnet ferrites (cf. Figs. 3 and 4 and the table). This must be explained by supposing that $Al^{3+}$ and $Ga^{3+}$ are distributed on tetragonal sites (in sublattice d), in consequence of which the resultant magnetic moment decreases. $Al^{3+}$ and $Ga^{3+}$ have smaller ionic radii than $Fe^{3+}$, therefore they have an affinity for the tetrahedral positions. $Sc^{3+}$ and $In^{3+}$, having larger radii than $Fe^{3+}$, preferentially occupy octahedral positions, therefore the magnetic moment of the ferrites increases (cf. table). The $Cr^{3+}$ ion, though also smaller than the $Fe^{3+}$, nevertheless occupies octahedral positions, perhaps by virtue of its peculiar electronic configuration. This leads, in a certain $Cr^{3+}$ concentration range, to an increase of magnetic moment.

Thus it follows from the experiments on substitution that the moment of a garnet ferrite can be increased by replacing an iron ion in sublattice a by any nonmagnetic ion, and can be decreased by replacing an iron ion in sublattice d by a nonmagnetic ion.

It should be noted that in all cases of replacement of an iron ion by another ion, the magnitude of the Curie temperature of the garnet ferrite decreases. This is explained as a consequence of the fact that the number of magnetic $Fe^{3+}$-$O^{2-}$-$Fe^{3+}$ interactions on a magnetic ion in the garnet ferrite decreases. Summarizing everything that has been said about the magnetic properties of garnet ferrites, we must point out that we still have only scanty data on the magnetic properties of these interesting materials. Up to now nothing is known about hysteretic, magnetostrictive, electrical, and other properties of the garnet ferrites. Meanwhile these data are necessary for an understanding of the nature of their spontaneous magnetization.

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