

Magnetic and Crystallographic Properties of Substituted Yttrium-Iron Garnet, $3\text{Y}_2\text{O}_3 \cdot x\text{M}_2\text{O}_3 \cdot (5-x)\text{Fe}_2\text{O}_3^\dagger$

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A solid solution of yttrium-iron garnet with yttrium-gallium or yttrium-aluminum garnet is formed over the entire range of composition; the lattice constant variation is nearly linear. The trivalent ions, Sc^{3+} , In^{3+} , and Cr^{3+} , may be substituted for Fe^{3+} to a limited extent. Substitution proceeds on a steric basis for nonmagnetic ions: those smaller than Fe^{3+} , namely Al^{3+} and Ga^{3+} , preferentially occupy the smaller, tetrahedrally coordinated sites, 24(d); larger ions, In^{3+} and Sc^{3+} , preferentially occupy larger, octahedrally coordinated sites, 16(a). The Cr^{3+} ion, though smaller than Fe^{3+} , preferentially occupies the octahedral site, presumably because of its electronic configuration. The magnetic moment initially rises with octahedral substitution of nonmagnetic ions and falls with tetrahedral substitution because the moment corresponds to the difference in the moments of the Fe^{3+} ions in the two octahedral sites and the three tetrahedral sites per formula unit, $\text{Y}_3\text{Fe}_2(\text{FeO}_4)_3$. The Curie temperature is decreased by the substitution of nonmagnetic ions for iron on account of the decrease in the number of $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ interactions.

INTRODUCTION

YTTTRIUM-IRON garnet is a prototype of new ferrimagnetic materials which have provoked great interest since their discovery.^{1,2} This interest has arisen in part from the value of single crystals grown by Nielsen³ to ferrimagnetic resonance,⁴ optical absorption and Faraday rotation⁵ (visible domain patterns) and crystallographic studies.⁶ Yttrium-iron garnet has properties which make it particularly suitable for magnetic studies, namely: very nearly cubic symmetry,⁷ definite composition, and the presence of only trivalent metal ions.

There are eight formula units, $\text{Y}_3\text{Fe}_2(\text{FeO}_4)_3$, in a unit cell of lattice constant $a = 12.376 \pm 0.004 \text{ \AA}$,^{6,8} the x-ray density is 5.17 g cm^{-3} at room temperature.⁶ Of the five iron ions present in a formula unit, three are in 24(d) sites tetrahedrally surrounded by oxygen ions and two are in 16(a) sites octahedrally surrounded by oxygen ions⁶ (Fig. 1). A magnetic moment of $5 \mu_B$ per formula unit results from negative superexchange (antiferromagnetic) interaction between Fe^{3+} ions in these two different sites through the intervening O^{2-} ions; it corresponds to the moment of the one Fe^{3+} ion

present in a tetrahedral site in excess of the number of Fe^{3+} ions in octahedral sites.

Substitution of nonmagnetic ions for iron will change the moment by altering the difference in the number of magnetic ions in tetrahedral and octahedral sites. The magnetic moment could be increased by predominant substitution in octahedral sites and reduced by predominant substitution in tetrahedral sites. In either case the Curie temperature, T_C , will be reduced below that of yttrium-iron garnet because the number of interactions per magnetic ion per formula unit will have been reduced.⁹

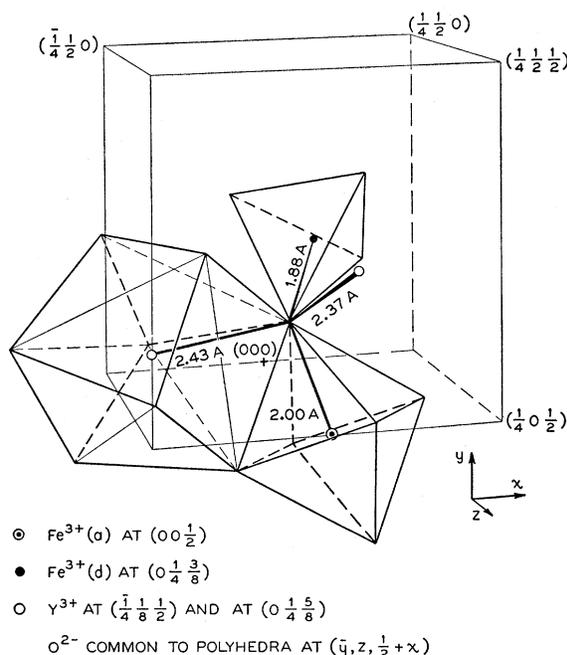


FIG. 1. The oxygen coordination of positive ions in yttrium-iron garnet.

[†]Portions of this paper were presented at the 1957 Washington Meeting of the American Physical Society [M. A. Gilles and S. Geller, *Bull. Am. Phys. Soc. Ser. II*, **2**, 238 (1957)] and at the Conference on Magnetism and Magnetic Materials in Washington, D. C., November, 1957, *J. Appl. Phys.* **29**, 380 (1958).

¹ F. Bertaut and F. Forrat, *Compt. rend.* **242**, 382 (1956).

² S. Geller and M. A. Gilles, *Acta Cryst.* **10**, 239 (1957).

³ J. W. Nielsen, *J. Phys. Chem. Solids* (to be published).

⁴ J. F. Dillon, Jr., *Bull. Am. Phys. Soc. Ser. II*, **2**, 22 (1957); *Phys. Rev.* **105**, 759 (1957).

⁵ J. F. Dillon, Jr., *Bull. Am. Phys. Soc. Ser. II*, **2**, 238 (1957).

⁶ S. Geller and M. A. Gilles, *J. Phys. Chem. Solids* **3**, 30 (1957); International Union of Crystallography, Fourth International Congress, Montreal, July, 1957, abstract 6-27; *Acta Cryst.* **10**, 787 (1957).

⁷ A magnetic material cannot truly be cubic because spontaneous magnetization appears in only one direction in a given domain. However, measurements, such as x-ray diffraction, which are insensitive to spontaneous magnetization, may not reveal deviation from cubic symmetry.

⁸ F. Bertaut and F. Forrat, *Compt. rend.* **244**, 96 (1957).

⁹ M. A. Gilles, *Phys. Rev.* **109**, 777 (1958).

The substitution, if possible, of trivalent transition-metal ions for Fe^{3+} would probably have a similar, though reduced, effect on the magnetic moment provided that they participate in superexchange interaction. A moment of $5 \mu_B$, the moment of Fe^{3+} , is the maximum available from a transition-metal ion when its orbital contribution is quenched by the crystalline field.

It might be expected that in the case of isostructural oxides a complete range of solid solution would exist. Therefore, such cases of substitution for iron in yttrium-iron garnet were considered first. Yttrium-aluminum garnet was first synthesized by Yoder and Keith.¹⁰ Synthesis of yttrium-gallium garnet was accomplished by Keith and Roy¹¹ and single crystals were made in these Laboratories by Remeika.² In addition to these obvious cases, partial substitution for iron by scandium and indium was attempted even though the garnet compounds corresponding to total substitution are not known and could not be made. Substitution for iron by chromium was suggested by its presence in 16(a) in uvarovite, $\text{Ca}_3\text{Cr}_2(\text{SiO}_4)_3$.

From crystallographic and magnetic studies of these substituted yttrium-iron garnets much can be learned about the steric aspects governing substitution, the distribution of the substituted ions over the tetrahedral and octahedral sites, and the geometry and strength of the $\text{Fe}^{3+}-\text{O}^{2-}-\text{Fe}^{3+}$ interactions.

EXPERIMENTAL

Synthesis of Materials

All materials employed in this work, with the exception of yttrium-iron garnet, were in ceramic form. A single crystal of yttrium-iron garnet was grown from PbO flux by Nielsen.³ It was selected on the basis of high perfection as a consequence of which the probability of occluded PbO and epitaxial magneto-plumbite would be minimized.

The substituted yttrium-iron garnet ceramic material was prepared by D. W. Mitchell of these Laboratories. The constituent metals, In and Ga, were dissolved in 8*N* HNO_3 ; Fe in 2*N* HNO_3 ; Al in 8*N* ($5\text{HNO}_3 + \text{HCl}$); the oxides, Y_2O_3 , In_2O_3 , and Sc_2O_3 , were dissolved in 5*N* HNO_3 ; CrO_3 was dissolved in 2*N* HCl and reduced with $\text{H}_2\text{C}_2\text{O}_4$. The hydroxides were coprecipitated with NH_4OH from a stoichiometric mixture of the metal-ion solutions. Impurities in all materials were less than 0.05 weight percent.

The coprecipitated hydroxides were dried at 230°C for 16 hours and then heated to 800 to 850°C over a period of 24 hours. The calcined material was mortared and pressed into pills which were fired by E. F. Dearborn at 1450°C in O_2 for 16 hours when substitution was for one Fe or less. For substitutional replacement

of Fe_2O_3 by highly refractory oxides, such as Al_2O_3 , firing at temperatures which ranged to 1730°C was carried out by W. F. Janssen.

Diffraction Data

X-ray powder photographs were taken with a Straumanis type Norelco camera of 114.59 mm diameter; Cr *K* radiation was used. A *V*-foil filter was arranged along one edge of the film to help in identification of Cr *K* β reflections.

Magnetic Measurements

A Sucksmith-type¹² apparatus was employed in measurements of magnetic moment as a function of field and temperature. Fields (H_a) up to 13 000 oersteds were obtained from a twelve-inch Varian magnet with plane pole faces and a $1\frac{3}{4}$ inch gap; the gradient was produced by current-carrying conductors mounted on the pole faces.¹³ Calibration was carried out with

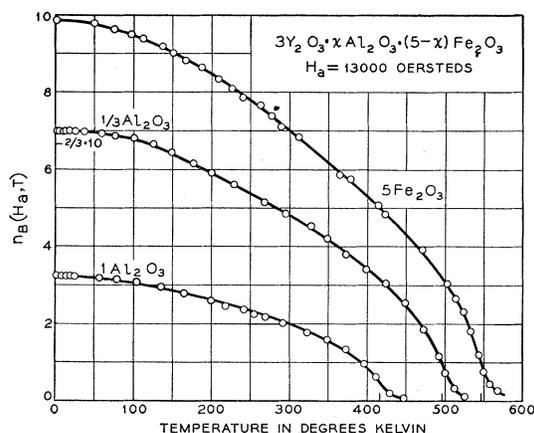
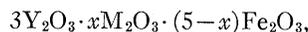


Fig. 2. n_B vs T for aluminum substituted yttrium-iron garnet.

spectroscopically pure Ni spheres (Johnson-Matthey 890). The garnet specimens were spheres ranging in weight from 35 to 150 mg. The atmosphere surrounding the specimens during measurements was He at a pressure of about 3 lb/in.² above atmospheric pressure.

MAGNETIC DATA

The data for n_B , the magnetic moment in Bohr magnetons per general formula unit,



as a function of temperature for all substituted yttrium-iron garnets studied may be most easily interpreted by comparison with the n_B vs T curve for yttrium-iron garnet itself. Of principal interest are the variation of the saturation moment, $n_B(\infty, 0)$, i.e., the moment at

¹⁰ H. S. Yoder and M. L. Keith, *Am. Mineralogist* **36**, 519 (1951).

¹¹ M. L. Keith and R. Roy, *Am. Mineralogist* **39**, 1 (1954).

¹² W. Sucksmith, *Proc. Roy. Soc. (London)* **A170**, 551 (1939).

¹³ Sucksmith, Clark, Oliver, and Thompson, *Revs. Modern Phys.* **25**, 34 (1953).

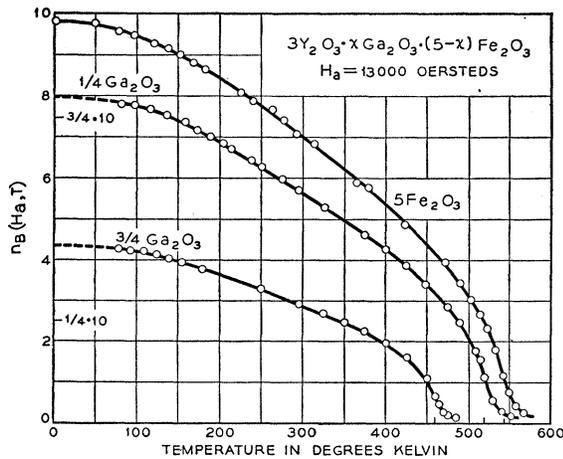


FIG. 3. n_B vs T for gallium substituted yttrium-iron garnet.

infinite field¹⁴ and zero temperature, and the change of the Curie temperature with substitution. In all cases an applied field, H_a , of 13 000 oersteds, was well in excess of the field required for saturation at liquid-nitrogen temperature.

In most cases $n_B(\infty, 0)$ may be determined sufficiently precisely by the extrapolation to absolute zero of measurements carried down to liquid-nitrogen temperature, 77°K. In cases for which this procedure is inadequate the authors have been aided by data which

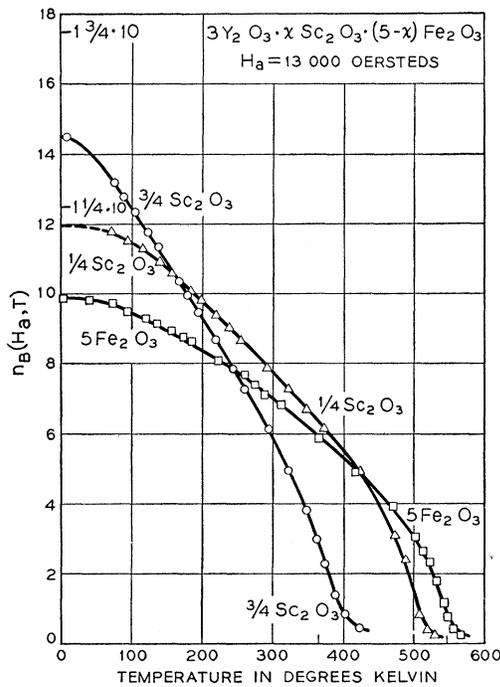


FIG. 4. n_B vs T for scandium substituted yttrium-iron garnet.

¹⁴ That is, a field adequate to achieve a close approach to saturation but not large in comparison with the Weiss molecular field.

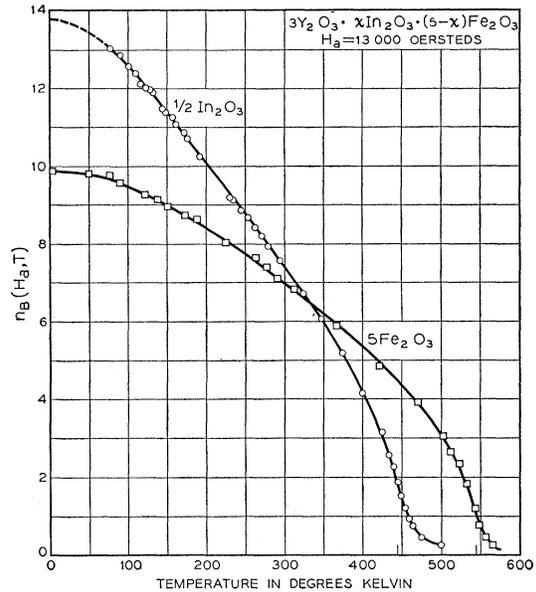


FIG. 5. n_B vs T for indium substituted yttrium-iron garnet.

were provided by Miss D. E. Walsh of these Laboratories for temperatures as low as 1.3°K.

With regard to magnetic moment the effects of substitution of other trivalent metal ions for Fe^{3+} divide into two categories. The substitution of Al^{3+} or Ga^{3+} for Fe^{3+} decreases $n_B(\infty, 0)$ (Figs. 2, 3) and the substitution of Cr^{3+} , Sc^{3+} , and In^{3+} for Fe^{3+} increases $n_B(\infty, 0)$ (Figs. 4-6). In all cases the Curie temperature decreases.

The Curie temperature has, in every case, been associated with the point of inflection of the n_B vs T curve after the method of Curie.¹⁵ In order to establish the suitability of this method to our purpose the Curie

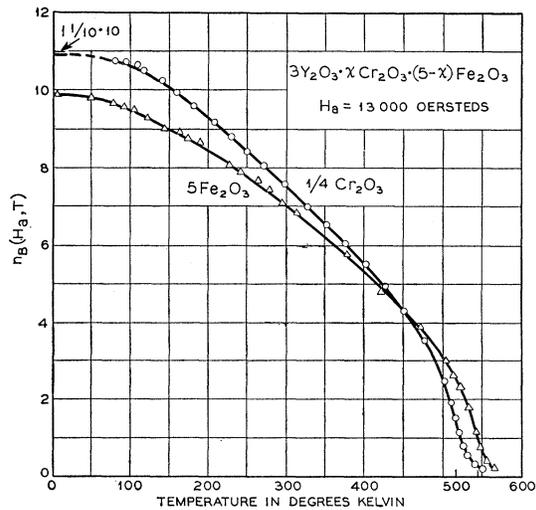


FIG. 6. n_B vs T for chromium substituted yttrium-iron garnet.

¹⁵ P. Curie, Ann. phys. 5, 289 (1895).

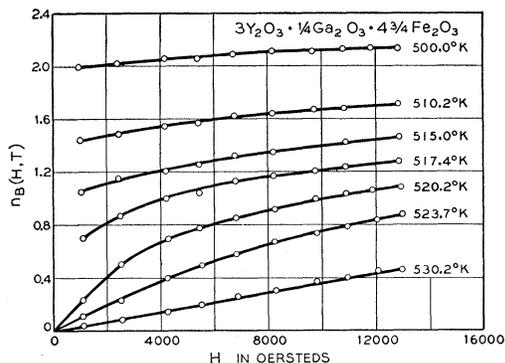


FIG. 7. n_B vs H at constant temperature for $3Y_2O_3 \cdot \frac{1}{4}Ga_2O_3 \cdot 4\frac{3}{4}Fe_2O_3$.

temperature for $3Y_2O_3 \cdot \frac{1}{4}Ga_2O_3 \cdot 4\frac{3}{4}Fe_2O_3$ was also determined by the method of Weiss and Forrer¹⁶ so that the error associated with the point of inflection method could be estimated. In the method of Weiss and Forrer the curve of $[n_B(0, T)]^2$ vs T is extrapolated to $n_B(0, T) = 0$, at which point $T = T_C$; $n_B(0, T)$ is the magnetic moment at $H = 0$ and temperature T . For the determination of $n_B(0, T)$, the magnetic moment was measured as a function of the internal field¹⁷ H at constant T (Fig. 7). From these curves a set of curves of n_B vs T at constant H was constructed. Then curves of H vs T at constant n_B were obtained from which $n_B(0, T)$ could be found by extrapolation. From the

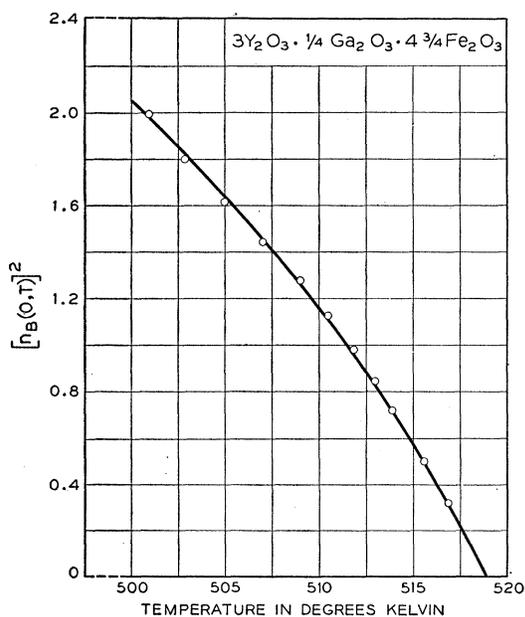


FIG. 8. $[n_B(0, T)]^2$ vs T at $H = 0$ for $3Y_2O_3 \cdot \frac{1}{4}Ga_2O_3 \cdot 4\frac{3}{4}Fe_2O_3$.

¹⁶ P. Weiss and R. Forrer, *Compt. rend.* **178**, 1670 (1924); see discussion by R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, 1951), p. 716.

¹⁷ The internal field, H , has been determined by subtracting from the applied field, H_a , the demagnetizing field of the sphere based on its moment at temperature T .

plot of $[n_B(0, T)]^2$ vs T (Fig. 8), it was determined that $T_C = 519.0 \pm 0.3^\circ K$; the point of inflection method yielded $520 \pm 3^\circ K$ at $H_a = 13,000$ oersteds. Consequently, the values of T_C obtained by the point of inflection method are satisfactory for our present purpose.

CRYSTALLOGRAPHIC DATA

The variation of lattice constant, a , of yttrium-iron garnet with the amount of substitution was observed for the entire range available (Table I). The variation of a with x is nearly linear in all cases (Fig. 9) even though only in the case of Ga or Al substitution is the system a solid solution of two isostructural oxides of different lattice constant. Attempts to form Y-Sc, Y-In, and Y-Cr garnets by solid-solid reaction were unsuccessful.

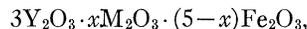
M-ION DISTRIBUTION AND MAGNETIC PROPERTIES

For the purpose of discussion and interpretation of the magnetic and crystallographic data obtained for

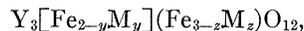
TABLE I. Lattice constants for substituted yttrium-iron garnet, $3Y_2O_3 \cdot xM_2O_3 \cdot (5-x)Fe_2O_3$.

xM_2O_3	a (Å)	xM_2O_3	a (Å)
0	12.376 ± 0.004	$\frac{1}{3}Ga_2O_3$	12.356 ± 0.004
		$\frac{5}{5}Ga_2O_3$	12.273
$\frac{1}{3}Al_2O_3$	12.353	$\frac{1}{3}Sc_2O_3$	12.392
$\frac{2}{3}Al_2O_3$	12.331	$\frac{2}{3}Sc_2O_3$	12.421
$1Al_2O_3$	12.306	$\frac{1}{3}Sc_2O_3$	12.438
$1\frac{1}{3}Al_2O_3$	12.265	$\frac{2}{3}Sc_2O_3$	12.498
$2\frac{1}{3}Al_2O_3$	12.215	$1\frac{1}{3}Sc_2O_3$	
$3Al_2O_3$	12.159		
$5Al_2O_3$	12.003	$\frac{1}{4}In_2O_3$	12.404
		$\frac{3}{4}In_2O_3$	12.435
$\frac{1}{4}Ga_2O_3$	12.374		
$\frac{3}{4}Ga_2O_3$	12.371	$\frac{1}{4}Cr_2O_3$	12.368
$\frac{3}{4}Ga_2O_3$	12.366		

substituted yttrium-iron garnet of the general formula unit,



it is necessary to use a formula unit in the following form:



where $x = y + z$. The ions in the octahedral, 16(a), positions are enclosed by square brackets and those in tetrahedral, 24(d), positions by curved brackets.

For small substitution ($x \ll 5$) for Fe^{3+} by a non-magnetic ion, M^{3+} , the magnetic moment, n_B , per general formula unit would, to first approximation, be

$$\begin{aligned} \frac{1}{2}n_B(\infty, 0; y, z) &= (3-z)5 - (2-y)5 \\ &= 5(1+y-z) \mu_B. \end{aligned}$$

For larger x the probability that an octahedral or tetrahedral Fe^{3+} ion may be linked only with non-magnetic M^{3+} ions becomes appreciable so that such an Fe^{3+} ion may not contribute to n_B . With allowance

for this condition

$$\begin{aligned} \frac{1}{2}n_B(\infty, 0; y, z) &= 5[(3-z) - (3-z)(y/2)^4 - (2-y) + (2-y)(z/3)^6] \\ &= 5\{(1+y-z) - [(3-z)(y/2)^4 - (2-y)(z/3)^6]\} \mu_B. \end{aligned}$$

The effect of M-ion distribution upon T_C may be approximated through its effect upon the average number, n , of $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ interactions per magnetic ion. In yttrium-iron garnet there are 24/5 interactions per magnetic ion per formula unit, $\text{Y}_3\text{Fe}_2(\text{FeO}_4)_3$. The introduction of a nonmagnetic ion, M, will reduce n so that

$$\begin{aligned} n(y, z) &= \left[\left(\frac{3-z}{3} \right)^4 \left(\frac{2-y}{2} \right)^3 \right. \\ &\quad \left. + \left(\frac{2-y}{2} \right)^6 \left(\frac{3-z}{3} \right)^2 \right] / (5-y-z) \\ &= (24 - 12y - 8z + 4yz) / (5 - y - z). \end{aligned}$$

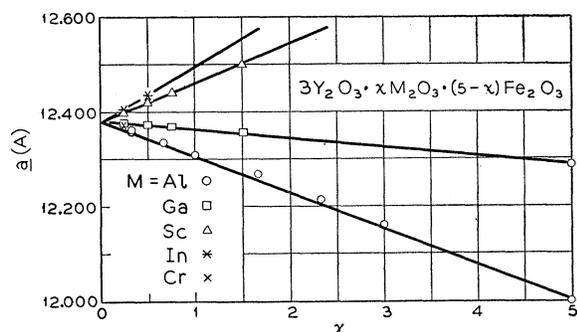


Fig. 9. Lattice constant vs x for substituted yttrium-iron garnets.

Therefore, the Curie temperature of a substituted yttrium-iron garnet, $T_C(y, z)$, will vary approximately as $n(y, z)$ so that it will be related to the Curie temperature of yttrium-iron garnet, $T_C(0, 0)$, by

$$T_C(y, z) = \frac{n(y, z)}{n(0, 0)} T_C(0, 0) = \frac{(1-y/2)(1-z/3)5}{5-y-z} T_C(0, 0).$$

In this approximation the effects of change in interionic distances and angles (lattice constant and parameter changes) which result from the substitution of M^{3+} for Fe^{3+} have been neglected. Another shortcoming of this approximation arises from the random variation of the number of interactions per Fe^{3+} ion as a consequence of the random distribution of M^{3+} ions in a given type of site.

Although it would appear that either $n_B(\infty, 0; y, z)$ or $T_C(y, z)$ would suffice to determine the distribution of M ions, it is considered that n_B would provide greater accuracy because less serious approximations have been made. On this basis the $n_B(\infty, 0)$ data have

TABLE II. The magnetic moment, $n_B(\infty, 0)$, and Curie temperature, T_C , observed, and values calculated for T_C and the fraction, f_t , of M ions in tetrahedral sites for $3\text{Y}_2\text{O}_3 \cdot x\text{M}_2\text{O}_3 \cdot (5-x)\text{Fe}_2\text{O}_3$.

$x\text{M}_2\text{O}_3$	$n_B(\infty, 0)$ obs (μ_B)	T_C obs ($^\circ\text{K}$)	T_C calc ($^\circ\text{K}$)	f_t calc
0	9.92	545	545	0
$\frac{1}{4}\text{Ga}_2\text{O}_3$	7.95	519	524	0.91
$\frac{1}{2}\text{Ga}_2\text{O}_3$	4.35	460	477	0.88
$\frac{3}{4}\text{Al}_2\text{O}_3$	7.00	497	518	0.95
$1\text{Al}_2\text{O}_3$	3.25	415	451	0.84
$\frac{1}{4}\text{Sc}_2\text{O}_3$	11.97	500	504	0.11
$\frac{1}{2}\text{Sc}_2\text{O}_3$	14.4	365	427	0.21
$\frac{3}{4}\text{In}_2\text{O}_3$	13.8	444	462	0.11
$\frac{1}{4}\text{Cr}_2\text{O}_3$	10.95	515	...	0.0

been used to determine the fraction, f_t , of M ions found in tetrahedral sites,

$$f_t = z/x = 1 - y/x = 1 - f_o,$$

where f_o is the fraction of M ions in the octahedral sites (Table II). The Curie temperatures have then been calculated from y and z thus obtained (Table II).

DISCUSSION

The magnetic and crystallographic observations made thus far form a consistent picture in terms of the crystal structure and $\text{Fe}^{3+}\text{-O}^{2-}\text{-Fe}^{3+}$ interactions as presented elsewhere by the authors.^{6,9} The magnetic measurements not only give further understanding of the ferrimagnetism in rare-earth iron type garnets but also help to confirm, and to establish, important crystallochemical relationships.

The M-ion distribution, which has thus far been examined only through its effect on magnetic properties, is consistent with steric considerations when M is a nonmagnetic ion. It appears, at least qualitatively, that the set of radii derived from the perovskite-like structures by Geller¹⁸ apply to the garnets.¹⁹

We have seen (Fig. 9) that the rate of change of the lattice constant of substituted yttrium-iron garnets with increasing x in all cases corresponds in relative magnitude and sign to the size of the M^{3+} ion relative to that of Fe^{3+} as found for perovskite-like structures. The more detailed steric influence observed is still more important, however. It is known⁶ that the tetrahedral site provides a smaller volume than does the octahedral site ($\text{Fe}^{3+}\text{-O}^{2-}$ distances of 1.88 and 2.00 Å, respectively, in yttrium-iron garnet). In every case we have observed that a nonmagnetic substituent M^{3+} -ion occupies predominantly an octahedral or tetrahedral

¹⁸ S. Geller, Acta Cryst. 10, 248 (1957).

¹⁹ The sequence of decreasing size for the ions in question for coordination number, C.N.(6), is Y^{3+} , In^{3+} , Sc^{3+} , Fe^{3+} , Ga^{3+} , Cr^{3+} , Al^{3+} . It should be noted that the feasibility of substitution of In^{3+} and Sc^{3+} for Fe^{3+} is suggested by the C.N.(6) ionic radii derived from the perovskites. These radii are 1.12 and 1.09, respectively, times that of Fe^{3+} . However, substitution probably would not have been considered to be possible on the basis of the C.N.(6) radii of Pauling and Goldschmidt which are 1.35, 1.35 and 1.42, 1.24, respectively, times that of Fe^{3+} .

site for small x according as it is larger or smaller than Fe^{3+} . In other words the smaller ion persistently seeks the smaller site.

The degree of preference of Ga^{3+} for the tetrahedral site with small substitution for Fe^{3+} in yttrium-iron garnet is remarkable because of the close similarity of these two ions and compounds. Both Fe^{3+} and Ga^{3+} are spherical ($3d^5$ and $3d^{10}$ electronic configurations, respectively) and Ga^{3+} is only about 2% smaller in radius than Fe^{3+} for C.N.(6).¹⁸ Furthermore the lattice constant of yttrium-gallium garnet (12.273 Å), which corresponds to total substitution, is only about 0.8% less than that of yttrium-iron garnet (12.376 Å). The absence of change of electrostatic energy as an important influence in the distribution of the metal ions when all have the same valence should be kept in mind when comparison is made with the distribution observed, for example, in iron spinels for the same substitution.

The problem of M-ion distribution has been examined by neutron diffraction by Prince²⁰ of these Laboratories. Neutron diffraction can provide valuable data because of the difference in the nuclear and electronic scattering powers of Fe^{3+} and Al^{3+} for neutrons of about 1 Å wavelength. Prince has been able to confirm the distribution of Al^{3+} in $3\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3 \cdot 4\text{Fe}_2\text{O}_3$ (Table II). At the same time he was able to substantiate the magnetization observed at 24 and -196°C , to verify its origin, and to determine the magnetization of the Fe^{3+} sublattices.

The electronic configuration of a metal ion appears to be a much more important factor than size with regard to its presence in the octahedral or tetrahedral sites. Furthermore the electronic configuration is much more important in the formation of a compound of garnet structure than it is for a compound of perovskite structure.^{18,21-24} All minerals of garnet structure²⁵ with the exclusion of uvarovite are found with the octahedral and tetrahedral sites occupied entirely by spherical ions (ions with closed p or d or half-filled d shells) except perhaps for small impurities.

Among the transition metals, Cr^{3+} is the only ion which has been substituted for Fe^{3+} in any quantity. In yttrium-iron garnet, as in uvarovite, Cr^{3+} enters the octahedral site, probably exclusively, even though Cr^{3+} is known to be smaller than Fe^{3+} in sites of C.N.(6).¹⁸ These observations suggest strongly that the electronic configuration of Cr^{3+} , which is favorable to the forma-

tion of d^2sp^3 (octahedral) type bonds, must be important.²⁶ Therefore it is not surprising that attempts by the authors to prepare yttrium-transition metal garnets have not met with success except in the case of iron.

In addition to the limitations which evidently are imposed on the formation of compounds of garnet structure by the electronic configuration of ions for the 16(a) and 24(d) positions, a size limitation has also been observed. Total substitution of In^{3+} or Sc^{3+} for Fe^{3+} has not been accomplished. The upper limits of substitution are not precisely known but probably are, x less than about one for In^{3+} and less than about two for Sc^{3+} , these ions apparently are too large to allow formation of yttrium-indium or yttrium-scandium garnets. Attempts to compensate for the large size of Sc^{3+} by replacement of Y^{3+} by a larger La^{3+} were unsuccessful. In^{3+} does not appear to replace Y^{3+} because attempts to synthesize indium-iron and indium-aluminum garnet were also unsuccessful. In the case of Cr^{3+} the substitution does not appear to proceed well for x much greater than $\frac{1}{4}$. This limitation probably is a consequence of the strong preference of a smaller ion, Cr^{3+} , for a larger site which quickly leads to a condition not compatible with the requirements of the structure.

The limit of feasible substitution for iron in yttrium-iron garnet by In^{3+} , Sc^{3+} , Cr^{3+} , and other transition metal ions is generally indicated by the appearance of a perovskite-like phase; this phase also appeared in an attempt to synthesize lanthanum-scandium garnet. The perovskite-like phase is known to be more stable than the garnet phase in the case of the rare-earth iron³ and aluminum sesquioxide systems²⁷; it does not appear in all of the rare-earth gallium sesquioxide systems.^{2,11} In this connection it should be borne in mind that the packing in the garnet structure is much less efficient than in the perovskite-like structure.⁶

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²⁰ E. Prince, International Union of Crystallography, Fourth International Congress, Montreal, July, 1957, abstract 6-28; Acta Cryst. **10**, 787 (1957).

²¹ S. Geller and E. A. Wood, Acta Cryst. **9**, 563 (1956).

²² S. Geller and V. B. Bala, Acta Cryst. **9**, 1019 (1956).

²³ M. A. Gilileo, Acta Cryst. **10**, 161 (1957).

²⁴ S. Geller, Acta Cryst. **10**, 243 (1957).

²⁵ In addition to silicates there are the minerals berzeliite, $(\text{Ca}_2\text{Na})\text{Mn}_2(\text{AsO}_4)_3$, and cryolithionite, $\text{Na}_3\text{Al}_2(\text{LiF}_4)_3$.

²⁶ Actually the 16(a) position in yttrium-iron garnet is surrounded by an octahedron of oxygen ions which is not regular. The regularity of the octahedra and tetrahedra appears to increase with the ratio of the radii of the ions in the octahedral and tetrahedral sites according to the work of S. C. Abrahams and S. Geller [Acta Cryst. (to be published)] on grossularite.

²⁷ The high-temperature yttrioalumite phase of Yoder and Keith (see reference 10) has been identified as perovskite-like YAlO_3 reported by Geller and Bala (see reference 22).