THE BELL SYSTEM
TECHNICAL JOURNAL

VOLUME XLIII   MARCH 1964   NUMBER 2

Importance of Intrasublattice Magnetic Interactions and of Substitutional Ion Type in the Behavior of Substituted Yttrium Iron Garnets

By S. GELLER, H. J. WILLIAMS, G. P. ESPINOSA and R. C. SHERWOOD

(Manuscript received November 6, 1963)

The results of measurements at moderate to high magnetic fields on a large number of nonmagnetic ion substituted yttrium iron garnets suggest that intrasublattice interactions play an important role in determining their spontaneous magnetizations and Curie temperatures. It is shown that the system $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ *is continuously related to the system* $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ *or* $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$*. It is concluded that in these systems the tetrahedral-tetrahedral (d-d) antiferromagnetic interactions are stronger than octahedral-octahedral (a-a) antiferromagnetic interactions. The changes in magnetic structure from an ideal ferrimagnet, yttrium iron garnet, to an end-member in which there are at least short-range antiferromagnetic interactions (i.e., in* $\{Ca_3\}[Fe_2](Si_3)O_{12}$ *or a hypothetical* $\{YCa_2\}[Zr_2](Fe_3)O_{12}$*) should bear an analogy to the crystal chemical changes. It is therefore proposed that when substitution is made exclusively in one sublattice, the moments of the* Fe^{3+} *ions in that sublattice remain parallel (as in the Yafet-Kittel theory), while the weakened average a-d interactions and the intrasublattice interactions lead to random canting of the* Fe^{3+} *ion moments of the other. This tendency occurs as soon as substitution begins. On continued substitution, a point is reached beyond which canting increases much more rapidly with increasing substitution. In this region, the intrasublattice interactions dominate the a-d interactions, but it is probable that the canting continues to be random.*

In the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system, the point at which the tetrahedral intrasublattice interactions dominate is reached at about $x = 0.95$ as contrasted with $x \approx 0.70$ for the $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ and $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ systems. The canting of the d-site ion moments increases at the same rate in the three systems to $x \approx 0.70$, but beyond this point, the canting in the Mg-Si substituted YIG is always substantially less than for the other two systems. This together with data on other substituted garnets indicates that the substitution of the Si^{4+} ions in the d-sites tends to decrease the average d-d interaction strength. Similarly, substitution in the a sites tends to decrease the average a-a interaction strength.

Measurements on some garnets in the systems $\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}](Si_yFe_{3-y})O_{12}$, $\{Y_{3-y+x}Ca_{y-x}\}[Mg_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$ and $\{Y_{3-x-y}Ca_{x+y}\}[Zr_xFe_{2-x}](Si_yFe_{3-y})O_{12}$ indicate that different nonmagnetic ions may produce different magnetic behavior. This is especially noticeable in the region in which the intrasublattice interactions are dominant. Comparative behavior of the systems $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ and $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ and of the systems $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}M_x)O_{12}$, $M \equiv Si$ and Ge, also indicates that the ion type is important in determining magnetic behavior. It is speculated that this results from effects on the interaction geometry, especially when the interactions are weak.

Results on garnets in systems $\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$, $\{Y_{3-y+x}Ca_{y-x}\}[Mg_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$, and $\{Y_{3-x-y}Ca_{x+y}\}[Zr_xFe_{2-x}](Si_yFe_{3-y})O_{12}$ also aided in substantiating the other ideas put forward as well as in determining the distribution of ions in the system $\{Y_3\}Fe_{5-x}Al_xO_{12}$, on which more extensive studies than heretofore were made. Some anomalies occur in this system for values of $x > 2.0$.

Application of the ideas derived from these studies are made to the ferrospinels, and it is shown that one may thereby account for the high Curie temperature of lithium ferrite, the lower Curie temperature of nickel ferrite, and the substantially lower Curie temperature and low 0°K moment of manganese ferrite.

It is noted that although the ideas presented may account in a general way for the behavior of the Sb^{5+} and V^{5+} ion substituted garnets, their behavior could not have been quantitatively predicted from the results of the present work. It is probable that the chemical bonding of the Sb^{5+} and V^{5+} ions has much greater effects on the magnetic behavior than does that of the various ions treated in this paper.

I. INTRODUCTION

Studies of substitutions for iron ions in yttrium iron garnet of nonmagnetic ions which prefer exclusively (or almost exclusively) octahedral sites have been reported earlier.[1,2] The results of the study of the tin-substituted yttrium iron garnets led to Gilleo's statistical treatment,[3] which appeared to account well for the 0°K moments and Curie temperatures in this system as well as in those involving zirconium,[2] scandium,[2-4] and indium[2-4] substitutions. However, the data available at the time of these developments were still not sufficient for a complete test of the method.

The study of substituted yttrium iron garnets has now been extended to systems in which substitution for Fe^{3+} ions is made exclusively in the tetrahedral sites (i.e., $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$), equally in both octahedral and tetrahedral sites

(i.e., $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$, $\{Y_{3-x}Ca_x\}[Sc_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$,

and

$$\{Y_{3-2x}Ca_{2x}\}[Zr_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}),$$

and unequally in the two sites

$$\text{(e.g.,}\quad \{Y_{3+x-y}Ca_{y-x}\}[Mg_xFe_{2-x}](Fe_{3-y}Si_y)O_{12},$$

$$\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}](Fe_{3-y}Si_y)O_{12},$$

and $\{Y_{3-x-y}Ca_{x+y}\}[Zr_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$). Analogous germanium-substituted systems have also been studied. The system $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ has been reinvestigated and the study of the $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ system extended to larger values of x. High-field measurements have been made on specimens when required. The study of the system $Y_3Al_xFe_{5-x}O_{12}$[4] has been extended to large values of x, and the distribution of the ions vs x deduced.

The results of these investigations indicate that the Gilleo treatment does not in general give good agreement with the observed 0°K moments of the substituted yttrium iron garnets. Application of the Yafet and Kittel theory[5] to the tin-substituted garnets was made by de Gennes.[6] Agreement of 0°K moments appeared to be good, although not nearly as good as that shown[2,3] by the Gilleo theory. However, an arithmetic error was made in de Gennes' calculation; when corrected, the agreement deteriorates. Furthermore, using the same approach as that of de Gennes for the silicon-substituted garnets, that is, assuming the Pauthenet[7] molecular field coefficients of yttrium iron garnet to remain constant for the whole system, no semblance of agreement is found.

Contrary to earlier assumptions, there is substantial evidence that *intra*sublattice interactions are not negligible; they appear to play an important role in determining the spontaneous magnetizations and Curie temperatures of the substituted garnets. It also must be concluded that different nonmagnetic ions may produce different effects on the magnetic behavior when the amounts of substituent for the Fe^{3+} ions in particular sites are the same.

In the course of our study of the yttrium iron garnet-calcium iron silicate system, on which a preliminary report was made some time ago,[8] we learned that Smolenskii, Polyakov, and Iodin[9] had reported on this system. However, their magnetic measurements were made at 77°K and presumably they did not make any high-field measurements.

The above description should make it clear that the problem of the behavior of the substituted garnets has increased in complexity with the number of experiments performed. Following the completion of the draft form of this manuscript, new garnets containing Sb^{5+} (Ref. 10), V^{5+} (Refs. 10–12), and Bi^{3+} (Refs. 10, 12, 13) ions were discovered. (Many of these no longer contain yttrium or rare earth ions.) The magnetic behavior of these garnets was in part unpredictable from the results given in the present paper. However, there are unifying consistent features of the garnet systems described herein and we feel it worthwhile to describe them.

Complete understanding, it is felt, will eventually come from various studies of single crystals in the various systems. Neutron diffraction studies should play an important rôle, but also of utmost importance, it would appear, are spectroscopic studies which would give an insight into the effects of changes in chemical bonding on changes in magnetic interactions.

II. EXPERIMENTAL

2.1 *Preparation of Specimens*

As we have recently described in some detail our present techniques for specimen preparation,[14] we shall not do so here. Utmost care is required in these preparations, including the use of pure starting materials, correction for adsorbed moisture or CO_2 in the starting materials, proper mixing and avoidance of inhomogeneous loss of constituents, the insuring of the theoretical weight losses on firing, the careful examination of powder photographs or diffractometer patterns to be sure that single phases, preferably sharply defined ones, are obtained, and careful measurement of lattice constants to be sure that these fit properly on the curves characterizing the systems. The preparation of the specimens in most cases required several regrindings and refirings.

2.2 *Magnetic Measurements*

Measurements of magnetic moment were made in the temperature range 1.4–298°K at applied fields, H_a, to 15.3 koe, by means of a pendulum magnetometer described elsewhere.[15] Calibration was carried out with spectroscopically pure Ni; measurements on Mohr's salt[16] corroborated the calibration with Ni.

Measurements at fields to 80 koe were made with the Bitter-type magnet and an extraction method used for determination of the moment. Calibration was carried out with spectroscopically pure Ni.

2.3 *Crystallographic Measurements*

Lattice constants were obtained from measurements of powder photographs taken with Norelco Straumanis-type cameras of 114.6-mm diameter and Cr*K* radiation.

III. MAGNETIC AND CRYSTALLOGRAPHIC DATA

3.1 *The Systems* $\{Y_{3-x}Ca_x\}Fe_{5-x}M_x^{4+}O_{12}$, $M \equiv Si, Ge$

3.1.1 *Magnetic Data*

In the system $\{\mathrm{Y}_{3-x}\mathrm{Ca}_x\}\mathrm{Fe}_{5-x}\mathrm{Si}_x\mathrm{O}_{12}$, specimens with $x \leqq 1.77$ were saturated at fields $\leqq 12.6$ koe at 1.4°K. For $x \geqq 1.88$, saturation was not attained at low fields, and therefore measurements were made at the high fields at 4.2°K. The specimen with $x = 1.88$ was saturated at 60 koe. None of the other specimens was saturated at fields below 80 koe and at 4.2°K. For these specimens the behavior of the magnetization at fields $\geqq 50$ koe was such that $n_B(H_a, T) = n_B(0, T) + \chi_n(H_a, T)H_a$; the values of $n_B(0, T)$ in these cases were determined by extrapolation to $H_a = 0$.

Typical curves of $n_B(H_a, T)$ vs T obtained with the pendulum magnetometer are shown in Figs. 1 and 2. When $x = 2.25$ (Fig. 2), the magnetization curves at the two higher fields appear to reach a maximum at about 40°K, then decrease, cutting the ordinate with positive slope. At 5 koe, the curve cuts the ordinate with zero slope. The curves for $x = 2.50$ behave similarly.

In Fig. 3, curves of n_B vs H_a at 4.2°K for $x = 2.00$, 2.25, and 2.50 are shown. For all these, measurements were made on sintered specimens. For $x = 2.25$, measurements were also made on the finely powdered specimen. Note that although the slope is greater for the sintered speci-

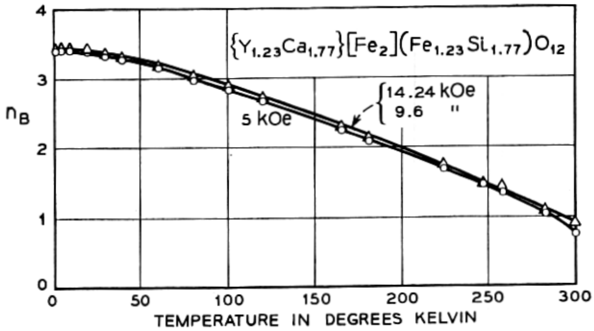

Fig. 1 — n_B vs T at different magnetic fields for $\{Y_{1.23}Ca_{1.77}\}[Fe_2](Fe_{1.23}Si_{1.77})O_{12}$.

men, extrapolation to $H_a = 0$ leads to insignificant difference in n_B. However, when a plot of n_B vs $1/H_a$ is extrapolated to $1/H_a = 0$, these values of n_B are 3.5 and 4.0 for the powdered and sintered specimens respectively.

In Table I, the spontaneous moments listed for specimens with $x \leqq 1.77$ are extrapolated to 0°K; for specimens with $x \geqq 1.88$, the values are those extrapolated to $H_a = 0$ at 4.2°K.[17] These are plotted vs x in Fig. 4. Negative values of n_B mean that the moment of the octahedral sublattice is dominant.

Where possible, Curie temperatures (Table I and Fig. 5) were obtained from extrapolation of a plot of $n_B^2(0,T)$ vs T to $n_B^2(0,T) = 0$

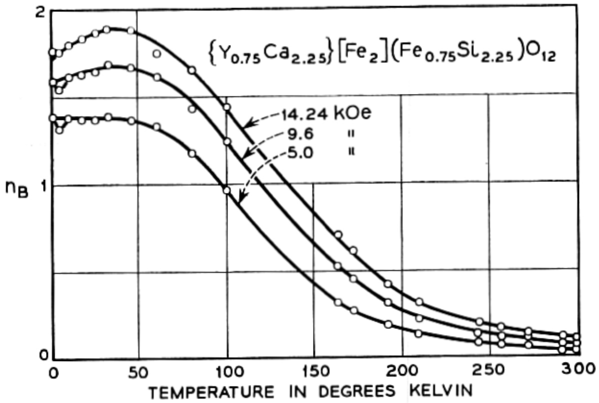

Fig. 2 — n_B vs T at different magnetic fields for $\{Y_{0.75}Ca_{2.25}\}[Fe_2](Fe_{0.75}Si_{2.25})O_{12}$.

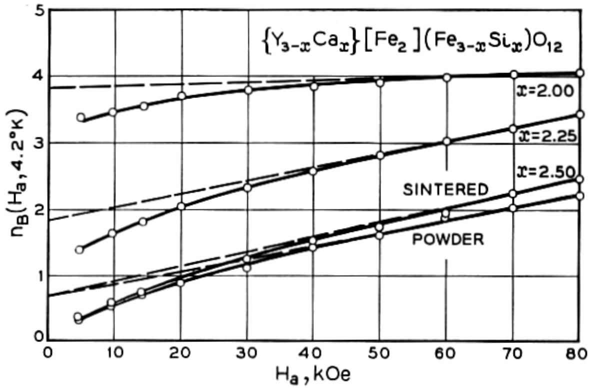

Fig. 3 — n_B vs applied field, H_a, at 4.2°K, for some specimens in the system $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$.

and from extrapolation of $1/\chi_n$ vs T to $1/\chi_n = 0$ when T_C was sufficiently below room temperature. (See Ref. 14.)

The garnet $\{Ca_3\}[Fe_2](Si_3)O_{12}$ cannot be made by solid-state reaction at atmospheric pressure. Small crystals were grown by Van Uitert and Bonner, and magnetic measurements were made on 2.99 g of these over

TABLE I — MAGNETIC AND CRYSTALLOGRAPHIC DATA FOR THE GARNETS $\{Y_{3-x}Ca_x\}Fe_{5-x}M_x^{4+}O_{12}$, M ≡ Si,Ge

x	M ≡ Si			M ≡ Ge		
	n_B[a]	T_C(°K)	a(Å)	n_B[a]	T_C(°K)	a(Å)
0.00	5.01	553[b]	12.376 ± 0.003	5.01	553[b]	12.376 ± 0.003
0.40	2.98	543[c]	12.344			
0.70						12.375
0.75		508[c]	12.314			
1.00	0.06		12.291	0.18		12.372
1.01	−0.07		12.291			
1.02	−0.14		12.291			
1.50	−2.36	367	12.243	−2.31	365	12.365
1.75				−3.15	316	12.360
1.77	−3.40	312	12.212			
1.88	−3.8	280	12.202			
2.00	−3.8	266	12.186 ± 0.005	−3.15	258	12.355
2.25	−1.9	180	12.157	−1.55	180	12.348 ± 0.004
2.50	−0.65	86	12.126	−0.35	80 (?)	12.339
2.75			12.093[d]	0		12.329
3.00	0		12.048[e] ± 0.003	0[f]		12.320[g]

[a] For M ≡ Si, Ge and $x < 1.88$, 1.75 respectively, values are those from extrapolation to 0°K; for $x \geqq 1.88$, 1.75 respectively, values are at 4.2°K, extrapolated to $H_a = 0$. [b] From J. Loriers and G. Villers, Compt. Rend., **252**, 1590 (1961). [c] Measured by E. A. Nesbitt. [d] Not single-phase: see text. [e] From Ref. 20. [f] From Ref. 21. [g] From Ref. 38.

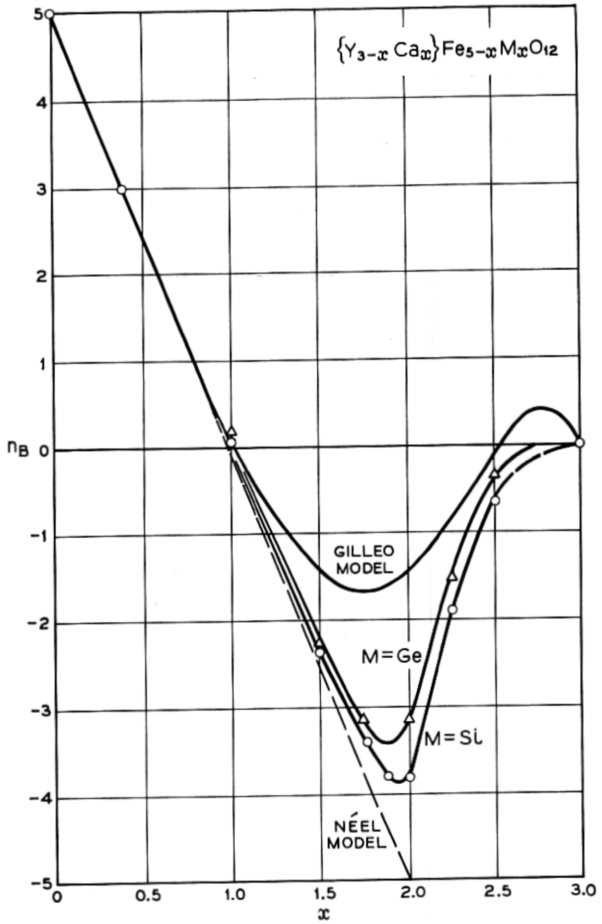

Fig. 4 — Spontaneous magnetizations vs composition for the silicon- and germanium-substituted yttrium iron garnets. For $x < 1.88$, saturation was attained at low fields and n_B values obtained by extrapolating $n_B(T)$ to $T = 0°K$. For $x \geqq 1.88$, saturation was not attained at low fields, and the n_B values were obtained by extrapolating $n_B(H_a)$ to $H_a = 0$ at 4.2°K (see Fig. 3). Shown also are the curves given by the Gilleo and Néel models for substitution by nonmagnetic ions exclusively on tetrahedral sites.

the temperature range 1.4 to 296°K. At a field of 5.0 koe, there was a peak in the susceptibility at about 9°K. However, the nature of the peak is not conclusive evidence of an antiferromagnetic transition. On the other hand, θ_p for the specimen is 29°K, which is indicative of antiferromagnetic interaction. The Curie constant $C = \Delta T/\Delta\ (1/\chi_n) = 1.47 \times 10^{-3}$, to be compared with the theoretical value of 1.56×10^{-3}.

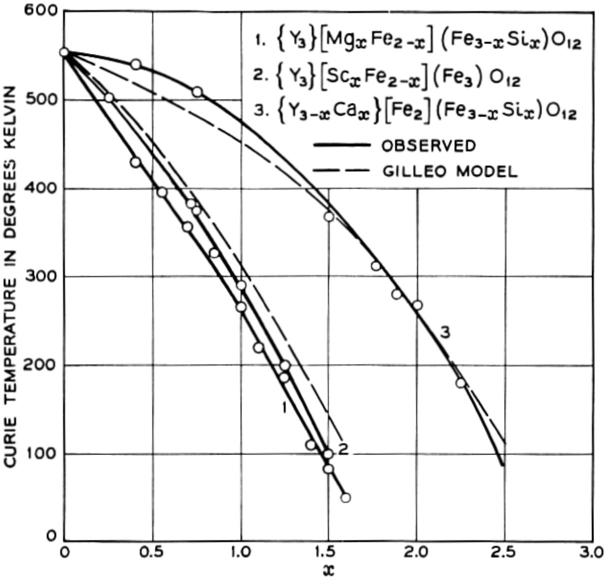

Fig. 5 — Curie temperatures vs x for the systems (1) $\{Y_3\}[Mg_xFe_{2-x}]$-$(Fe_{3-x}Si_x)O_{12}$, (2) $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$, (3) $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$.

In the system $\{Y_{3-x}Ca_x\}Fe_{5-x}Ge_xO_{12}$, specimens with $x \leqq 1.50$ were saturated at fields $\leqq$12.6 koe at 1.4°K. In measurements with the pendulum magnetometer, the specimen with $x = 1.75$ appeared to be saturated at 9.6 koe at both 1.4 and 4.2°K. Measurements on the sintered specimen at high fields at 4.2°K indicated that saturation was not attained until about 50 koe. However, the difference in n_B is only 0.1 μ_B . For the specimens with $x \geqq 2.00$, saturation was not attained at 1.4° or at 4.2°K at fields below 80 koe. As in the case of the first system discussed, n_B (0, 4.2°K) was determined by extrapolation of the straight line portion of the $n_B(H_a\ ,4.2°\mathrm{K})$ vs H_a curve to $H_a = 0$. The magnetization curves in this system were similar in character to those of the specimens in the analogous Si system. Curie temperatures (Table I) were determined as described above. The spontaneous magnetizations extrapolated to $T = 0$, $H_a = 0$ or at $T = 4.2°\mathrm{K}$,[17] $H_a = 0$ are listed in Table I and plotted vs x in Fig. 4.

3.1.2 *Crystallographic Data*

The lattice constants of specimens in these systems are listed in Table I and plotted vs x in Fig. 6. All garnets involving Ge substitution gave

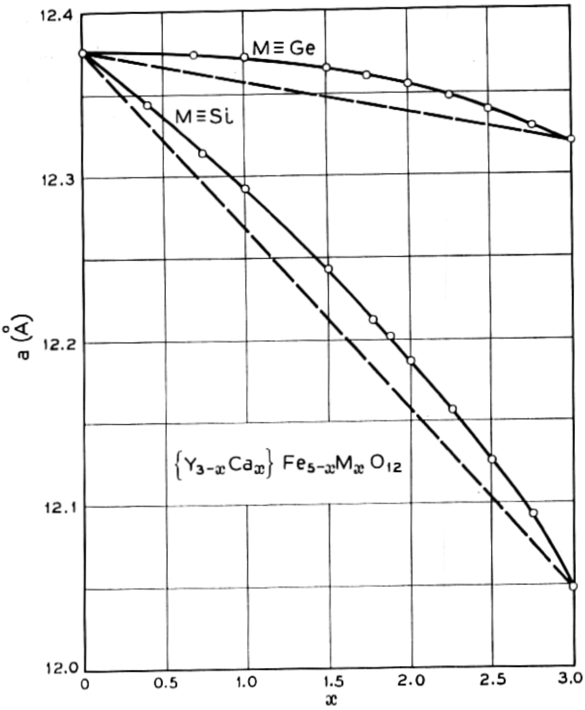

Fig. 6 — Lattice constants vs composition of silicon- and germanium-substituted garnets.

final powder photographs having sharp back-reflection lines. However, in a few cases of the silicon-rich specimens (that is, with $x = 2.25$ and 2.50) sharp back-reflection lines appeared to be unattainable. Because no extraneous phases appeared to be present, it seemed worthwhile to carry out the magnetic measurements on these anyway. In some cases, the indicated larger limits of error on the lattice constants are a result of only few back-reflection lines on which the measurements are based. However, because of the smoothness of the curves which may be passed through the central values, all the indicated estimates of limits of error (Table I) are felt to be conservative.

In both systems, the lattice constant vs composition behavior is nonlinear; such behavior has been observed in other garnet systems.[1,14,18,19] We might expect the larger volumes than given by the straight line joining the lattice constants of the end-members to indicate greater entropies, the disorder apparently arising from the disparity of the sizes and possibly of the electrostatic charges of tetrahedrally coordinated ions of Fe^{3+} vs Si^{4+} or vs Ge^{4+}. However, the lattice constant itself is not always indicative of the disorder which may exist in a solid solution. The latter cannot obey the third law of thermodynamics because the crystalline fields about space group equipoints cannot all be the same, even if the lattice constant-composition behavior is a linear one.

An attempt was made to prepare the specimen with $M \equiv Si$, $x = 2.75$; a slight amount of an extra unidentified phase was observed in this case. The lattice constant (Table I) indicated that the garnet phase present had almost the composition sought. However, it is possible that some excess silicon with divalent iron could be present in this garnet.[14]

The specimen of $Ca_3Fe_2Si_3O_{12}$ prepared by Van Uitert and Bonner had a lattice constant of 12.067 ± 0.003 Å. This is substantially larger than the 12.048 Å reported[20] for a specimen prepared at high pressure. The difference in lattice constant implies that at least one of the specimens contains impurity ions. However, our main interest was to show the presence of antiferromagnetic interaction in $Ca_3Fe_2Si_3O_{12}$, and it does not seem that the impurity ion (or ions) could introduce it in this case. Magnetic measurements were also made on a mineral specimen from Graham County, Arizona, having a lattice constant of 12.068 ± 0.003 Å, with essentially the same results as obtained on the synthetic.

3.1.3 *Discussion of the Garnets* $\{Y_2Ca\}[Fe_2](Fe_2Si)O_{12}$ *and* $\{Y_2Ca\}Fe_4GeO_{12}$

The present work indicates that earlier results[21] on these garnets are erroneous. The 0°K moments reported earlier were 0.5 and 1.5 μ_B respectively, as compared with 0.06 and 0.18 μ_B obtained in the present work. That the latter two results are the more reliable is easily ascertained by examination of Fig. 4; these points lie well on the curves for the appropriate systems.

It is precisely in sensitive regions where the greatest care in preparation must be exercised. In the case of the Si-substituted garnet, we can only guess that perhaps there was present in the earlier preparation an extraneous phase which was not observed on the powder photograph or, that despite the good agreement between lattice constants (see Tables I of Ref. 21 and of this paper), the stoichiometry was not exact. For example, excess Si^{4+} ions would cause the reduction of some Fe^{3+} to Fe^{2+} ions. While the excess Si^{4+} ions would tend to reduce the lattice constant, the presence of Fe^{2+} would tend to increase it.[14] Also, any deviation in stoichiometry would tend to increase the absolute value of the spontaneous moment.

In fact, the observed deviation, 0.06 μ_B from exactly 0.00 μ_B for $\{Y_2Ca\}[Fe_2](Fe_2Si)O_{12}$, amounts to only 0.5 mg of SiO_2 in the 0.001 mole of specimen prepared. The specimens with $x = 1.01$ and 1.02 were also prepared in an attempt to find the exact zero spontaneous magnetization at 0°K for this system. However (see Table I), neither of these gave exactly zero values. It would appear from the results that the experimental error could be as large as the equivalent of 0.01 of a Si^{4+} ion or 0.05 μ_B in this region of the system.

The high value previously obtained for the garnet $\{Y_2Ca\}Fe_4GeO_{12}$ is more easily explained, and a number of experiments (see Table II) were carried out to prove this contention. Examination of Fig. 6 shows that the change of lattice constant with x in the system $\{Y_{3-x}Ca_x\}Fe_{5-x}Ge_xO_{12}$ is not very large over rather large ranges of x. At $x = 1.00$, a change of ±0.003 Å (our quoted limits of error) implies a change of -0.25 or $+0.20$ respectively in x, which in turn implies a change (Fig. 4) of ±1.00 μ_B in 0°K moment. The broadness of back-reflection lines in the x-ray powder photograph may indicate a variation in range greater than $0.75 \leqq x \leqq 1.20$. As shown in Table II, repro-

TABLE II — EXPERIMENTS TO OBTAIN THE CORRECT DATA FOR $\{Y_2Ca\}Fe_4GeO_{12}$

Specimen	a(Å)	n_B (1.4°K)	n_B (77°K)	Description
594	12.372	1.00		After firing 16 hrs. at 1300°C, then 16 hrs. at 1350°C. Specimen contained 6.5% excess GeO_2 (based on total GeO_2). Broad 116[a] line.
	12.371	0.23		After third firing 39 hrs. at 1425°C. Specimen contained 4.1% excess GeO_2. Sharp 116 line.
602	12.371	0.18	0.17	After firing 19 hrs. at 1405°C, then 63 hrs. at 1400°C. Sharp 116 line.
	12.372		0.17	After third firing 66 hrs. at 1300°C. Sharp 116 line.
606		1.12	1.08	After firing 16 hrs. at 1315°C, then 16 hrs. at 1300°C. Broad 116 line.
			0.96	After third firing 64 hrs. at 1275°C. 116 line still broad.
			0.28	After fourth firing 17 hrs. at 1410°C. 116 line much sharper.
	12.372		0.18	After fifth firing 16 hrs. at 1410°C. 116 line sharp.

[a] That is, $h^2 + k^2 + l^2 = 116$.

ducible results are obtained for single sharply defined stoichiometric phases.

The preparation of $\{Y_2Ca\}Fe_4GeO_{12}$ requires a temperature of about 1400°C; even rather long firings at about 1300°C did not produce homogeneity. On the other hand (see Table II, specimen 602), firing at 1300°C for a long period produced no significant change in a homogeneous specimen formed at 1400°C.

Because of its volatility, an excess of GeO_2 is usually added to the reactants required for the preparation of Ge^{4+} ion substituted garnets. Firings are carried out until this excess is lost. It is possible, however, to add too great an excess and it is then best to discard the specimen. However, as seen in Table II, for specimen 594, an excess of 4.1 per cent GeO_2 was not as important as the correct firing temperature.

3.2 *The Systems* $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ *and* $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$

3.2.1 *Magnetic Data*

Part of the $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ system[4] and the whole $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ system[2] have been investigated earlier in these laboratories. In the present investigation several new specimens have been prepared and high-field measurements made on specimens with $x \geqq 0.72$. For values of $x \leqq 0.60$, specimens were magnetically saturated at an applied field of 9.6 koe at 1.4°K. For $x = 0.72$, the specimens were saturated at 60–70 koe at 4.2°K, and for $x > 0.72$, saturation was not attained at fields to 80 koe at 4.2°K. In these cases the spontaneous magnetizations, $n_B(0,4.2°)$, were obtained by extrapolating the straight line portions of the $n_B(H_a, 4.2°)$ to $H_a = 0$. The values thus obtained are listed in Table III; the actual spontaneous magnetizations of 0°K may, of course, be slightly higher.[17] Spontaneous magnetizations obtained by extrapolating $n_B(H_a, 4.2°)$ vs $1/H_a$ to $1/H_a = 0$ are also shown in Table III. The spontaneous magnetizations are plotted vs x in Fig. 7. Curie temperatures (Table III, Fig. 5) of specimens in these systems were determined as described above. For $x \geqq 1.50$, results were inconclusive. Examples of plots of n_B vs T for specimens in these systems have been given in other papers. The behavior of n_B vs T for high substitution is similar to that of the $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ system for high x.

The values $n_B(H_a, 4.2°)$ vs H_a for high x of specimens in both sys-

TABLE III — MAGNETIC AND CRYSTALLOGRAPHIC DATA FOR GARNETS $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ AND $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$

x	Sc				Zr			
	n_B[a]		T_C(°K)	a(Å)	n_B[a]		T_C(°K)	a(Å)
	$H_a = 0$	$H_a = \infty$			$H_a = 0$	$H_a = \infty$		
0.20[b]					5.9	5.9		12.404
0.25[c]	5.99	5.99	504	12.392				
0.40[b]					6.7	6.7		12.434
0.60	7.44	7.44	408	12.424	7.39	7.39		12.470
0.72	7.65	7.65	386	12.433	7.6	7.6	386	12.490
0.75[c]			375	12.438				
0.80	7.1	8.1		12.442	6.9	8.2		12.501
1.00	5.7	7.6	294	12.457	5.2	6.6	288	12.534
1.25	3.1	6.2	200	12.478	2.8	5.7	200	12.573
1.50	1.4	4.6	100(?)	12.497	1.1	4.0	65(?)	12.614
1.75					0.4	2.0	48(?)	12.653
1.95					0.0			12.684

[a] For $x < 0.72$, n_B was obtained by extrapolation to $T = 0$; for $x \geqq 0.72$, n_B is at 4.2°K. [b] Data from Ref. 2. [c] Data from Ref. 4.

tems are plotted in Fig. 8. In all cases, for the same value of x, the values of n_B at the same H_a are higher for Sc substitution than for Zr substitution. This will be discussed further later.

A plot of $1/\chi_n$ vs T for $\{Y_{1.05}Ca_{1.95}\}[Zr_{1.95}Fe_{0.05}](Fe_3)O_{12}$ is given in Fig. 9. A conclusive antiferromagnetic transition was not observed at fields as low as 4.9 koe. Above 70°K, $1/\chi_n$ follows a Curie-Weiss law with C equal to the calculated theoretical value for 3.05 Fe^{3+} ions per formula unit. The linear portion of $1/\chi_n$ vs T intersects the abscissa at −66°K, indicating that there is antiferromagnetic interaction among the Fe^{3+} ions at low temperatures.

Shown also in Fig. 9 is a plot of $1/\chi_n$ vs T for $\{YCa_2\}[Zr_2](Ga_{0.25}Fe_{2.75})O_{12}$. In this case again, there was no conclusive evidence of a transition to long-range antiferromagnetic order, but the intersection of the extrapolated linear portion of $1/\chi_n$ vs T with the abscissa, −40°K, indicates that antiferromagnetic interaction is present at low temperatures. As one would expect, the interaction strength is weaker than for $\{Y_{1.05}Ca_{1.95}\}[Zr_{1.95}Fe_{0.05}](Fe_3)O_{12}$.

For both specimens, there does not appear to be any indication of weak ferromagnetism.[22] Below the linear portions of $1/\chi_n$ vs T, the curves are concave upwards and neither specimen appears to have a residual moment at 1.4°K.

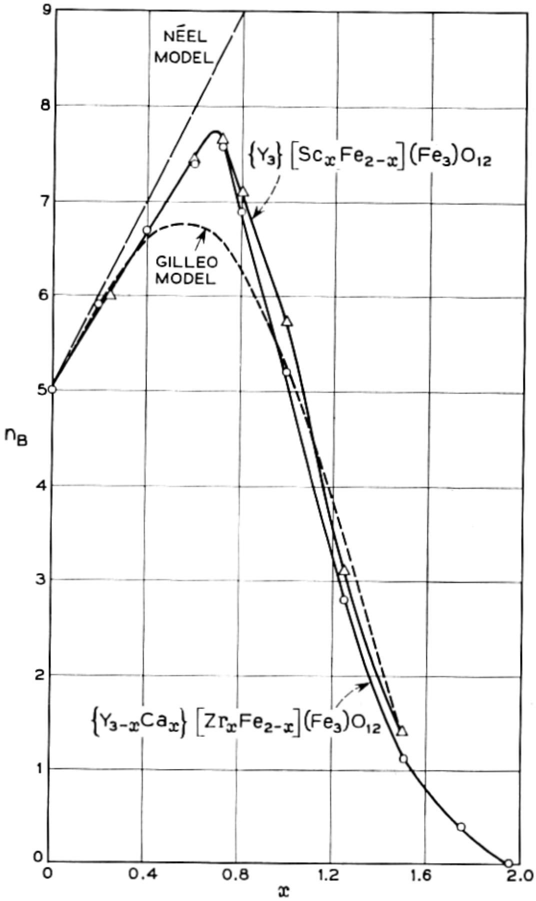

Fig. 7 — Spontaneous magnetizations vs composition for the zirconium- and scandium-substituted yttrium iron garnets. For $x < 0.72$, saturation was attained at low fields and the n_B values were obtained by extrapolating $n_B(T)$ to $T = 0°K$. For $x \geqq 0.72$, saturation was not attained at low fields and the n_B values were obtained by extrapolating $n_B(H_a)$ to $H_a = 0$ at 4.2°K (see Fig. 8). Shown also are the curves given by the Gilleo and Néel models for substitution by nonmagnetic ions exclusively on octahedral sites.

3.2.2 *Crystallographic Data*

Lattice constants for these systems are given in Table III and plotted vs x in Fig. 10. Shown also in Fig. 10 are values obtained in the former studies made in these laboratories. For the most part, agreement of the former with the present values is good. However, in the present study,

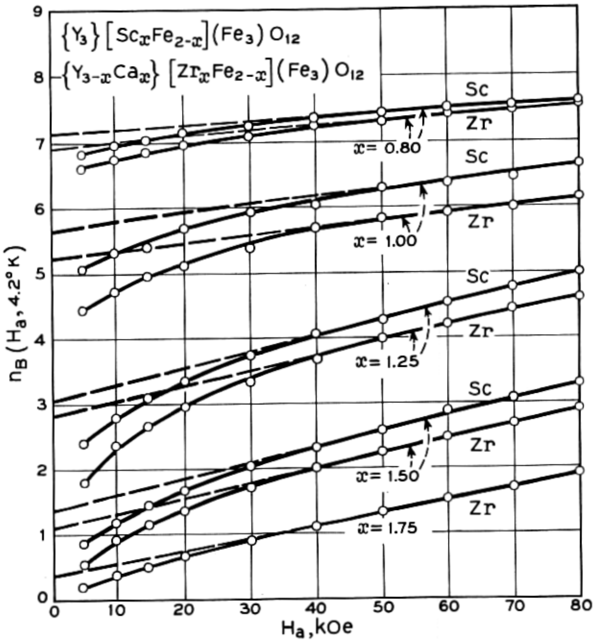

Fig. 8 — n_B vs applied field H_a, at 4.2°K, for some scandium- and zirconium-substituted yttrium iron garnets.

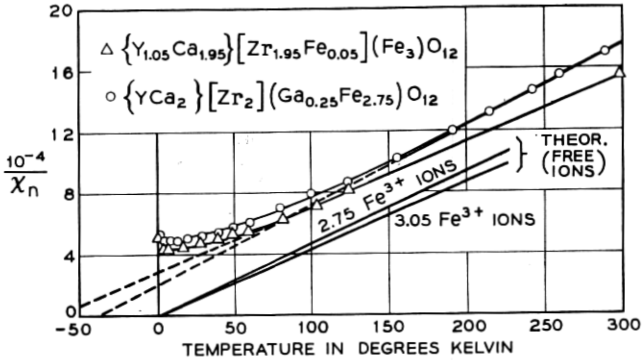

Fig. 9 — Reciprocal susceptibility (χ_n in Bohr magnetons per oersted per formula unit) vs temperature for the garnets $\{Y_{1.05}Ca_{1.95}\}[Zr_{1.95}Fe_{0.05}](Fe_3)O_{12}$ and $\{YCa_2\}[Zr_2](Ga_{0.25}Fe_{2.75})O_{12}$.

all points for both systems lie almost exactly on the two straight lines (Fig. 10) and, where differences occur, the present values are considered to be the more reliable ones.

An attempt to prepare $\{Y_3\}[Sc_2](Fe_3)O_{12}$ produced a specimen containing an extraneous perovskite-type phase and a garnet phase with lattice constant 12.508 Å. This value corresponds to the composition $x = 1.62$, which is the maximum value attainable, at least under the conditions of preparation.

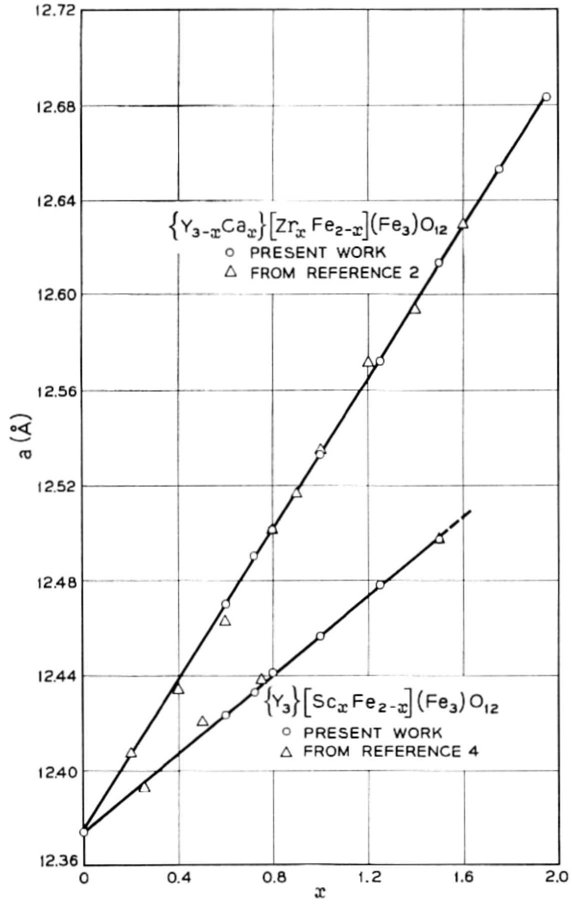

Fig. 10 — Lattice constants vs composition for the scandium- and zirconium-substituted yttrium iron garnets.

In the case of Zr substitution, previously we reported[2] obtaining a specimen with $x = 2.00$. However in attempting to reproduce this composition, very careful examination of x-ray data indicated a slight amount of extraneous phase. The garnet present had a lattice constant 12.686 Å, indicating a maximum $x = 1.96$. It was possible, however, to make the garnet $\{YCa_2\}[Zr_2](Ga_{0.25}Fe_{2.75})O_{12}$[23] with lattice constant 12.681 ± 0.003 Å.

3.3 *The System* $Y_3\,[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$

3.3.1 *Magnetic Data*

For values of $x \leqq 0.85$, all specimens in this system were essentially saturated over the whole temperature range at fields of 9.6–12.6 koe. For $x = 0.90$, measurements were made only at 1.4°K; the specimen was saturated at 11.3 koe. For $x = 1.00$, saturation was attained at 11.3 koe at 1.4°K, yielding a spontaneous magnetization of 3.5 μ_B per formula unit. However, subsequent high-field measurements showed that this specimen was more likely saturated at 70 koe with a moment of 3.8 μ_B.

For $x \geqq 1.10$, saturation was not attained at 1.4°K and at fields $\leqq 14.24$ koe; therefore high-field measurements were made on these specimens at 4.2°K. The specimen with $x = 1.10$ was saturated at 70 koe. All others were not saturated below 80 koe; in these cases the values of spontaneous magnetization were obtained by extrapolation of the linear portions of the n_B vs H_a curves to $H_a = 0$. Values of moments were also obtained by extrapolation of n_B vs $1/H_a$ to $1/H_a = 0$. Both sets of values are given in Table IV and plotted vs x in Fig. 11. Note that the points for $x = 1.00$ and 1.10, which must lie on a reasonable curve representing the system, fit distinctly better on the $n_B(0)$ than on the $n_B(\infty)$ curve.

Curves of n_B vs T at 14.24 koe for various specimens are given in Fig. 12. To show the effect of different fields on the magnetization when saturation is not attained, typical curves for the specimen with $x = 1.25$ are given in Fig. 13.

When $x = 1.7$, there appears to be an antiferromagnetic transition at about 10°K. This is seen at fields of 9.6 koe or lower. There appears also to be a residual moment of $\approx 0.2\ \mu_B$ at 4.2°K.

Measurements were made on the specimen with $x = 0.55$ at fields from 4.8 to 80 koe at 4.2°K. Saturation was attained at 4.8 koe; the moment obtained was 4.62 μ_B, an excellent corroboration of the value obtained with the pendulum magnetometer (Fig. 12).

Curie temperatures, obtained from plots of $n_B^2\,(0,T)$ vs T (see above)

TABLE IV — CRYSTALLOGRAPHIC, MAGNETIC AND PREPARATION DATA FOR $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ SYSTEM

x	a(Å)	n_B[a]	T_C(°K)	Firing Procedure,[b] Temp., °C (hr)
0.40	12.348	4.65	432	1250(2), 1425($2\frac{1}{2}$), 1445($2\frac{1}{2}$)
0.55	12.336	4.60	396	1400($\frac{1}{2}$), 1450($2\frac{1}{2}$), 1465($2\frac{1}{2}$)
0.70	12.321	4.35	356	1450($\frac{1}{2}$), 1480(3), 1500(3)
0.85	12.308	4.25	327	1400($\frac{1}{2}$), 1490(2), 1500(2), 1550(2)
0.90	12.305	4.17		1400($\frac{1}{2}$), 1460(2), 1540(2)
1.00	12.289	3.8(3.8)[c]	265	1420($\frac{3}{4}$), 1480(3), 1520(3), 1500(2)
1.10	12.282	3.2(3.2)	220	1420(1), 1480–1500($4\frac{1}{2}$), 1520(4)
1.25	12.265	2.2(3.4)	187	1450($\frac{1}{2}$), 1525(3), 1550(3)
1.40	12.252	1.25(2.7)	110	1400($\frac{1}{2}$), 1500(2), 1560(2)
1.50	12.237	0.9(2.4)	84	1400($\frac{1}{2}$), 1500(4), 1525(5), 1550(5)
1.60	12.229	0.55(2.0)	50(?)	1400($\frac{1}{2}$), 1500($3\frac{1}{2}$), 1525(2), 1560(2)
1.70	12.220	0.35(2.25)		1375(1), 1500(2), 1550(4), 1590(4), 1575(4)
1.85	12.197			1300(1), 1500(4), 1525(4), 1535(7)

[a] For $x \leqq 0.90$, n_B was obtained by extrapolation to $T = 0$; for $x > 0.90$, n_B is at 4.2°K. [b] All specimens were first calcined at 500–900°C over a period of 1 hr. [c] Numbers in parentheses are from extrapolation to $H_a = \infty$, others to $H_a = 0$.

and $1/\chi_n$ vs T when possible, are listed in Table IV and plotted vs x in Fig. 5. The Curie temperatures obtained from the Gilleo treatment agree almost perfectly with those observed. The discrepancies are noticeable only at high x: for $x = 1.5$, it is 9°K, for $x = 1.6$ it is 14°K.

3.3.2 *Crystallographic Data*

Lattice constants for this system are given in Table IV and plotted vs x in Fig. 14. The limits of error assigned to each lattice constant are ±0.003 Å. All points but one deviate no more than 0.002 Å from the curve a vs x, and in no case is more than a deviation of $x = 0.02$ implied by any deviation of lattice constant; in fact, a deviation of $x = 0.02$ is implied for only three out of thirteen specimens, namely for those with $x = 0.90$, 1.00 and 1.70.

Careful examination of the powder data, both photographic and diffractometric, indicated that specimens with $x = 1.90$, 1.95 and 2.00 were not single-phase. As it is known that the Mg^{2+} ion may also occupy c sites in garnets, at least one specimen was made in which substitution was made in both c and a sites simultaneously. The garnet $\{Y_{2.8}Mg_{0.2}\}$-$[Mg_{1.7}Fe_{1.3}](Fe_{1.1}Si_{1.9})O_{12}$ has a lattice constant of 12.177 ± 0.003 Å.

Because such substitution is feasible, the *exact* maximum value of x in the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system cannot really be obtained and the preparation of specimens in this system requires more care perhaps than those in which a substituent ion prefers one site exclusively. (For this reason, we have included the firing data in Table IV.)

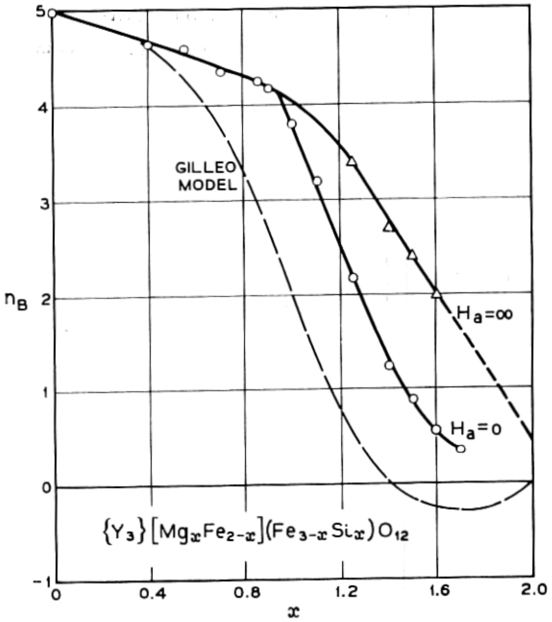

Fig. 11 — Spontaneous magnetizations vs composition for the system $\{Y_3\}$-$[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$. For $x \leqq 0.90$, saturation was attained at low fields and the n_B values were obtained by extrapolating $n_B(T)$ to $T = 0$°K. For $x \geqq 1.00$, saturation was not attained at low fields and the n_B values were obtained at 4.2°K by extrapolating $n_B(H_a)$ to $H_a = 0$ and $n_B(1/H_a)$ to $1/H_a = 0$. Shown also is the curve given by the Gilleo model.

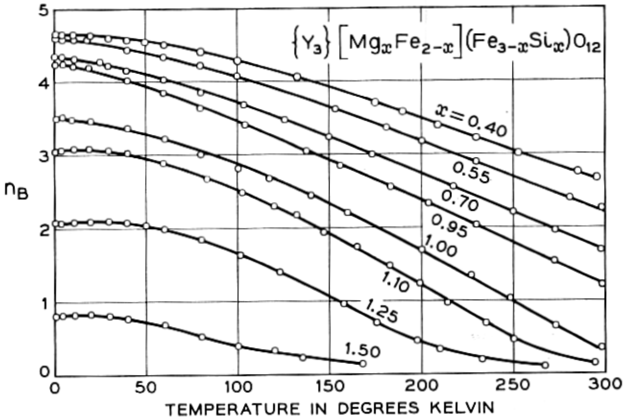

Fig. 12 — $n_B(14.24\text{ koe},T)$ vs T for specimens in the system $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$.

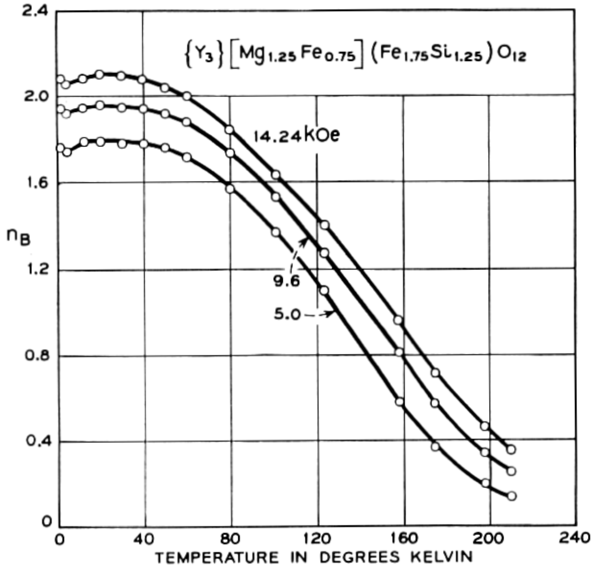

Fig. 13 — n_B vs T at different magnetic fields for $\{Y_3\}[Mg_{1.25}Fe_{0.75}](Fe_{1.75}Si_{1.25})O_{12}$.

The behavior of the lattice constant vs composition (Fig. 14) is again not linear for the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system. However, as will be shown later, of all the ions substituted for trivalent iron, the Mg^{2+} ion appears to make the "best fit," in the octahedral sites.

3.4 *Miscellaneous Specimens in the Systems* $\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}](Si_yFe_{3-y})O_{12}$, $\{Y_{3-y+x}Ca_{y-x}\}[Mg_xFe_{2-x}](Si_yFe_{3-y})O_{12}$ *and* $\{Y_{3-x-y}Ca_{x+y}\}[Zr_xFe_{2-x}](Si_yFe_{3-y})O_{12}$

Measurements were made on various specimens in these systems for the purpose of making certain points to be given later. In some cases, magnetic saturation was attained at low fields, in some at high fields, and not in some at fields to 80 koe. Results are given in Table V. Several Ge-substituted garnets analogous to the Si-substituted ones were also made. Data for these are given in Table VI.

3.5 *The System* $Y_3Al_xFe_{5-x}O_{12}$

3.5.1 *Magnetic Data*

Results obtained in these laboratories on part of this system were reported several years ago.[4] In the present investigation, the range of

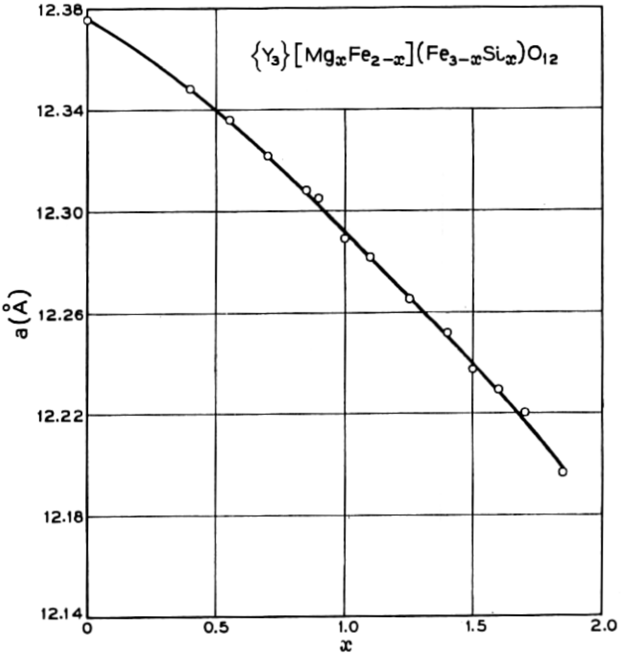

Fig. 14 — Lattice constant vs composition for the system $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$.

substitution has been extended. In this system, for $x \leqq 1.75$, magnetic saturation was attained at 1.4°K at applied fields $\leqq$9.6 koe.

Although there is no doubt that the specimen with $x = 2.0$ has a spontaneous magnetization, the results on the two specimens with $x = 2.5$ and 3.0 are not conclusive. In both cases, there appears to be an antiferromagnetic transition at about 10°K (see Fig. 15) which appears at fields of 4.8 and 9.6 koe, but not at 14.24 koe. The plots of $1/\chi_n$ vs T follow a Curie-Weiss law. For $x = 2.5$, the straight line portion of $1/\chi_n$ vs T intersects the T axis at -40°K and for $x = 3.0$ at -20°K. (See Fig. 16.) The values of μ_{eff} are 3.29 and 3.34 μ_B respectively. These results indicate that at least short-range antiferromagnetic interaction is present over a wide temperature range.

High-field measurements at 4.2°K were made on specimens with $x = 2.0$, 2.5, and 3.0. Each showed a residual moment when $n_B(H_a)$ was extrapolated to $H_a = 0$. The values obtained lie on the smooth curve joining the points at values of $x < 2.0$. This, however, may be fortuitous.

Table V — Magnetic and Crystallographic Data for Garnets $\{Y_{3-y+x}Ca_{y-x}\}[Mg_xFe_{2-x}](Si_yFe_{3-y})O_{12}$, $\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}]$-$(Si_yFe_{3-y})O_{12}$ and $\{Y_{3-x-y}Ca_{x+y}\}[Zr_xFe_{2-x}](Si_yFe_{3-y})O_{12}$

Octahedral Ion	x	y	n_B[a]	T_C, (°K)	Approx. Saturation Field, koe	a(Å)
Mg^{2+}	0.175	0.825	1.64	450	4.8	12.309
	0.30	1.47	−0.92		4.8	12.246
	0.18	1.57	−1.83		7.3	12.237
	0.90	1.10	3.2	294	9.6	12.283
	0.50	1.50	−0.24	325	9.6	12.244
	0.44	1.76	−1.29	298	9.6	12.223
	0.22	1.98	−3.1	245	60	12.191
	0.75	1.75	−0.18	250	11.3	12.214
Sc^{3+}	0.85	0.85	4.0		12.6	12.381
	0.30	1.47	−0.92		4.8	12.270
	0.30	1.52	−1.12		<4.8	12.265
	0.30	1.60	−1.39		<4.8	12.258
	1.10	0.90	2.8	220	>70	12.398
	1.00	1.00	2.9	235	>70	12.380
	0.90	1.10	2.8	260	>70	12.362
Zr^{4+}	0.76	0.24	5.9	340	>70	12.475
	0.60	0.60	4.39	360	9.6	12.421
	0.35	1.15	0.88	370	4.8	12.331
	0.30	1.20	0.41		9.6	12.319
	0.85	0.85	3.6		70	12.440
	0.30	1.60	−1.40		4.8	12.277
	1.10	0.90	1.8	190	>70	12.477
	1.00	1.00	2.1	200	>70	12.450
	0.90	1.10	1.9	210	>70	12.426
	0.60	1.60	−0.3	200		12.32
	1.25	1.25				12.466

[a] When approximate saturation field is ≧60 koe, these values are at 4.2°K; when >70, they are extrapolated to $H_a = 0$. All others at 0 or 1.4°K.

Table VI — Magnetic and Crystallographic Data for Garnets $\{Y_{3-y+x}Ca_{y-x}\}Mg_xFe_{5-x-y}Ge_yO_{12}$, $\{Y_{3-y}Ca_y\}Sc_xFe_{5-x-y}Ge_yO_{12}$ and $\{Y_{3-x-y}Ca_{x+y}\}Zr_xFe_{5-x-y}Ge_yO_{12}$

Octahedral Ion	x	y	n_B*	T_C(°K)	Saturation Field, koe	a(Å)
Mg^{2+}	1.00	1.00	3.9		60	12.364
	1.25	1.25	2.2		>70	12.362
Sc^{3+}	1.00	1.00	2.9		>70	12.457
Zr^{4+}	0.60	0.60	4.35	360	9.6	12.467
	0.85	0.85	2.9		>70	12.506
	1.00	1.00	1.6		>70	12.530

* See footnote, Table V.

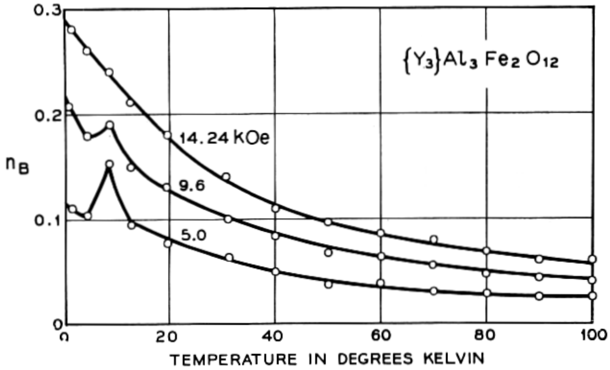

Fig. 15 — n_B vs T at different magnetic fields for $Y_3Al_3Fe_2O_{12}$.

The values of n_B at $H_a = 0$, $T = 0$ are listed in Table VII and plotted vs x in Fig. 17. The value for the specimen with $x = 1.00$ fits the curve somewhat better than that obtained in the previous work.[4] Curie temperatures, obtained as described earlier, are given in Table VII and plotted vs x in Fig. 18. Shown also are the values of T_C obtained from the Gilleo theory (see discussion).

3.5.2 *Crystallographic Data*

The lattice constants for specimens in this system are listed in Table VII and plotted vs x in Fig. 19. Shown also are the values obtained in

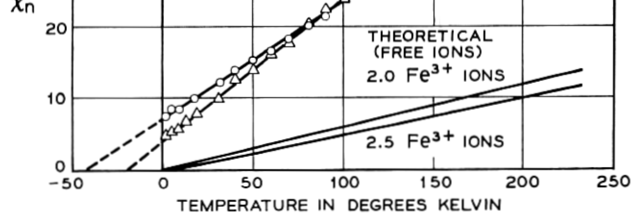

Fig. 16 — Reciprocal susceptibility vs temperature for $Y_3Al_{2.5}Fe_{2.5}O_{12}$ and for $Y_3Al_3Fe_2O_{12}$.

Table VII — Magnetic and Crystallographic Data for Garnets $Y_3Al_xFe_{5-x}O_{12}$

x	n_B		T_C(°K)		a(Å)	
	Present Work	Ref. 4	Present Work	Ref. 4	Present Work	Ref. 4
0.00	5.01	4.96		545	12.376	12.376
0.33		3.50		497		12.353
0.67						12.331
1.00	1.73	1.63	430	415	12.311	12.306
1.50	0.94		365		12.276	
1.67						12.265
1.75	0.55		295		12.256	
2.00	0.15		240		12.239	
2.33						12.215
2.50	−0.15(?)				12.206	
3.00	−0.25(?)				12.164	
3.00					12.161	12.159
5.00						12.003

the earlier investigation in these laboratories. Except for $x = 1.00$, the latter values lie within individual experimental error on the curve given by those more recently obtained and which are considered to be improved. To a value of $x = 2.5$, the a vs x behavior of the $Y_3Fe_{5-x}Al_xO_{12}$ system is linear (and extrapolates to a value of 12.030 Å for $Y_3Al_2Al_3O_{12}$). However, beyond this point, there appears to be an inflection toward the abscissa. Two specimens with $x = 3.00$ were carefully prepared,

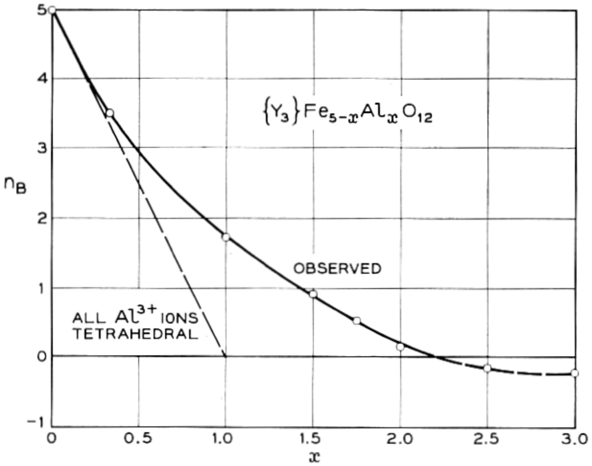

Fig. 17 — Spontaneous magnetization vs composition for aluminum-substituted yttrium iron garnets. (See text for explanation of values for $x > 2.0$.) Shown also is the line expected, when $0 \leqq x \leqq 1.0$, if all Al^{3+} ions replaced Fe^{3+} ions in tetrahedral sites.

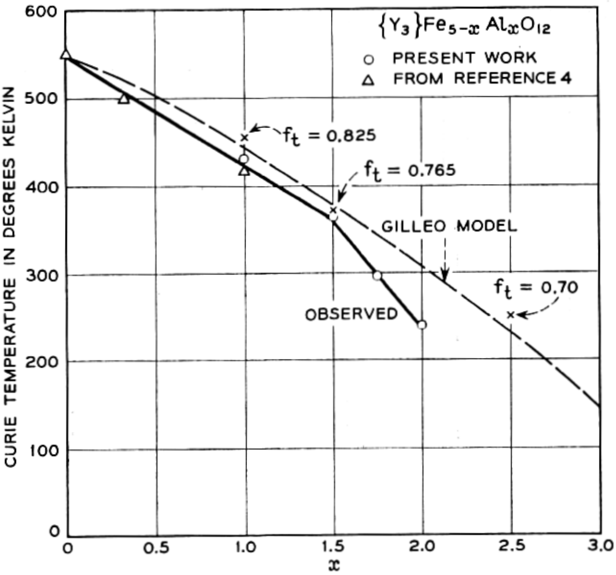

Fig. 18 — Curie temperatures vs composition for the aluminum-substituted yttrium iron garnets. Shown also is the curve obtained from the Gilleo model based on the distributions given in Fig. 29. The points denoted by crosses were obtained from specimens in which Mg^{2+} or Zr^{4+} were substituted for Fe^{3+} ions in octahedral sites and Si^{4+} for Fe^{3+} ions in tetrahedral sites, with required electrostatic balance by Ca^{2+} ions in dodecahedral sites (see text).

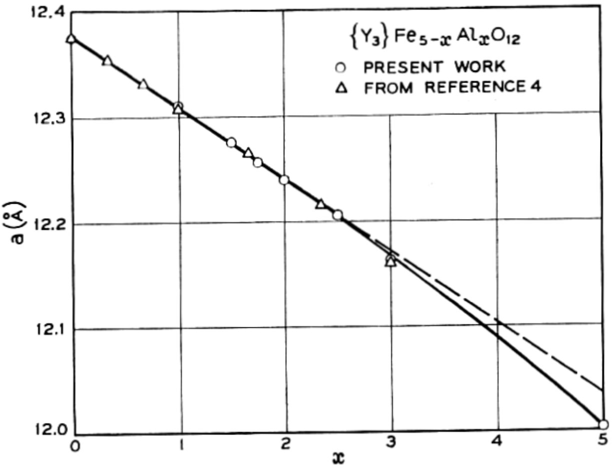

Fig. 19 — Lattice constant vs composition for aluminum-substituted yttrium iron garnets.

one with ultra-pure Al_2O_3 ; the lattice constants obtained for the two specimens are 12.164 and 12.161 Å (the latter for the ultra-pure specimen). The larger of the two values still is far from the straight line of the first half of the system (Fig. 19). As will be shown in a subsequent paper, a vs x for the $Gd_3Fe_{5-x}Al_xO_{12}$ system also does not behave exactly linearly, although the inflection occurs at a much lower value of x.

IV. GENERAL DISCUSSION

The original purpose of this investigation was to test further the Gilleo theory[3] and the extension thereof to substituted rare earth iron garnets.[25] Following this paper, we shall publish one concerned with the latter systems which will show, unfortunately, that this extension[25] of the theory does not fit the results because, as the present paper will show, the Gilleo theory for substituted yttrium iron garnets does not fit the results. In fact, no existing theory accounts for the observations quantitatively, and though the over-all agreement is rather poor, the Gilleo theory comes the closest.

In this paper, we shall develop a descriptive theory for substituted yttrium iron garnets which draws on various theories of Néel,[26] Yafet and Kittel,[5] Gilleo[3] and Anderson.[27] The possibility of a quantitative theory which can *predict* the magnetic behavior of the substituted garnets is complicated by the various effects of substitution on the magnetic structure. These effects appear to be more complex for higher substitution, and in fact there is now evidence that, especially for high substitution, *different* nonmagnetic ions in the *same* site produce different behavior (see also Refs. 10–13 and Section 4.3). In a sense, this is a rather unfortunate result because, before we discovered it, we believed that even without a quantitative theory, we should be able from limited data to predict the magnetic behavior of any substituted yttrium iron garnet. Actually, as will be shown later, this can still be done within a certain range of substitution and for particular ions.

The present data strongly indicate that the Si^{4+} ion has a preference exclusively for tetrahedral sites in the garnets.[28] The preference of the Ge^{4+} ion for tetrahedral sites is not quite as great as that of the Si^{4+} ion; that is, with increasing Ge^{4+} ion substitution, there does appear to be some tendency for a small percentage of these ions to go into octahedral sites. However, this percentage is not nearly as large as previously[21] indicated.

Assuming that our present conclusion regarding the site preference of the Si^{4+} ion is correct, we may compare Fig. 4 with the observed data,

$n_B(0°\mathrm{K})$ vs x calculated on the basis of a simple Néel model[26] and on that proposed by Gilleo.[3] It is seen that neither model gives satisfactory agreement with the observations over the whole range of substitution. In the range to $x \approx 1.9$ there is apparently better agreement with the simple Néel model than with the Gilleo one. The observed minimum, $-3.85\ \mu_B$, occurs at $x = 1.94$; the minimum predicted by the Gilleo model is $-1.8\ \mu_B$ at $x = 1.77$; the Néel theory does not predict a minimum, but does not preclude one (see Section 11 of Ref. 26). Agreement of observed 0°K moments for octahedral substitution (see Fig. 7) with those calculated with the Gilleo theory is somewhat better than for tetrahedral ion substitution, but it cannot be said to be satisfactory. For the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system (see Fig. 11), the moments calculated with the Gilleo theory are also not in good agreement with the observed values. Thus, although the Gilleo theory predicts a maximum for octahedral and a minimum for tetrahedral substitution, it does not appear to account quantitatively for the observed moments in any of the systems. It should be pointed out, however, that unlike others, this theory takes into account the statistical nature of the problem, while on the other hand it has neglected the importance of intrasublattice interactions.

Wojtowicz[29] has shown that intrasublattice interactions are negligible in the (unsubstituted) yttrium and lutecium iron garnets, while the results of Pauthenet[7] and of Aleonard[30] based on the Weiss molecular field theory (as applied by Néel to ferrospinels) show that they are important. The theory of Yafet and Kittel,[5] also based on the Weiss molecular field theory, leads to the result that at a certain concentration of nonmagnetic ions in a particular site in a ferrospinel, a transition occurs to a ground state in which there is canting of moments in the unsubstituted sublattice. We shall show below that this theory also does not account for the behavior of the substituted garnets. Nevertheless, an important implication of our structural argument is the importance of intrasublattice interactions.

As indicated earlier, there is an arithmetic error in the de Gennes application[6] of the Yafet-Kittel theory to the Sn^{4+} ion substituted garnets: the molecular field equations for YIG determined by Pauthenet[7] should have been written

$$H_A = -7000\ M_A - 14{,}800\ M_B$$

$$H_B = -14{,}800\ M_A - 4200\ M_B$$

from which $n = +14{,}800$, $\alpha_2 = -0.95$, $\gamma_2 = -0.57$. Thus according to the theory it is at $y = 0.57$ or $x = 0.29$ that the canting first occurs.

Also, the maximum moment, 6.45 μ_B, in the system should then be attained at $x = 0.29$. Actually, if this system is assumed to behave similarly to those of Fig. 7, the maximum moment of 7.8 μ_B is attained at about $x = 0.7$ and the canting appears experimentally to occur earlier (see later discussion).

But the discrepancies for the silicon-substituted yttrium iron garnet are even worse. Again using the Pauthenet equations, the triangular configuration (c) of the Yafet-Kittel theory would be expected, that is, for $1/|\alpha_2| < y$. The system is $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$; thus $y = 2/(3 - x)$. Canting should therefore begin at $x = 1.1$. For $x < 1.1$, $n_B(0°K) = 5(1 - x)$ while for $x > 1.1$,

$$n_B(0°\mathrm{K}) = 5(3 - x)(1 - 1/|\alpha_2|) = -0.25(3 - x).$$

The algebraic minimum, $-0.5\ \mu_B$, should occur at $x = 1.1$; the observed values are $-3.85\ \mu_B$ at $x = 1.94$.

For the $\{Ca_3\}[Fe_2](Si_3)O_{12}$ specimen, the value of $1/\chi_o$ in units comparable to those used by Aleonard,[30] is -1.9. Thus $n_{aa} = -1.9$, which is about $\frac{1}{12}$ the value of n_{aa} in YIG. This value of n_{aa} indicates very weak magnetic interaction in line with the θ_p of 29°K and the possible Néel temperature of 9°K and also implies that the interaction coefficients change with substitution. Thus it appears that the use of the interaction coefficients of YIG to predict the behavior of the entire system is not correct.

In a first approximation, it appears now that the following picture of the behavior of the substituted yttrium iron garnets (discussed in this paper) is a plausible one. Yttrium iron garnet itself may be considered an ideal Néel ferrimagnet; that is, at 0°K, the moments of all a-site Fe^{3+} ions are exactly parallel, the moments of all d-site Fe^{3+} ion moments are exactly parallel and the moments of a-site Fe^{3+} ions are exactly antiparallel to those in the d-sites. Under these circumstances the theoretical moment, 5.0 μ_B per formula unit, should be and is observed. When the d-sites are filled with nonmagnetic ions, as in $Ca_3Fe_2Si_3O_{12}$, at the very least, short-range antiferromagnetic order occurs among the moments of the a-site Fe^{3+} ions. When the a-sites are filled with nonmagnetic ions, as for example in hypothetical $\{YCa_2\}[Zr_2](Fe_3)O_{12}$, at the very least, short range antiferromagnetic order occurs among the moments of the d-site Fe^{3+} ions (see also Ref. 27).

Thus, on a structural basis, replacement of Fe^{3+} ions in a particular site by nonmagnetic ions must ultimately change a ferrimagnetic to some type of antiferromagnetic structure. Figs. 4 and 7 show that this occurs continuously; Figs. 20 and 21 show the connection between the

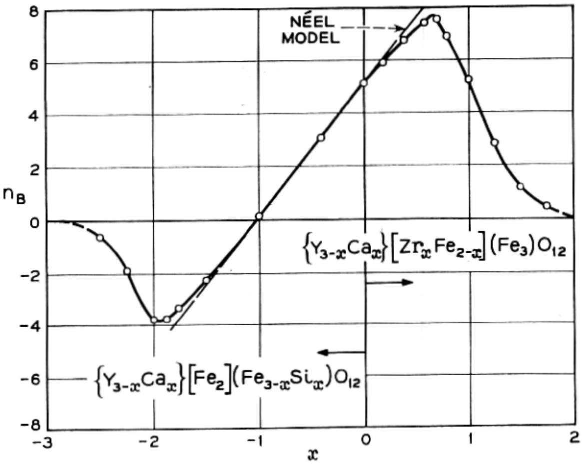

Fig. 20 — Continuous relation between the systems $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ and $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$.

silicon- and zirconium-substituted yttrium iron garnet systems and give a pictorial summary of the behavior of these systems. Now, let us assume (see Fig. 21) that in the silicon-substituted garnets at 0°K, only the effective moment[31] of the octahedral Fe^{3+} ion sublattice is reduced by *canting* of the moments of these ions because of linkages to tetrahedral nonmagnetic ions and the effect of *a*-*a* antiferromagnetic interaction. Analogously, we assume (see Fig. 21) that in the zirconium (or similar) ion substituted garnets, only the effective moment of the tetrahedral Fe^{3+} ion sublattice is reduced. We can then determine the average effective[31] moment per octahedral and per tetrahedral Fe^{3+} ion, respectively, as a function of x. The results (Fig. 22, curves 1 and 4) indicate that far more silicon than zirconium substitution is always required to cause reduction of the average Fe^{3+} ion moment in the octahedral and tetrahedral sublattice, respectively.

A small part of the arrangement of cations in the *a* and *d* sites of a zirconium-substituted garnet crystal is shown in Fig. 23. For further clarity, we show in Fig. 24 the arrangement of cations in the three types of sites in four octants of the garnet unit cell. In yttrium iron garnet,[32] each ion on an *a* site is linked through pairs of oxygen ions to eight *a*-site ions at distance 5.36 Å and through single oxygen ions to six *d*-site ions at 3.46 Å. Each *d*-site ion is linked through pairs of oxygens to four *d*-site ions at 3.79 Å and through single oxygens to four *a*-site ions at 3.46 Å. These distances and linkages through oxygen ions imply

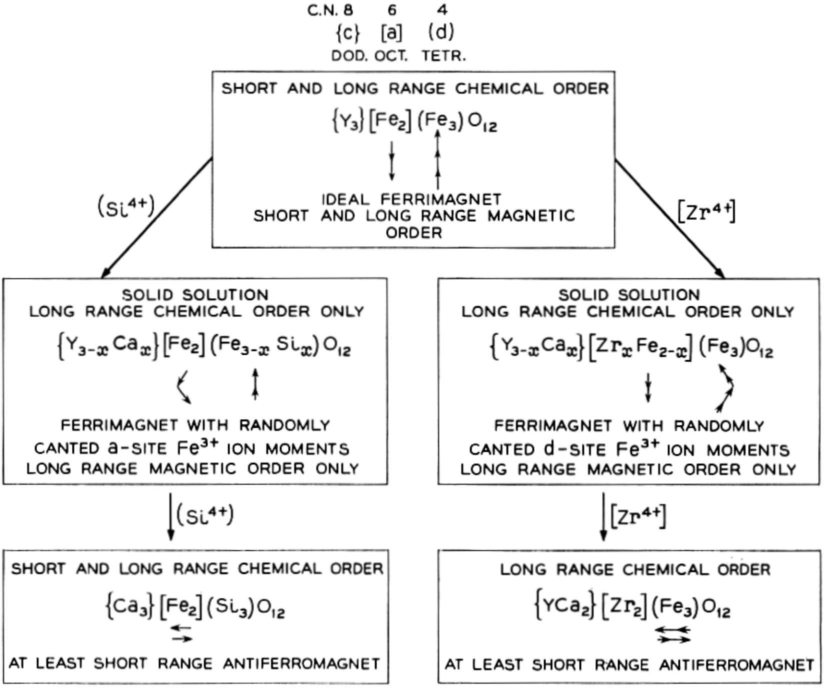

Fig. 21 — Summary of proposed explanation for the magnetic behavior of the systems $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ and $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$.

that in YIG the *a-d* interaction should be strongest, next the *d-d* and finally the *a-a*.

The results shown in Fig. 22 indicate that the average *a-d* interaction weakens as substitution of nonmagnetic ions is made in either site. Nevertheless the *a-d* interactions remain dominant until the changes in direction of the curves are reached. At $x_o = 0.70$, a transition occurs to a state in which the *d-d* interactions are dominant.[33] Similarly at $x_t = 1.92$, a transition occurs to a state in which the *a-a* interactions are dominant.[33] Because the transition occurs for $x_t = 1.92$ as against $x_o = 0.70$, there is little question that the *d-d* interactions in the Zr^{4+} ion substituted garnets are stronger than the *a-a* interactions in the Si^{4+} ion substituted system. Moreover, as shown in Fig. 25, the ratio of x_t/x_o required to reduce the effective Fe^{3+} ion moment to a particular value is everywhere greater than 1.75.

The decreases in effective moments of the sublattices with increasing x are small but real until the transition points are reached. However, it

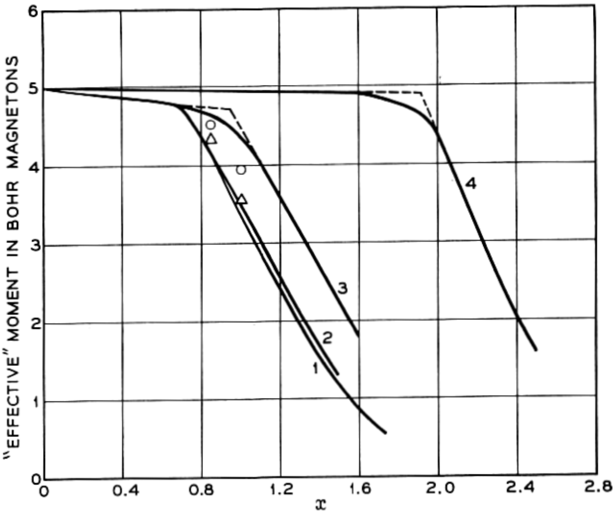

Fig. 22 — "Effective" moment (see Ref. 28) per Fe^{3+} ion in (1) tetrahedral sites for $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ system; (2) tetrahedral sites for $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ system; (3) tetrahedral sites for $\{Y_3\}[Mg_xFe_{2-x}]$-$(Fe_{3-x}Si_x)O_{12}$ system; (4) octahedral sites for $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ system. Circle points are for $\{Y_{3-x}Ca_x\}[Sc_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ specimens and triangles for $\{Y_{3-2x}Ca_{2x}\}[Zr_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ specimens (see text).

would appear from the Yafet-Kittel theory that if there were no short-range disorder, there should actually be no decrease in effective moments before the transitions are reached, since the ground state before the transition should be an ideal ferrimagnetic one, with no splitting of the sublattices. That is, because the *a-d* interactions are dominant, the molecular field of the *d* sublattice, in the case of tetrahedral substitution, would act to keep the *a* sublattice moments aligned antiparallel to the *d*; while in the case of octahedral substitution, the molecular field of the *a* sublattice would act to keep the *d* sublattice moments aligned antiparallel to the *a*. On the other hand, it would appear that chemical disorder which always exists in a solid solution would cause magnetic disorder. This chemical disorder implies further that distinct "sublattice splitting" does not really occur in these substituted garnets, but rather that the canting of the moments within a sublattice is random, and that since the crystals are ferrimagnetic, a statistical long-range order must exist.

We see also in Fig. 22 that although until the transition points are reached the rates of decrease in effective moments of the sublattices with increasing x are both small, that for tetrahedral substitution is

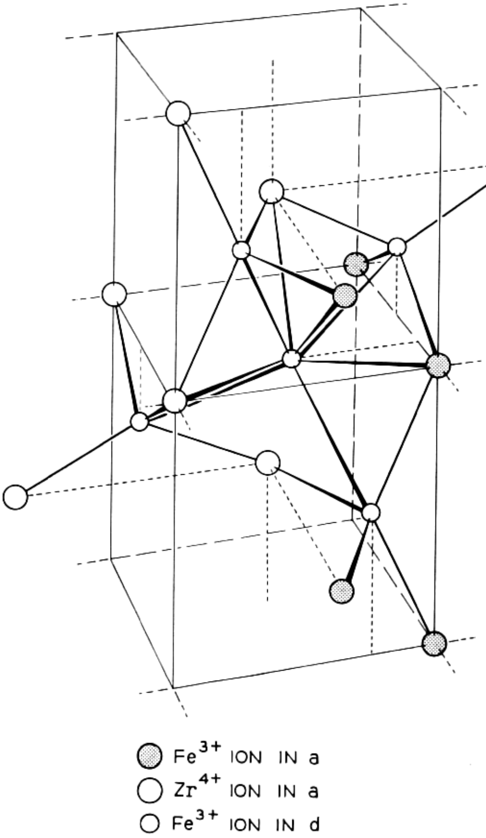

Fig. 23 — Part of the arrangement of cations in the *a* and *d* sites of a zirconium-substituted yttrium iron garnet crystal.

much smaller than for octahedral substitution. This shows again that the *d-d* interactions are stronger than the *a-a*. Now it is unlikely that short-range magnetic disorder occurs before the transition and not beyond it. Thus it appears that what is occurring differs from the idealization given by the Yafet-Kittel theory. The transition is almost surely one at which a change from dominance of the *a-d* to *a-a* or *d-d* interactions occurs, but not one in which there is an abrupt change from a strictly ferrimagnetic to a canted ground state. That is to say, there is always a competition among the various interactions, and as soon as the strictly antiparallel one is disrupted, one of the others may begin to manifest itself.

To emphasize at this point the importance of the competing inter-

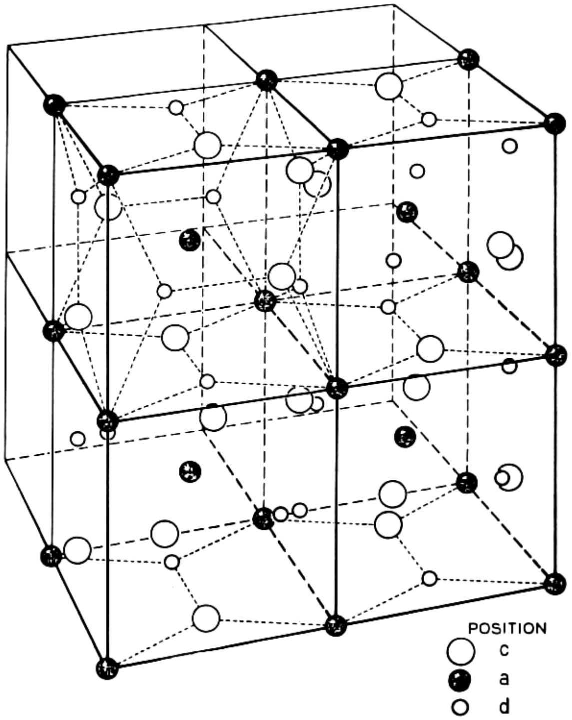

Fig. 24 — Arrangement of cations in *c*, *a*, and *d* sites in four octants of the garnet unit cell.

actions, we outline some further evidence to be discussed in more detail later. Suppose we look at a system in which substitution of nonmagnetic ions is made in both sites. We choose ions such as Sc^{3+} and Si^{4+} which we believe have exclusive preference for octahedral and tetrahedral sites respectively. A formula representing such a system is $\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$. Suppose we begin with $y = 0$ and $x = 0.30$. We see from Fig. 22 that some canting will occur among the Fe^{3+} ion moments on the tetrahedral sites. Now we keep x constant and increase y. As y increases, the canting of the *d*-site Fe^{3+} ion moments will decrease. A value of y will be reached for which the particular garnet will again appear to be an ideal Néel ferrimagnet. The value of y for which this occurs (see Table V) is 1.52, that is to say, for the garnet $\{Y_{1.48}Ca_{1.52}\}[Sc_{0.30}Fe_{1.70}](Si_{1.52}Fe_{1.48})O_{12}$. For this garnet, the difference in the number of Fe^{3+} ions in the two sites is 0.22, which according to the Néel model would give a 0°K spontaneous magnetization of $-1.10\ \mu_B$; the

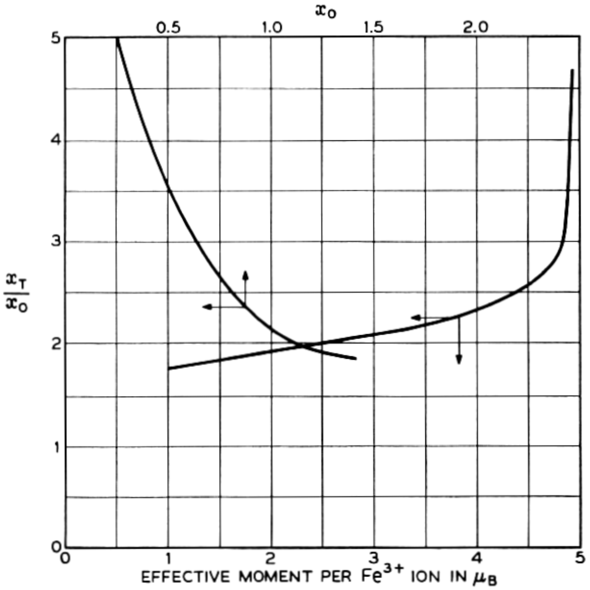

Fig. 25 — The ratio, x_t/x_o, of tetrahedral to octahedral nonmagnetic ions, required to produce the same effective moment per Fe^{3+} ion in the appropriate sublattice. Also shown is the curve x_t/x_o vs x_o.

observed value, $-1.12\ \mu_B$, is in good agreement with this value. Note (Table V) that for the garnet $\{Y_{1.53}Ca_{1.47}\}[Sc_{0.3}Fe_{1.7}](Si_{1.47}Fe_{1.53})O_{12}$, the observed 0°K spontaneous magnetization is $-0.92\ \mu_B$, to be compared with $-5 \times 0.17 = -0.85\ \mu_B$ from the Néel model. Thus for this garnet canting of the Fe^{3+} ion moments occurs in the tetrahedral sites. On the other hand, in the case of the garnet $\{Y_{1.4}Ca_{1.6}\}[Sc_{0.3}Fe_{1.7}]$-$(Si_{1.6}Fe_{1.4})O_{12}$, the observed 0°K spontaneous magnetization is $-1.39\ \mu_B$, to be compared with $-5 \times 0.30 = -1.50\ \mu_B$ from the Néel model. Thus for this garnet canting of the Fe^{3+} ion moments occurs in the octahedral sites. (This example also demonstrates that the 0.3 Sc^{3+} ions are in octahedral sites exclusively.)

The above discussion has been concerned only with what occurs at or very near 0°K. It appears, however, that the behavior of these substituted garnets may be similar at higher temperatures. We note (see Fig. 5) that x_t/x_o required to give the same Curie temperature is everywhere greater than 1.68. Fig. 5 also shows the effect of transition from *a-d* to intrasublattice interaction dominance, even though, except for the $Y_3[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ systems, it does not show as clearly as Fig. 22 where the transition values of x are.

Also shown in Fig. 5 is the plot of T_C vs x obtained from the Gilleo theory. The agreement with observed Curie temperatures is rather good; for the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system, it is almost perfect. Thus it is possible that, although the Gilleo theory does not hold at low temperatures, it does at higher temperatures. However, it is also possible that this good agreement of Curie temperatures is fortuitous (see later discussion).

In the system $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ there is always 1.0 more Fe^{3+} ion per formula unit in the tetrahedral than in the octahedral sites. Thus the apparently continuous decrease in total 0°K moment (Fig. 11) in the early stages of substitution must, according to our model, mean that canting of the Fe^{3+} ion moments is occurring in the tetrahedral sites. If we assume that the moments of the a-site Fe^{3+} ions remain parallel we may determine for each composition the effective moment contributed to the ferrimagnetism by each tetrahedral Fe^{3+} ion, as shown in Fig. 22, curve 3.

We note that there are two main regions of behavior similar to those in the systems in which substitution of nonmagnetic ions is made exclusively either in octahedral or in tetrahedral sites. The decrease in effective moment (or increase in canting) is initially at the same rate as in the $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ or $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ systems, but beyond $x \approx 0.7$ the rate of decrease of effective moment is lower than in the latter system. Thus we conclude tentatively (see later discussion) that:

(1) canting of Fe^{3+} ion moments in the tetrahedral sublattice occurs from the beginning of substitution;

(2) in the region $0 < x \leqq 0.7$, the replacement of d-site Fe^{3+} ions by Si^{4+} ions does not have a significant effect on the average d-d interaction strength, but when $x > 0.7$, decreases the average d-d interaction strength; thus

(3) in the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system, the transition to the dominance of the d-d interactions over the a-d interactions (see Ref. 33) occurs at $x \approx 0.95$ as against $x = 0.70$ in the $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ system.

The Curie temperatures of the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system are shown in Fig. 5 (curve 1). The latter are almost everywhere smaller than those of the $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ system for the same x. However, the differences are nowhere greater than 35°K even though x in the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system represents as many nonmagnetic ions in d as in a sites, or twice as much *total* substitution of nonmagnetic ions. This comparison already indicates that the canting may also have an effect on the Curie temperature; that is, that the intrasublattice interactions are important over a wide temperature range and not only at 0°K.

We may obtain a clearer idea of the effect of the intrasublattice interactions on the Curie temperatures by plotting T_C vs total per cent substitution of nonmagnetic for Fe^{3+} ions as in Fig. 26 for exclusively *a*-site, *d*-site and equal *a*-*d*-site substitution. Now we see that on this basis, the Curie temperatures for the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system are everywhere substantially greater than those for the $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ system for the same total per cent replacement of Fe^{3+} ions. Further, to about 37 per cent substitution, the values of T_C for the $Y_3[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system are lower than for the $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ system. (The actual values of x are about 0.9 and 1.85 for the systems, respectively.) In the region below 37 per cent substitution, canting of *d*-site moments in the former system is greater than canting of *a*-site moments in the latter (Fig. 22). In the region above 37 per cent the

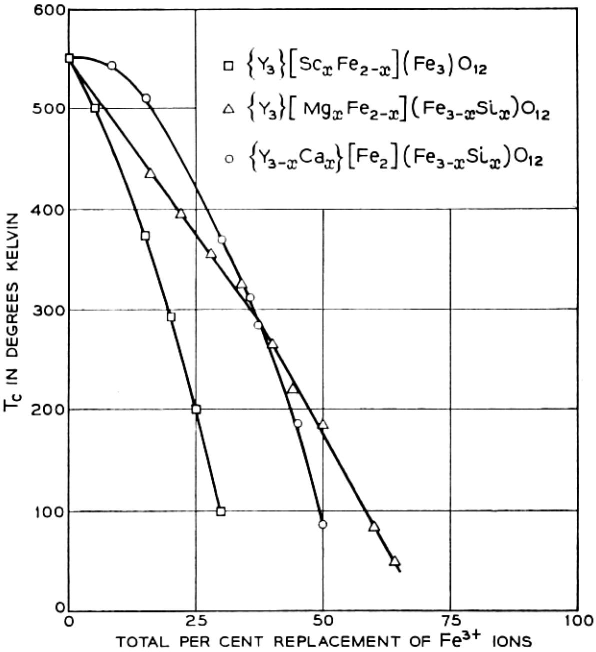

Fig. 26 — Curie temperatures vs total per cent replacement of Fe^{3+} ions.

reverse is true. For example, for 50 per cent substitution the formulas are respectively $Y_3[Mg_{1.25}Fe_{0.75}](Fe_{1.75}Si_{1.25})O_{12}$ and $\{Y_{0.5}Ca_{2.5}\}[Fe_2]$-$(Fe_{0.5}Si_{2.5})O_{12}$; Fig. 22 shows that the effective moment of the *d*-site Fe^{3+} ion in the former is 3.35 μ_B while that of the *a*-site Fe^{3+} ion in the latter is 1.6 μ_B. [Thus we see also why even when there are only 1.8 Fe^{3+} ions left per formula unit, i.e., $\{Y_3\}[Mg_{1.6}Fe_{0.4}](Fe_{1.4}Si_{1.6})O_{12}$, we still have a ferrimagnetic specimen with $T_C = 50°K$. In fact, even when $x = 1.7$ (1.6 total Fe^{3+} ions per formula unit), the garnet may still be ferrimagnetic.]

We should expect that in the general system $\{Y_{3+x-y}Ca_{y-x}\}[Mg_xFe_{2-x}]$-$(Fe_{3-y}Si_y)O_{12}$ there will be, for a given $(x + y)$, a value of x (or $f_t = y/x + y$) such that there will be no canting of Fe^{3+} ion moments in either sublattice. We saw above for $x + y = 2.50$ (50 per cent substitution) that the effective moments when $x = y = 1.25$ ($f_t = 0.5$) and when $x = 0$, $y = 2.50$ ($f_t = 1.0$) are both lower than 5.0 μ_B. Because canting occurs in different sublattices for these two garnets, the garnet in which no canting will occur [for this value of $(x + y)$] should have $0.5 < f_t < 1.0$. Moreover, this garnet should have the maximum Curie temperature for $x + y = 2.50$. We have not attempted to obtain this particular garnet, but in the course of our investigations we have made one very close to it. The garnet with formula $\{Y_2Ca\}[Mg_{0.75}Fe_{1.25}](Fe_{1.25}Si_{1.75})O_{12}$ ($f_t = 0.70$) has a 0°K moment of -0.18 μ_B (Table V). Our accumulated data indicate that the canting occurs in the tetrahedral sites (the octahedral sublattice then dominates, therefore the choice of negative sign); the effective moment of a tetrahedral Fe^{3+} ion is 4.85 μ_B. The Curie temperature is 250°K; for $f_t = 0.50$ and 1.00, the Curie temperatures (see Tables I and IV, respectively) are 187 and 86°K respectively. It is also noteworthy that the garnet with $f_t = 0.70$ saturates at low temperatures at about 10 koe, whereas the other two do not.

In the foregoing discussion, it would appear that it was tacitly assumed that the 0°K moments and Curie temperatures do not depend significantly on the *type* of nonmagnetic ion substituted for the Fe^{3+} ion in yttrium iron garnet. That is to say, it would appear that we had implied that a garnet such as $\{Y_{3-x-y}Ca_{x+y}\}[Zr_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$ will have the same 0°K moment and Curie temperature as

$$\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$$

or as $\{Y_{3+x-y}Ca_{y-x}\}[Mg_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$ provided all x's are the same and all y's are the same. This appears to be a generally accepted idea.

However, there now appears to be some evidence that this is not generally true (see also Refs. 10–13 and Section 4.3). In Fig. 7 and Table III, it will be noted that beyond about $x = 0.7$ the moments for the system $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ are lower than those for the system $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$. The differences are outside experimental error. We shall discuss substituted gadolinium iron garnets fully in a future paper, but as further evidence of the reality of the differences in the two systems we point out here the moments obtained from high-field measurements at 4.2°K of $\{Gd_2Ca\}[ZrFe](Fe_3)O_{12}$ and $\{Gd_2Y\}[ScFe](Fe_3)O_{12}$. Extrapolation of $n_B(H_a)$ vs H_a to $H_a = 0$ gives 5.3 and 4.6 μ_B for these, respectively. Extrapolations of $n_B\ (H_a)$ vs $1/H_a$ to $1/H_a = 0$ give 7.1 and 6.7 μ_B for these respectively. Regardless of which values are more nearly the correct ones for these garnets, the moment of the Zr-substituted gadolinium iron garnet is significantly higher than that for the Sc-substituted one. Because the net moments from the iron sublattices of these garnets are antiparallel to those of the gadolinium sublattices, the net moment per formula unit of the Zr-substituted gadolinium iron garnet *should* be larger than that of the Sc-substituted gadolinium iron garnet, if the moments of the analogous substituted yttrium iron garnets are in the reverse order.

One may well ask whether these differences are a result of some Zr^{4+} or Sc^{3+} ions being in tetrahedral sites. While this possibility cannot be completely eliminated, evidence will be presented which indicates that it does not account for the results. Now, the Zr^{4+} ion is a rather large one; in ZrO_2 it prefers eight-coordination,[34] while in zirconates it prefers six-coordination. Lower coordination for Zr^{4+} has, as far as we know, not been reported, although there is no *a priori* reason to deny its possibility. If we, however, assume that all Zr^{4+} ions go into octahedral sites in the garnets, we may ask if some Sc^{3+} ions go into tetrahedral sites. Consideration of this possibility leads to the conclusion that if some Sc^{3+} ions do go into tetrahedral sites, the percentage doing so decreases to a minimum and then increases again.

We arrive at this conclusion in the following way. We assume that a small amount of Sc^{3+} ions in the tetrahedral sites does not alter the effect of the presence of the large amount of Sc^{3+} ions in octahedral sites on the moments of the Fe^{3+} ions in the tetrahedral sites. Thus for one Sc^{3+}, if we assume a formula of $\{Y_3\}[Sc_{0.9}Fe_{1.1}](Fe_{2.9}Sc_{0.1})O_{12}$, the effective moment (Fig. 23) of a tetrahedral Fe^{3+} ion will be 3.85 μ_B. The 0°K spontaneous magnetization per formula unit would then be 5.7 μ_B, in agreement with the observed value. A distribution given by $\{Y_3\}[Sc_{0.95}Fe_{1.05}](Fe_{2.95}Sc_{0.05})O_{12}$ gives a moment per formula unit of

5.4 μ_B. For 1.25 Sc^{3+} ions with a distribution given by $\{Y_3\}[Sc_{1.2}Fe_{0.8}](Fe_{2.95}Sc_{0.05})O_{12}$, the effective tetrahedral Fe^{3+} ion moment is 2.43 μ_B and the 0°K moment per formula unit is 3.16 μ_B, which is in good agreement with the observed value. The distribution $\{Y_3\}[Sc_{1.15}Fe_{0.85}](Fe_{2.90}Sc_{0.10})O_{12}$, however, leads to a 0°K moment per formula unit of 3.4 μ_B. For 1.50 Sc^{3+} ion with a distribution given by $\{Y_3\}[Sc_{1.4}Fe_{0.6}](Fe_{2.9}Sc_{0.1})O_{12}$, the derived 0°K moment per formula unit is 1.4 μ_B, in agreement with the observed values.

One can see then from these examples that if the assumptions were correct, the percentages of Sc^{3+} ions entering tetrahedral sites would be 10, 4 and 6.7 respectively. Such a situation is felt to be rather unlikely; one would expect the fraction of Sc^{3+} ions going into tetrahedral sites to increase monotonically. Under such conditions, the curves of Fig. 7 for the Zr- and Sc-substituted yttrium iron garnets should actually cross at a value of $x > 0.70$. It is still possible that very small amounts of Zr^{4+} ions may go into tetrahedral sites, in which case, if Sc^{3+} ions also go into tetrahedral sites, the situation would be more complex; but there is further evidence that this alone would still not account for the observations.

Fig. 4 indicates a resemblance of the behavior of the Ge- and Si-substituted yttrium iron garnets to those of the Zr- and Sc-substituted garnets. At $x > 1.0$, the 0°K moments per formula unit (absolute values) of the Ge-substituted garnets are lower than those for the Si-substituted garnets. Now, in Figs. 7 and 23 and Table III it will be noted that to $x = 0.70$ the Zr and Sc-substituted garnet systems behave in very nearly the same way. Below $x = 0.70$, it is expected that all these garnets will saturate magnetically at moderate fields. It is mainly in the region in which the intrasublattice interactions become dominant that substantial differences occur (but see Refs. 10–13 and Section 4.3); this is the region in which saturation is not attained at fields to 80 koe.

As pointed out earlier, it is now felt that it is unlikely that Si^{4+} ions enter the octahedral sites in the garnets. Thus it may be concluded that because between $x \approx 1.0$ and 1.92 the Ge-substituted garnets have lower moments (absolute values) than the analogous Si^{4+} ion substituted garnets, some Ge^{4+} ions do enter octahedral sites. When $x = 1.00$, the distribution of ions is probably given by $\{Y_2Ca\}[Fe_{1.99}Ge_{0.01}](Fe_{2.01}Ge_{0.99})O_{12}$. When $x = 1.92$, the distribution is probably given by $\{Y_{1.08}Ca_{1.92}\}[Fe_{1.94}Ge_{0.06}](Fe_{1.14}Ge_{1.86})O_{12}$. However, if the percentage of Ge entering octahedral sites increases with increasing total substitution, and if there are no other effects on the spontaneous magnetization resulting from the particular ion, the curve for Ge substitution should cross that for Si substitution.

If, for the sake of discussion, a linear relation between percentage Ge in octahedral sites vs total Ge substitution is assumed for $x > 1.0$, the distribution for $x = 2.0$ would be given by $\{YCa_2\}[Fe_{1.93}Ge_{0.07}]$-$(Fe_{1.07}Ge_{1.93})O_{12}$ and for

$$x = 2.25, \{Y_{0.75}Ca_{2.25}\}[Fe_{1.91}Ge_{0.09}](Fe_{0.84}Ge_{2.16})O_{12} .$$

Using Fig. 22, the effective moments of the octahedral Fe^{3+} ions would be 4.70 and 3.40 μ_B respectively. The 0°K moments then should be -4.0 and -2.3 μ_B respectively, as compared with the observed values -3.15 and -1.55 μ_B respectively. Note (see Fig. 4) that the observed value for 2.0 Si is -3.8 μ_B. It is probable that for $x = 1.92$ there is somewhat less than 0.06 Ge in octahedral sites, but regardless of the actual amounts, the single assumption of some Ge^{4+} ions in octahedral sites *cannot* account for the observations if it is also assumed that Si^{4+} ions go only into tetrahedral sites in the garnets. But even if the latter assumption were unacceptable, it is certain that the Si^{4+} ions would have a greater preference for the tetrahedral sites than Ge^{4+} ions. And it would then still appear necessary for the Ge curve to cross the Si curve if there were no additional effect resulting from the substitution of a particular ion.

This conclusion also is perhaps contrary to the thinking on ferrimagnetic materials. Generally, it is believed that for a given total substitution, when the net difference in the number of Fe^{3+} ions is greater, the moment per formula unit should be greater. However, there is concrete evidence that the conclusion is correct.

This may be illustrated by the following example. The garnet $\{Y_{1.24}Ca_{1.76}\}[Mg_{0.22}Fe_{1.78}](Fe_{1.02}Si_{1.98})O_{12}$ has a 0°K moment of -3.1 μ_B[35] and a Curie temperature of 245°K. The garnet $\{Y_{0.8}Ca_{2.2}\}[Fe_2]$-$(Fe_{0.8}Si_{2.2})O_{12}$ has a 0°K moment (see Fig. 4) of -2.3 μ_B and a Curie temperature (see Fig. 5) of 200°K. (Note that the difference in the number of Fe^{3+} ions in the former is 0.76 and in the latter 1.2.) If it is again assumed that the tetrahedral Fe^{3+} ion moments remain parallel, then in the former the effective moment of an octahedral Fe^{3+} ion is 4.5 μ_B. Examination of Fig. 22 shows that this is just slightly larger than the effective moment of the octahedral Fe^{3+} ion in $\{Y_{1.02}Ca_{1.98}\}$-$[Fe_2](Fe_{1.02}Si_{1.98})O_{12}$. The 45°K lower Curie temperature of $\{Y_{0.8}Ca_{2.2}\}$-$[Fe_2](Fe_{0.8}Si_{2.2})O_{12}$ than that of $\{Y_{1.24}Ca_{1.76}\}[Mg_{0.22}Fe_{1.78}](Fe_{1.02}Si_{1.98})O_{12}$ is in accord with the stronger interactions in the latter. The Curie temperature of the latter is 25°K lower than that of $\{Y_{1.02}Ca_{1.98}\}[Fe_2]$-$(Fe_{1.02}Si_{1.98})O_{12}$ (Fig. 5), which has a larger *number* of interactions of about the same strength.

The effects of different ions on magnetic behavior are more marked in several of the specimens shown in Tables IV and V. The systems involved are $\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}](Si_yFe_{3-x})O_{12}$, $\{Y_{3-y+x}Ca_{y-x}\}[Mg_xFe_{2-x}]$-$(Si_yFe_{3-y})O_{12}$, and $\{Y_{3-x-y}Ca_{x+y}\}[Zr_xFe_{2-x}](Si_yFe_{3-y})O_{12}$. The results for specimens with values of x and y: $x = y = 0.85$; $x = y = 1.00$; $x = 0.90$, $y = 1.10$; and $x = 1.10$, $y = 0.90$ are retabulated in Table VIII. In the last case, it is not now possible to prepare the specimen in which $M = Mg^{2+}$ because electrostatic balance with a tetravalent ion in the c-sites would be required. It is seen that the moments and Curie temperatures decrease in the order Mg, Sc, Zr and that saturation is more easily attained in those garnets containing magnesium than in the others. If we assume for the time being that all the Mg^{2+} ions go into octahedral sites, it appears that if it were possible to find a tetravalent ion to balance electrostatically the Mg^{2+} ions as in a hypothetical system $\{Y_{3-x}Me_x{}^{4+}\}[Mg_x{}^{2+}Fe_{2-x}](Fe_3)O_{12}$, the effective moment of a tetrahedral Fe^{3+} ion for given x would be higher than for an analogous Sc^{3+}-substituted yttrium iron garnet. This, of course, neglects any effect that the ions substituted in the c-sites would have on the magnetic structure. There are probably effects of the c-site substituted ions,[13] but it is impossible to determine them for divalent ions such as Ca^{2+} separately. It should be pointed out that when $x = y$ no substitution for Y is necessary when $M = Mg^{2+}$; x Ca^{2+} is necessary when $M = Sc^{3+}$, and $2x$ Ca^{2+} is necessary when $M = Zr^{4+}$.

The important question again arises: are some of the ions assumed to be in octahedral sites actually in tetrahedral sites? To try to answer this question directly, we have taken quantitative x-ray intensity data

TABLE VIII — RETABULATION OF DATA FROM SELECTED SPECIMENS FROM TABLES IV, V AND VI

Octahedral Ion	n_B $H_a = 0$	T_C, °K	Saturation Field, koe
	$x = y = 0.85$		
Mg	4.25	327	11.3
Sc	4.0		12.6
Zr	3.6		70
	$x = y = 1.00$		
Mg	3.8	265	70
Sc	2.9	235	>70
Zr	2.1	200	>70
	$x = 0.90$, $y = 1.10$		
Mg	3.2	294	9.6
Sc	2.8	260	>70
Zr	1.9	210	>70
	$x = 1.10$, $y = 0.90$		
Sc	2.8	220	>70
Zr	1.8	190	>70

from the specimens of $\{Y_{0.5}Ca_{2.5}\}[Zr_{1.25}Fe_{0.75}](Fe_{1.75}Si_{1.25})O_{12}$ and $\{Y_3\}[Mg_{1.85}Fe_{0.15}](Fe_{1.15}Si_{1.85})O_{12}$. The data were collected with the Norelco powder diffractometer using CuK_α radiation. Integrated intensities were measured on the charts with a Keuffel and Esser polar planimeter. In the calculations of intensities, corrections were made for anomalous dispersion,[36] the imaginary parts being included.[37] Estimates of oxygen ion positions were as far as possible based on interatomic distances expected between the ions involved. Calculations were made for the above distributions and also for $\{Y_{0.5}Ca_{2.5}\}[Zr_{1.00}Fe_{1.00}]$-$(Fe_{1.50}Zr_{0.25}Si_{1.25})O_{12}$ and $\{Y_3\}[Mg_{1.70}Fe_{0.30}](Fe_{1.0}Mg_{0.15}Si_{1.85})O_{12}$.

The results indicated that the x-ray data cannot give unequivocal conclusions regarding the exact distribution of the ions in these garnets. However, the assumptions that the Mg^{2+} and Zr^{4+} ions substitute only in the octahedral sites in the two garnets are certainly compatible with the data. Furthermore, examination of powder photographs of related garnets indicates that it is more likely that the Zr^{4+} and Mg^{2+} ions prefer octahedral sites exclusively than that some enter tetrahedral positions.

If, however, we examine the Curie temperatures in each x,y (for $x + y = 2.0$) group of Table VIII, we might be led to believe that if all Zr^{4+} ions are considered to be in octahedral sites, because substitution in the octahedral sites has a far greater effect on Curie temperature than tetrahedral substitution in this region of x and y, some Sc^{3+} ions go into tetrahedral sites and more Mg^{2+} ions do. On the other hand, we note that for Zr^{4+} ion substitution the highest moment is obtained for $x = y = 1.00$, those for $x = 0.90$, $y = 1.10$ and $x = 1.10$, $y = 0.90$ being lower. In fact, the same seems to be true for Mg^{2+} and for Sc^{3+} substitution. It thus appears unlikely that the results can be explained on the basis that the distributions of ions are different from those assumed.

To examine this conclusion further, we note the results on several other specimens. Table VI lists some Ge^{4+} ion substituted specimens analogous to those in Tables IV and V. For $Y_3MgFe_3GeO_{12}$, $Y_3Mg_{1.25}$-$Fe_{2.50}Ge_{1.25}O_{12}$ and for $\{Y_2Ca\}ScFe_3GeO_{12}$, Ge does not have a significant effect. But for $\{Y_{1.3}Ca_{1.7}\}Zr_{0.85}Fe_{3.3}Ge_{0.85}O_{12}$ and for $\{YCa_2\}ZrFe_3$-GeO_{12} the differences are substantial. These differences may be partly a result of a substantially different effect on the interaction geometry by the Ge^{4+} ion as compared with the Si^{4+} ion and partly because some of the Ge^{4+} ions enter octahedral sites in these garnets.

We have also prepared and made measurements on $\{Y_{1.8}Ca_{1.2}\}$-$[Zr_{0.6}Fe_{1.4}](Si_{0.6}Fe_{2.4})O_{12}$ and $\{Y_{1.8}Ca_{1.2}\}Zr_{0.6}Fe_{3.8}Ge_{0.6}O_{12}$ (Tables V and VI) for comparison with $\{Y_3\}[Mg_{0.6}Fe_{1.4}](Si_{0.6}Fe_{2.4})O_{12}$ (Fig. 11).

Although the differences are small, they could be real. The Mg-substituted garnet has the highest moment and the Zr-Ge substituted one the lowest. Again in the latter case, it is possible that some Ge^{4+} ions substitute in octahedral sites.

For the most part, however, in the region in which magnetic saturation is attained, differences in behavior for different nonmagnetic ions are either insignificant or small, as can be seen from an examination of Tables IV, V and VI and from later discussion. There is one garnet listed in Table V which behaves anomalously, as will be seen more clearly later; it is $\{Y_{0.8}Ca_{2.2}\}[Zr_{0.6}Fe_{1.4}](Fe_{1.4}Si_{1.6})O_{12}$. Although its moment appears to be right, its Curie temperature appears to be too low. This garnet, however, was very difficult to make. Although its lattice constant indicates that the composition is as given, the back-reflection lines in the powder photograph were not sharp.

It appears then that we must conclude that, especially in the regions of substitution in which intrasublattice interactions are dominant, there is a substantial effect on the magnetic structure of the types of ions substituted. Once it is realized that this occurs, it is not too difficult to find reasons that it should.

It has been shown that the *geometry* of different garnets may differ substantially. For example in a grossularite ($\{Ca_3\}[Al_2](Si_3)O_{12}$),[38] the oxygen octahedron is much more nearly regular than in yttrium iron garnet.[32] Also, the oxygen tetrahedron about the Si^{4+} ion is more regular than that about the Fe^{3+} ion in yttrium iron garnet. However the oxygen dodecahedron about the Ca^{2+} ion is more irregular than that about the Y^{3+} ion in yttrium iron garnet. The Si-O-Al angle in the grossularite is 136°, while the Fe(a)-O-Fe(d) angle in yttrium iron garnet is 127°.

Because ions of different valence and size produce different effects on the geometry (a manifestation of differences in chemical bonding) or crystal structure, it may be speculated that they will also produce different effects on the magnetic structure, especially when weak interactions are important (see also Refs. 21, 24 and 10–13).

In the earlier discussion of the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system, it was pointed out that the substitution of Si^{4+} ions in the tetrahedral sites, had, beyond $x = 0.70$, the tendency to weaken the d-d interactions. However, it is now seen that the Mg^{2+} ion appears also to disrupt the magnetic structure less than does Sc^{3+} or Zr^{4+} substitution. Unfortunately, it is again not possible to determine experimentally the separate effect of the Mg^{2+} ion. Nevertheless, if our assumption requiring the moments in one sublattice to remain parallel is valid, then our conclusions appear thus far to be plausible. In Fig. 22 we have plotted points for the effective moments of the tetrahedral Fe^{3+} ions for $x = 0.85$ and 1.00 in the garnets $\{Y_{3-2x}Ca_{2x}\}[Zr_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ and $\{Y_{3-x}Ca_x\}[Sc_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$. It is seen that these are higher than for the analogous garnets $\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ and $\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$ respectively.

If there were no effect of particular nonmagnetic ions substituted for the Fe^{3+} ions, it would be possible to plot a series of curves of 0°K moment vs $f_t = y/(x + y)$, where x,y equals the number of nonmagnetic ions in the octahedral, tetrahedral sites respectively. Thus it would have been possible with limited data to predict the moments for all nonmagnetic ion substituted yttrium iron garnets. Within the range that the *a-d* interactions are everywhere dominant, this is still possible for the garnets discussed here. We have seen that even when $x + y$ is large, if y is substantially larger than x, the *a-d* interactions may still be dominant and therefore such curves would still be valuable.

Some curves of this type are plotted in Fig. 27. Included are curves

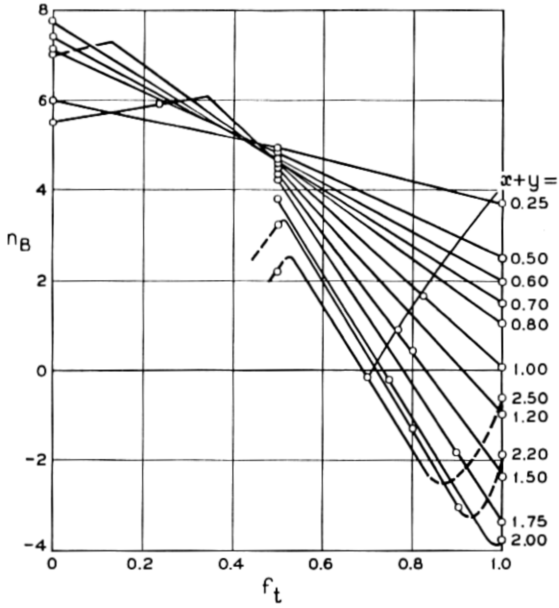

Fig. 27 — Spontaneous magnetizations, $n_B(0,0)$ of substituted yttrium iron garnets vs f_t, the fraction of nonmagnetic ions in the tetrahedral sites. [x = number of nonmagnetic ions in octahedral sites; y = number of nonmagnetic ions in tetrahedral sites; $f_t = y/(x + y)$.] Shown also is the curve for the $Y_3Fe_{5-x}Al_xO_{12}$ system.

which have regions in which the intrasublattice interactions are dominant. Points in the region $f_t \geqq 0.5$ are mostly from the system $\{Y_{3+x-y} \cdot Ca_{y-x}\}[Mg_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$. In Fig. 28, Curie temperatures vs f_t are shown for some values of $x + y$. The curves should be considered rather rough, because not many points have been obtained.

Fig. 27 shows that for $x + y = 2.0$, there is an algebraic minimum in the curve at $f_t \approx 0.98$. For $x + y = 2.20$ the algebraic minimum is more pronounced and occurs at $f_t \approx 0.93$. This makes clearer the discussion given above regarding the occurrence of garnets in which, for a given $x + y$, there is a higher (absolute value) moment when $|(3 - y_1) - (2 - x_1)| < |(3 - y_2) - (2 - x_2)|$. Note also that there are algebraic maxima in the curves for values of $x + y > 0.70$. The value of $x + y$ at which the maximum or the minimum first occurs appears to be at the point at which the intrasublattice interactions become dominant in the exclusively octahedral and tetrahedral ion substituted garnets respectively (see above). The crossover point for the Ge-substituted system should then be at the point of the algebraic minimum for the Si-substituted system. Examination of Fig. 4 shows that extension of the curve for the former system does intersect that of the latter system at about the predicted point.

The arguments regarding the effects of particular ions may be made still clearer. Referring again to Table VIII, we see that if one wished to

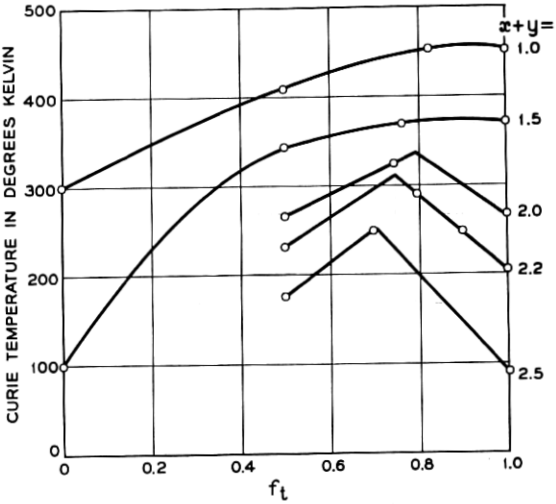

Fig. 28 — Curie temperatures vs f_t for various substituted yttrium iron garnets. (The lines connecting the points are, in this case, somewhat speculative.)

assume that the lower moments for Sc^{3+} and Zr^{4+} substitution when $x = y = 1.0$ (that is, with one Si^{4+} in tetrahedral sites) resulted from some Sc^{3+} or Zr^{4+} ions entering tetrahedral sites, f_t for the former would be 0.56 and for the latter 0.60 (Fig. 27). But then in Fig. 28 we see that the Curie temperatures should be in reverse order from those observed. Furthermore, magnetic saturation should also be more, rather than less, easily attainable than for the analogous Mg^{2+} ion substituted garnet. The garnet $\{Y_2Ca\}[Mg_{0.5}Fe_{1.5}](Fe_{1.5}Si_{1.5})O_{12}$ ($f_t = 0.75$) saturates at $\approx$9.6 koe at 1.4°K (see Table V).

Fig. 28 also appears to corroborate the idea that the intrasublattice interactions are effective over the whole temperature range, since for a given value of $x + y$, the maximum value of T_C is almost surely attained when the effective moments are at a maximum. It should be kept in mind, however, that Figs. 27 and 28 are based mainly on data from garnets which are magnetically saturated at 1.4°K and the data from the system $\{Y_{3+x-y}Ca_{y-x}\}[Mg_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$. The data from the system $\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$ in the region where saturation is *not* attained must be treated separately, as must the data from such a system as $\{Y_{3-x-y}Ca_{x+y}\}[Zr_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$. This results, as shown above, from the effect of the individual nonmagnetic ions on the magnetic structure.

Knowing that the Gilleo theory does not account for the 0°K moments of the substituted garnets and also that the x-ray method is not apt to give very narrow limits for the ionic distribution in the system $Y_3Fe_{5-x}Al_xO_{12}$, it was felt that it might be determined from such data as plotted in Fig. 27. If the particular ion effect is neglected, one may draw a curve (see Fig. 27) intersecting those for particular[39] $x + y$ at values of n_B found in the $Y_3Fe_{5-x}Al_xO_{12}$ system and thereby find f_t for each $x + y$ in this system, as plotted in Fig. 29.

The results obtained appear to be reasonable. It will be noted first

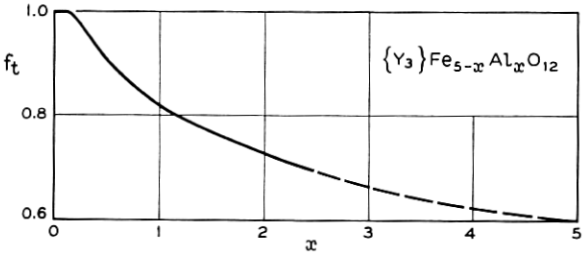

Fig. 29 — f_t vs x for the system $Y_3Fe_{5-x}Al_xO_{12}$ as derived from Fig. 27.

that the curve extends naturally from[39] $x + y = 2.5$ to $x + y = 5.0$, in which f_t must be 0.60. Secondly, for $x < 2.00$, (x as in $Y_3Fe_{5-x}Al_xO_{12}$) magnetic saturation is obtained at low fields at 1.4°K. Furthermore, two specimens in the system $\{Y_{3+x-y}Ca_{y-x}\}[Mg_xFe_{2-x}](Fe_{3-y}Si_y)O_{12}$, namely those for $x = 0.175$, $y = 0.825$ and $x = 0.75$, $y = 1.75$ and a third $\{Y_{1.50}Ca_{1.50}\}[Zr_{0.35}Fe_{1.65}](Fe_{1.85}Si_{1.15})O_{12}$ give very good checks on the moments found in the $Y_3Fe_{5-x}Al_xO_{12}$ system (see Tables V and VII). The Curie temperatures for the three specimens are plotted vs $x + y$ in Fig. 18 together with those found for the specimens in the $Y_3Fe_{5-(x+y)}Al_{(x+y)}O_{12}$ system. The agreement in the region $x + y \leqq 1.50$ is good but deteriorates in the region $x + y > 1.50$. This may again be an indication of the "particular ion effect."

Now consider a set of substituted garnets which have the same Curie temperature and which saturate magnetically at low fields. It is uncertain whether at a given temperature below T_C the values of the intrinsic spontaneous moments per octahedral Fe^{3+} ion, M_o, will all be the same, and similarly whether those of the tetrahedral Fe^{3+} ions, M_t, will be the same. It is unlikely, however, that they will differ greatly, and we shall assume that they are the same.

We take the three garnet specimens with measured extrapolated or interpolated Curie temperatures 367–375°K:

(1) $\{Y_{1.50}Ca_{1.50}\}[Zr_{0.35}Fe_{1.65}](Fe_{1.85}Si_{1.15})O_{12}$ $(T_C = 370°\text{K})$

(2) $\{Y_{1.50}Ca_{1.50}\}[Fe_2](Fe_{1.50}Si_{1.50})O_{12}$ $(T_C = 367°\text{K})$

(3) $\{Y_3\}[Mg_{0.62}Fe_{1.38}](Fe_{2.38}Si_{0.62})O_{12}$ $(T_C = 375°\text{K})$.

(For all these, the values calculated on the basis of the Gilleo model differ by $\leqq$11°K.) The observed spontaneous moments at 0, 100, 200, and 300°K are respectively as follows:

(1) 0.88, 0.79, 0.59, 0.38 μ_B

(2) −2.36, −2.15, −1.65, −1.08 μ_B

(3) 4.46, 4.00, 3.04, 2.00 μ_B (by interpolation; see Fig. 30).

In specimen (1) the canting must take place in the d sites, the sine of the angle being 0.99 [i.e., $\{5(1.65) + 0.88\}/(1.85)5$]. In (2) the canting occurs in the octahedral sites, the sine of the angle being 0 .99. Designating the octahedral and tetrahedral moments M_o and M_t respectively, we have from (1) and (2) at 100°K:

$$1.85(0.99)M_t - 1.65M_o = 0.79\ \mu_B$$

$$1.50M_t - 2(0.99)M_o = -2.15\ \mu_B$$

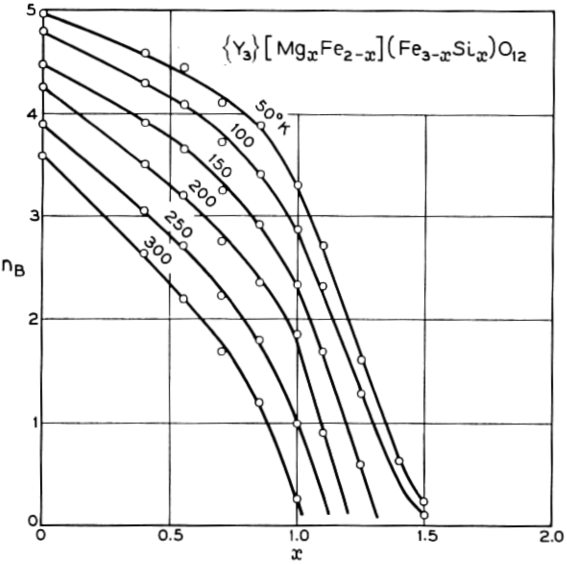

Fig. 30 — Spontaneous magnetizations, $n_B(H_a = 0)$, vs x for given temperatures in the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system.

for which

$$M_t = 4.44\ \mu_B$$

and

$$M_o = 4.45\ \mu_B .$$

For (3), we should have

$$2.38(0.96)M_t - 1.38M_o = 4.00\ \mu_B ,$$

the canting angles being obtained from the effective moments given in Fig. 22. Putting the moments obtained from (1) and (2) into the expression for (3), we obtain 4.00 μ_B .

To obtain the other values for (3) we substitute the 200 and 300°K moments in turn for the 100°K ones. At 200°K, we obtain from (1) and (2) $M_t = 3.36$, $M_o = 3.38\ \mu_B$, and the net moment for (3) calculated from these Fe^{3+} ion moments is 3.01 μ_B , to be compared with 3.04 μ_B observed. At 300°K, (1) and (2) yield $M_t = 2.14\ \mu_B$, $M_o = 2.17\ \mu_B$; the net moment calculated for (3) from these is 1.89 μ_B , to be compared with 2.00 μ_B observed. The agreement of calculated with observed values is generally good.

Now we try the same procedure with the Gilleo model. The three equations would be

$$(1)\ 1.85(0.97)M_t - 1.65(0.96)M_o = n_B^{(1)}(T)$$

$$(2)\ 1.50M_t - 2.00(0.89)M_o = n_B^{(2)}(T)$$

$$(3)\ 2.38(0.91)M_t - 1.38(0.99)M_o = n_B^{(3)}(T).$$

If we solve (2) and (3) of the Gilleo model for $T = 100°\text{K}$, we obtain $M_t = 5.57\ \mu_B$ and $M_o = 5.90\ \mu_B$, clearly impossible values, and there is therefore no point in checking these equations further.

It therefore appears that the intrasublattice interactions in these garnets may be important over the whole temperature range to or near T_C and that the Gilleo model is inapplicable in this range. However, the agreement of observed Curie temperatures with those predicted by the Gilleo theory is so good as to indicate either that the Gilleo theory is applicable very near the Curie temperature or that agreement is somehow fortuitous. In any case the Gilleo formula for Curie temperature is useful for the garnets of the systems discussed here.

When the canting model favored in this paper is used to calculate the intrinsic moments of the Fe^{3+} ions in the two different sites, the values obtained are only slightly different; in fact, the difference is so slight as to appear insignificant. The work of Bertaut et al.,[40] Prince[41] and Kuzminov et al.,[42] indicates that in yttrium iron garnet itself, the moments at temperatures above 110°K of the crystallographically different Fe^{3+} ions are substantially different. This is not corroborated, at least by the results on the substituted garnets.

There is some question as to how the determinations of the spontaneous magnetizations should be made when saturation is not attained at fields up to 14.24 koe. This "unsaturation" occurs noticeably after the intrasublattice interactions become dominant, an indication that the tendency not to saturate is associated with the canting. It is probable that when a specimen appears not to be saturated it is, in a sense, "oversaturated"; that is, the applied field disrupts the true zero-field structure by causing some alignment of the canted moments. If such were the case, it would appear that extrapolation to zero field would yield the more nearly correct results. This was especially well demonstrated by the results on the $\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ system. It is possible, however, that increased anisotropy also plays a role in preventing saturation. Measurements on single crystals, not now available, should aid in clarifying this situation.

In Gilleo's theory, an Fe^{3+} ion in one coordination not linked to at least two Fe^{3+} ions in the other coordination does not participate in the ferrimagnetism, at least at temperatures above 20°K. Gilleo points out[3] that the ions thus excluded should behave nearly as free ions at these temperatures, i.e., between 20°K and T_C. We do not find this to be the case. For example, in the $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ system, for substitutions which have the *a-d* interactions dominant, that is, for $x_t < 1.92$ and $x_o < 0.70$, the specimens are saturated or very nearly so at nominal fields. Beyond $x_t = 1.92$ or $x_o = 0.70$ saturation is not attained even at 1.4°K. But generally we observe that $n_B(H_a, T) - n_B(0, T)$ for fixed $H_a < 14.24$ koe is essentially constant to temperatures somewhat below the Curie temperature. For example, in the case of $\{YCa_2\}[Fe_2](FeSi_2)O_{12}$ with $T_C = 266°K$, $n_B(H_a, T) - n_B(0, T)$ is approximately equal to 0.2 μ_B at $H_a = 14$ koe to $T \approx 220°K$. In the case of $\{Y_{0.5}Ca_{2.5}\}[Fe_2](Fe_{0.5}Si_{2.5})O_{12}$ with $T_C = 86°K$, $n_B(H_a, T) - n_B(0, T)$ is approximately equal to 0.5 μ_B at $H_a = 14$ koe to $T \approx 80°K$.

4.1 *Application to Ferrospinels*

In the present article, it has been shown that the substitution of any nonmagnetic ion for an Fe^{3+} ion in the garnets tends to weaken the average *a-d* interaction. In a previous paper,[14] it was shown that divalent paramagnetic ions and Cr^{3+} ions also tend to weaken the average *a-d* interaction when substituted for the Fe^{3+} ions. The weakening of these interactions also results in an apparent reduction of the effective moment of the magnetic ions in at least one of the sublattices. We have put forward the idea that this reduction may be the result of random canting of these moments resulting from the intrasublattice antiferromagnetic interactions.

The ideas discussed in this paper should be applicable to the ferrimagnetic spinels. In a spinel, there is one cation in a tetrahedral site and there are two cations in octahedral sites per formula unit AB_2O_4. The antiferromagnetic interactions between magnetic ions on the two different sites would be expected to be the strongest present in the crystal; the antiferromagnetic interactions within the octahedral sublattice would be expected to be stronger than the antiferromagnetic interactions within the tetrahedral sublattice.

In the system $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$, there is very little effect on the effective moment of the Fe^{3+} ions in octahedral sublattice of substitution to $x = 1.0$, and only small effect even to $x = 1.50$. Thus one would predict that substitution in the octahedral sublattice of a ferrospinel would give similar behavior. On the other hand, substitution for *a*-site Fe^{3+} ions in the garnets has almost an immediately obvious effect on the effective moments of the Fe^{3+} ions in the *d* sites. Similarly, substitution in the tetrahedral sites of the ferrospinel might be expected to have a substantially larger effect than an analogous (twofold) substitution in the octahedral sites.

Lithium ferrite, $(Fe)[Li_{0.5}Fe_{1.5}]O_4$, accordingly has the highest Curie temperature, 953°K,[43] among the ferrospinels. Any substitution — i.e., by paramagnetic or nonmagnetic ions — for trivalent Fe^{3+} ions in this spinel reduces the Curie temperature.[43] Now the spinel nickel ferrite is inverse,[44] i.e., the formula may be written $(Fe)[NiFe]O_4$. In the garnet $\{Y_3\}[Ni_2](FeGe_2)O_{12}$, the Ni^{2+}-O^{2-}-Fe^{3+} interaction is about $\frac{1}{3}$ as strong as the Fe^{3+}-O^{2-}-Fe^{3+} interaction.[14] In $(Fe)[Li_{0.5}Fe_{1.5}]O_4$, each tetrahedral Fe^{3+} ion is linked through oxygen ions, on the average, to three Li^{3+} and nine Fe^{3+} ions in the octahedral sublattice; in $(Fe)[NiFe]O_4$ each tetrahedral Fe^{3+} ion is linked, through oxygen ions, on the average to six Ni^{2+} and six Fe^{3+} octahedral ions. In both cases, octahedral ions are linked only to Fe^{3+} ions in the tetrahedral sublattice. The average interaction strength in $(Fe)[Li_{0.5}Fe_{1.5}]O_4$ is then $\approx 9/8$ of that in $(Fe)[NiFe]O_4$. If there were at least an approximately linear relationship between Curie temperature and interaction strength,[45] the Curie temperature of $(Fe)[NiFe]O_4$ should be $\approx$ 850°K. This value compares favorably with that observed, 853°K.

Several investigators have sought an explanation for the low 0°K moment observed for manganese ferrite. As far as we know, there has been no *direct* evidence of other than divalent manganese and trivalent iron in a carefully prepared ferrite of composition $MnFe_2O_4$. Now manganese ferrite has a low Curie temperature, 603°K, as compared with nickel ferrite. Our work on the garnets would indicate that the strength of the Mn^{2+}-O^{2}-Fe^{3+} interaction should not differ substantially from that of the Ni^{2+}-O^{2-}-Fe^{3+} interaction. Thus, the low Curie temperature must be associated with the evidence that $MnFe_2O_4$ is actually an almost normal spinel, that is, the distribution of ions is given by

$$(Mn_{0.81}Fe_{0.19})[Fe_{1.81}Mn_{0.19}]O_4 . ^{46,47}$$

But this is analogous to the substitution in the *a* sites in yttrium iron garnet. Now an Fe^{3+} ion in an octahedral site in the ferrite is linked to mostly Mn^{2+} ions in tetrahedral sites; thus the average *a-d* interaction is substantially weaker in this ferrite than in lithium ferrite, and accordingly the Curie temperature is substantially lower.

We have shown[14] also that even substitution of 0.4 Mn^{2+} in the *a* sites of yttrium iron garnet causes canting of the *d*-site ion moments.

We propose that the behavior of manganese ferrite is similar to that of the divalent magnetic ion substituted garnets; that is, that the substitution of *any* ions for Fe^{3+} ions causes a weakening of the *a*-*d* interactions, whereupon the competing intrasublattice interaction manifests itself. For $MnFe_2O_4$ the usually observed value of the spontaneous magnetization at 4.2°K is 4.6 μ_B. Hastings and Corliss[46] have measured three specimens which give this value and very nearly the same ionic distribution. However, they could not resolve the problem of the low moment.

It is possible that if the specimens were not stoichiometric a low value could be obtained. However, if it is accepted that 4.6 μ_B is the correct value of spontaneous magnetization at 4.2°K, then we have, analogously to the garnets, that the canting may occur among the Fe^{3+} and Mn^{2+} ion moments on the *d*-sites. The effective moment (i.e., the component antiparallel to the *a* sublattice Fe^{3+} ion moments) of a *d*-site ion would then be 4.8 μ_B. In the garnet $\{Y_3\}[Mn_{0.4}Fe_{1.6}](Fe_{2.6}Si_{0.4})O_{12}$, the effective *d*-site Fe^{3+} ion moment is 4.96. Comparisons (see Fig. 22) with the effects of substitution of nonmagnetic ions in the garnets lead intuitively to the conclusion that the proposed amount of canting of the octahedral cation moments in manganese ferrite is plausible.

In discussing this conclusion with Hastings and Corliss, they have informed us that in the course of their investigation of $MnFe_2O_4$ they considered the moments proposed by us but concluded that the value of 4.6 μ_B for the average moment per ion in each sublattice gave a better fit with the observed data. This conclusion has not been changed after recent further consideration; however, the authors inform us that the model proposed by us cannot be ruled out by the existing data.

4.2 *Neutron Diffraction Studies*

We should mention what our ideas mean as far as neutron diffraction studies are concerned. First, consider a crystalline substance which is a solid solution. Coherent x-ray diffraction effects average over the crystal; that is, they do not tell us about local or short-range structure. For example, if two chemically different kinds of atoms may be thought to occupy highly specialized space group positions (i.e., with no allowable degrees of freedom), these are seen by the coherent x-ray "reflections" as having a weighted average atomic form factor of the two different atoms. Further, it could happen that these atoms, in the short range, may not lie exactly on the space group sites, but over the crystal space; that is, in the long range, appear to lie on these sites. In such a case the average thermal parameter may look too high, because the displacements of the atoms from the exact sites will appear from the coherent x-ray diffraction effects to be vibrations. Only the incoherent scattering will contain the information sought, but this may be too complicated to interpret.

Similarly, coherent neutron diffraction reflections may not give us a direct insight into the short-range magnetic disorder of the substituted garnets. They will give us only the average effective moment per ion of the particular sublattice. Incoherent neutron scattering might, however, be more elucidating.

4.3 *Garnets Containing Pentavalent Vanadium and Antimony*

Recently we have discovered new garnets containing pentavalent vanadium and antimony ions. In the case of V^{5+} ion substitution Smolenskii et al.[9] had reported on the system $x\ \{YCa_2\}Fe_4VO_{12}$-$(1-x)\ Y_3Fe_2Fe_3O_{12}$ but could not obtain a single-phase specimen with $x = 1.0$. We found that we could obtain a single-phase garnet with formula $\{Ca_3\}[Fe_2](Fe_{1.5}V_{1.5})O_{12}$ and that the complete solid solution range in the system $\{Y_{3-2x}Ca_{2x}\}[Fe_2](Fe_{3-x}V_x)O_{12}$ exists.[11,12] The end member, i.e., with $x = 1.5$, has a 0°K moment not significantly different from that of the Si^{4+} ion substituted garnet $\{Y_{1.5}Ca_{1.5}\}[Fe_2](Fe_{1.5}Si_{1.5})O_{12}$, but its Curie temperature, 493°K, is 126°K higher than that of the Si^{4+} ion substituted garnet. In the range of x studied, the Curie temperatures of the system $\{Y_{3-2x}Ca_{2x}\}[Fe_2](Fe_{3-x}V_x)O_{12}$ are all higher than those for $\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$ for the same x. In fact, the Curie temperature, 563°K, of $\{Y_{2.2}Ca_{0.8}\}[Fe_2](Fe_{2.6}V_{0.4})O_{12}$ is even higher than that of YIG itself. This behavior could not have been predicted from the results on the systems discussed in detail in this paper.

It was also found[12] that garnets in the yttrium-free $\{Bi_{3-2x}Ca_{2x}\}[Fe_2]$-$(Fe_{3-x}V_x)O_{12}$ system could be prepared, the probable range of x being $1.5 > x > 0.8$. In particular the magnetic behavior of $\{Bi_{0.5}Ca_{2.5}\}[Fe_2]$-$(Fe_{1.75}V_{1.25})O_{12}$ is essentially the same as that of the yttrium analog, despite the fact that Bi^{3+} for Y^{3+} ion substitution in YIG, i.e., in the system $\{Y_{3-x}Bi_x\}Fe_2Fe_3O_{12}$, resulted in increased Curie temperature.[13]

Pentavalent antimony may be put into garnets,[10] as in the system $\{Y_{3-2x}Ca_{2x}\}[Fe_{2-x}Sb_x](Fe_3)O_{12}$; garnets exist over the whole range $0 \leqq x \leqq 1.5$. To $x \approx 0.6$ this system behaves similarly to the Sc^{3+} and Zr^{4+} ion substituted systems at 0°K, but with some differences at higher temperatures. In the high substitution region, 0°K moments of the system are substantially lower than those of the Sc^{3+} and Zr^{4+} ion substituted systems. The turn down (see Fig. 4) of 0°K moment occurs sooner for the Sb^{5+} ion substituted system[10] than for the other two.

The end-member $\{Ca_3\}[Sb_{1.5}Fe_{0.5}](Fe_3)O_{12}$ forms a complete solid solution range with $\{Ca_3\}[Fe_2](Fe_{1.5}V_{1.5})O_{12}$; the system may be written $\{Ca_3\}[Sb_xFe_{2-x}](Fe_{1.5+x}V_{1.5-x})O_{12}$. The behavior of this system[10] could, in part, have been predicted from the results given in this paper. However, for $x = 0.75$, for example, the specimen does not saturate at moderate fields and its moment at 4.2°K is 2.5 μ_B . This may be compared with the 0°K moment, 4.35 μ_B , of $\{Y_3\}[Mg_{0.75}Fe_{1.25}](Fe_{2.25}Si_{0.75})O_{12}$, which is magnetically saturated at moderate fields.

Further details regarding these garnets and others involving Sb^{5+} and V^{5+} ion substitution will be found in Refs. 10–12. In the cases of Sb^{5+} and V^{5+} ions, their effects on the magnetic interactions occur even when substitution is not large. Therefore, even in these regions, all the results could not have been predicted from those of the present paper. Nevertheless, the ideas given in the present paper may still account for the behavior; we have pointed out earlier that systems which show large differences must be treated separately.

IV. ACKNOWLEDGMENTS

We wish to thank Y. Yafet for discussions of the theory of which he is coauthor, E. A. Nesbitt for the Curie temperature measurements as indicated in Table I, and A. J. Williams for technical assistance. Fig. 23 was drawn by H. J. Seubert and Fig. 24 is reproduced from Ref. 48.

Note Added in Proof

To ensure that the reader who so wishes may be able to duplicate our results, we have decided to list the preparation conditions of all specimens, rather than only those of Table IV. In Table IX the firing temperature is given, followed by the number of hours at that temperature. Each comma represents a regrinding and recompacting of the specimen. All firings were carried out in air except as indicated. In garnets containing Ca^{2+} and Mg^{2+} ions, starting materials were carbonates of these; in such cases a calcining was carried out. Usually, this consisted of varying the temperature in the initial firing from 500 to 900°C over a period of 1–2 hours.

It should be emphasized that the magnetic and crystallographic measurements were always made on the specimens quenched rapidly in air from the last firing temperature.

TABLE IX — PREPARATION DATA

x	y	Firing conditions, °C (hr.)
		$\{Y_{3-x}Ca_x\}[Fe_2](Fe_{3-x}Si_x)O_{12}$
0.00		1405(16)
0.40		1435(15)
0.75		1150(½), 1375(23)
1.00		1410(16), 1435(16), 1400(18), 1450(66)
1.01		1250(2), 1380(16), 1330(18), (75)
1.02		1250(½), 1285(17), 1275(20), 1415(7)
1.50		1280(16), 1300(19), (68), 1350(40)
1.77		1235(1), 1275(4), 1295(2), 1300(40), (?)[a]
1.88		1225(1), 1265(5), 1280(18), 1300(16)
2.00		1200(2), 1270(2), 1300(2½), (18), (19)
2.25		1225(½), 1265(2), (2), 1285(6)
2.50		1225(1), 1260(2), 1265(48), 1260(1), 1270(2½)
2.75		1225(½), 1200(64), 1220(22), 1240(19), 1245(64)
		$\{Y_{3-x}Ca_x\}Fe_{5-x}Ge_xO_{12}$
0.70		1225(½), 1350(8), 1390(19)
1.00		1340(16), 1320(16), 1300(66), 1435(17), (6)
1.50		1280(16), 1300(19), (68), 1350(40)
1.75		1225(½), 1260(1½), 1300(2), 1350(2½), 1385(1½)
2.00		1225(1), 1250(2), 1280(2), 1330(2½), 1385(1½)
2.25		1225(½), 1250(2), 1300(2), 1350(2)
2.50		1225(1), 1260(1)[b], 1280(2)[b], 1330(3)[b], 1360(2)[b], 1400(4½) 1420–1370(17)
2.75		1225(1½), 1300(2), 1350(3), 1365(2), 1225(7)
		$\{Y_3\}[Sc_xFe_{2-x}](Fe_3)O_{12}$
0.60		1300(1), 1350(2½), 1395(21)
0.72		1250(½), 1300(2), 1350(2½), 1400(2), 1425–1450(4)
0.80		1300(½), 1400(3), 1420(17)
1.00		1250(½), 1325(4), 1400(16), 1440(21)
1.25		1300(1), 1350(2½), 1400(4½), 1420(21)
1.50		1300(1), 1350(2½), 1400(4½), 1420(21)
		$\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$
0.60		1280(1), 1320(19), 1300(65), 1325(40)
0.72		1300(½), 1350(2½), 1350(3), 1380(2), 1425(14), 1400(19)
0.80		1350(½), (5), (5), 1355(22), 1400(16), 1450–1430(18)
1.00		1250(½), 1325(4), 1350(4), 1400(16)
1.25		1300(½), 1350(5), (16)
1.50		1300(½), 1350(3), 1320(16½)
1.75		1300(½), 1350(5), (16)
1.95		1300(½), 1350(3), 1320(16½)
		$\{Y_{3-y+x}Ca_{y-x}\}[Mg_xFe_{2-x}](Si_yFe_{3-y})O_{12}$
0.175	0.825	1275(½), 1350(2), 1390(2), 1400(2½), 1315(18)
0.30	1.47	1300(1), 1350(4), 1375–1400(5), 1180(63), 1275(16), 1360(16)
0.18	1.57	1205(½), 1300(3), 1330(4), 1390–1360(22)
0.90	1.10	1300(½), 1450–1420(17), 1400(6)
0.50	1.50	1300(½), 1375(2), 1380(3), 1385(2)
0.44	1.76	1300(½), 1375(2), 1385(2), 1380(3½)
0.22	1.98	1250(½), 1300(2), 1315(2), 1300(2½), (16), 1200(19), 1340-1345(68)
0.75	1.75	1290(½), 1325(5), 1395(4), 1340(70), 1400(20), 1190(17)

TABLE IX—PREPARATION DATA—*continued*

x	y	Firing conditions °C (hr.)
		$\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}](Si_yFe_{3-y})O_{12}$
0.85	0.85	1225(½), 1350(3), 1400(16), 1395(20), 1425(5)
0.30	1.47	1285(1), 1325(4), 1350–1310(21), 1345(29)
0.30	1.52	1275(1), 1300(5), 1340(23), 1320(19), 1350(17)
0.30	1.60	1250(1), 1300–1330(3), 1340(21), 1360(22)
1.10	0.90	1300(½), 1400(3), (16), 1450(16)
1.00	1.00	1300(½), 1325(2½), 1400(5), 1450(3), 1500(4)
0.90	1.10	1300(1), 1355(3), 1400(20), (16)
		$\{Y_{3-x-y}Ca_{x+y}\}[Zr_xFe_{2-x}](Si_yFe_{3-y})O_{12}$
0.76	0.24	1285(½), 1360(2), (2), 1395(3), 1330(16), (42)
0.60	0.60	1275(1), 1300(4), 1310(22), 1340(23), 1365(70)
0.35	1.15	1225(½), 1325(3½), 1360(2), 1250(16), 1300(21)[b]
0.30	1.20	1250(½), 1350(4), 1375–1400(20), 1400(65), 1315(21), 1300–1275(41)
0.85	0.85	1200(½), 1325(4), 1375(5), 1360(16), 1210(68)[b]
0.30	1.60	1200(½), 1325(4), 1330(20), 1210(68), [b]1330(16), 1350(21)
1.10	0.90	1300(1), 1355(3), 1375(23)
1.00	1.00	1275(½), 1350(2), 1360(2½), (2½), 1305(21), 1300(16), 1360(20), 1400–1385(66)
0.90	1.10	1200(½), 1325(4), 1375(5), 1360(16), 1210(68)[b], 1280(23)
0.60	1.60	1200(1), 1260(4), 1300(4), 1350(4), 1375(4), 1360(16), 1355(16), 1300(70), (118), 1180(63)
1.25	1.25	1250(½), 1325(4), 1350(4), 1355(16), 1375(20), 1270(64), 1350(19)
		$\{Y_{3-y+x}Ca_{y-x}\}Mg_xFe_{5-x-y}Ge_yO_{12}$
1.00	1.00	1250(½), 1300(4), 1395(5), 1450–1460(3), 1500–1525(28), 1340(16)
1.25	1.25	1330(½), 1400(4), 1410(16), 1400(22)
		$\{Y_{3-y}Ca_y\}Sc_xFe_{5-x-y}Ge_yO_{12}$
1.00	1.00	1200(½), 1300(4½), 1390(21), 1400(22)
		$\{Y_{3-x-y}Ca_{x+y}\}Zr_xFe_{5-x-y}Ge_yO_{12}$
0.60	0.60	1275(1), 1300(4), 1310(22), 1340(22), 1365(70), 1385(16)
0.85	0.85	1200(½), 1300(3½), 1330(16), 1340(21), 1315(16), 1340(23), 1375(18)
1.00	1.00	1250(½), 1325(2½), 1375(4), 1425(20), 1450(3)
		$Y_3Al_xFe_{5-x}O_{12}$
1.00		1400(1), 1440(16), 1475(48)
1.50		1450(2), 1500(16), 1475(40)
1.75		1300(1), 1450(2), 1490(2), (2), 1510(4)
2.00		1400(1), 1500(19)
2.50		1450(1), 1525(2½), 1540(17), 1530(64), 1600–1660(5)
3.00		1300–1340(2), 1350–1430(3), 1420(40), 1520(42)
3.00		1425(1), 1445–1520(5), 1480(40), 1500(16), 1535(24)

[a] Unknown because of furnace burn-out.

[b] Fired in O_2.

REFERENCES

1. Geller, S., Bozorth, R. M., Gilleo, M. A., and Miller, C. E., J. Phys. Chem. Solids, **12,** Jan., 1960, p. 111.
2. Geller, S., Bozorth, R. M., Miller, C. E., and Davis, D. D., J. Phys. Chem. Solids, **13,** May, 1960, p. 28.
3. Gilleo, M. A., J. Phys. Chem. Solids, **13,** May, 1960, p. 33.
4. Gilleo, M. A., and Geller, S., Phys. Rev., **110,** Apr., 1958, p. 73.
5. Yafet, Y., and Kittel, C., Phys. Rev., **87,** July, 1952, p. 290.
6. de Gennes, P. G., Phys. Rev. Letters, **3,** Sept. 1, 1959, p. 209.
7. Pauthenet, R., Ann. Phys., **3,** Apr., 1958, p. 424.
8. Geller, S., Williams, H. J., Espinosa, G. P., and Sherwood, R. C., Bull. Amer. Phys. Soc., Ser. II, **7,** 1962, p. 279.
9. Smolenskii, G. A., Polyakov, V. P., and Iodin, V. M., Akad. Nauk. SSSR, Izvestia, Ser. fiz., **25,** 1961, p. 1396.
10. Geller, S., Williams, H. J., Espinosa, G. P., and Sherwood, R. C., J. Appl. Phys., Mar., 1964.
11. Geller, S., Espinosa, G. P., Williams, H. J., Sherwood, R. C., and Nesbitt, E. A., Appl. Phys. Letters **3,** Aug. 15, 1963, p. 60.
12. Geller, S., Espinosa, G. P., Williams, H. J., Sherwood, R. C., and Nesbitt, E. A., J. Appl. Phys., Mar., 1964.
13. Geller, S., Williams, H. J., Espinosa, G. P., Sherwood, R. C., and Gilleo, M. A., Appl. Phys. Letters, **3,** July 15, 1963, p. 21.
14. Geller, S., Williams, H. J., Sherwood, R. C., and Espinosa, G. P., J. Phys. Chem. Solids, **23,** 1962, p. 1525; see also J. Appl. Phys. **33,** Mar., 1962, p. 1195.
15. Bozorth, R. M., Williams, H. J., and Walsh, D. E., Phys. Rev., **103,** Aug. 1, 1956, p. 572.
16. Candela, G. A., and Mundy, R. E., Rev. Sci. Instr., **32,** 1961, p. 1056.
17. In subsequent discussion, these will be considered to be indistinguishable from the 0°K moments, although they may differ slightly from them.
18. Geller, S., and Miller, C. E., Amer. Min., **44,** Nov.-Dec., 1959, p. 1115.
19. Yoder, H. S., and Keith, M. L., Amer. Min., **36,** July–Aug., 1951, p. 519.
20. Skinner, B. J., Amer. Min. **41,** May–June, 1956, p. 428.
21. Bozorth, R. M., and Geller, S., J. Phys. Chem. Solids, **11,** Oct., 1959, p. 263.
22. In a previous paper,[2] it was reported that $\{YCa_2\}[Zr_2](Fe_3)O_{12}$, $\{YCa_2\}[Zr_2](Al_{0.5}Fe_{2.5})O_{12}$ and $\{YCa_2\}[Zr_2](Ga_{0.5}Fe_{2.5})O_{12}$ had residual moments at 1.4° K. It now appears (see text which follows) that both $\{YCa_2\}[Zr_2](Fe_3)O_{12}$ and $\{YCa_2\}[Hf_2](Fe_3)O_{12}$, also reported in that paper, could not have been *precisely* single-phase garnet specimens and that this was not discernible at the time of that investigation. With regard to the 0.5 Al and 0.5 Ga specimens, although these should exist as single-phase garnets, it is possible that these also were not phase pure; the present result on the 0.25 Ga specimen is considered to be more reliable.
23. The successful preparation of this garnet is a consequence of the fact that the tetrahedral Ga^{3+}-O^{2-} distance is expected to be substantially shorter than the tetrahedral Fe^{3+}-O^{2-} distance. See Geller, S., J. Chem. Phys. **33,** 1960, p. 676, and Refs. 14 and 24.
24. Geller, S., J. Appl. Phys. **31,** May, 1960, p. 30S.
25. Geller, S., J. Phys. Chem. Solids, **16,** 1960, p. 21.
26. Neel, L., Ann. Phys., **3,** 1948, p. 137.
27. Anderson, P. W., Phys. Rev., **102,** May 15, 1956, p. 1008.
28. Until recently, silicon has been known to have only tetrahedral coordination to oxygens in oxide systems. A rutile type SiO_2 (i.e., with Si having octahedral coordination to oxygens) was shown to occur at very high pressure, 160,000 kg/m², and a temperature of 1200–1400°C. (Stishov, S. M. and Popova, S. V., Geokhimiya, 1961, p. 837.)
29. Wojtowicz, P. J., J. Appl. Phys., **33,** June, 1962, p. 1957.
30. Aleonard, R., J. Phys. Chem. Solids, **15,** Aug., 1960, p. 167.
31. The term "effective moment" is used rather loosely here to prevent awkwardness in the presentation. Throughout the discussion, we shall mean

by this term the average *component* of the moment which is antiparallel to the Fe^{3+} ion moments of the sublattice in which there is no canting.

32. Geller, S., and Gilleo, M. A., J. Phys. Chem. Solids, **3,** 1957, p. 30; **9,** 1959, p. 235.
33. That is, the average d-d (a-d) interaction strength multiplied by the number of nearest neighbor $d(a)$ cations, 4(8), is greater than six times the average a-d interaction strength.
34. v. Náray-Szabó, St., Z. Kristallogr., (A), **94,** 1936, p. 414.
35. The minus sign, as usual, indicates that the octahedral sublattice contribution to the spontaneous magnetization is dominant. The Gilleo theory predicts a moment of $-0.65\ \mu_B$, but a Curie temperature of 242°K for this garnet.
36. Dauben, C. H., and Templeton, D. H., Acta Cryst., **8,** 1955, p. 841.
37. Geller, S., Miller, C. E., and Treuting, R. G., Acta Cryst., **13,** 1960, p. 179.
38. Abrahams, S. C., and Geller, S., Acta Cryst., **11,** 1958, p. 437.
39. In $Y_3Fe_{5-x}Al_xO_{12}$, x is the *total* substitution of Al distributed over a and d sites, and therefore is equivalent to $x + y$ of Fig. 27.
40. Bertaut, F., Forrat, F., Herpin, A., and Meriel, P., Compt. Rend. **243,** 1956, p. 898.
41. Prince, E., Acta Cryst., **10,** 1957, p. 787.
42. Kuzminov, U. S., Yamzin, I. I., and Belov, N. V., Kristallografiya, **7,** 1962, p. 1946.
43. Gorter, E. W., Philips Res. Rept., **9,** August, 1954, p. 403.
44. Hastings, J., and Corliss, L., Rev. Mod. Phys., **25,** Jan., 1953, p. 114.
45. Gilleo, M. A., Phys. Rev., **109,** Feb. 1, 1958, p. 777 and pertinent references therein.
46. Hastings, J., and Corliss, L., Phys. Rev., **104,** 1956, p. 328.
47. Nozik, Yu. Z., and Yamzin, I. I., Kristallografiya, **6,** 1961, p. 923.
48. Geller, S.. Acta Cryst., **12,** 1959, p. 944.