Crystal chemistry of the garnets*

By S. GELLER

North American Aviation Science Center, Thousand Oaks, California

Dedicated to Professor G. Menzer on his 70th birthday

Auszug

Die Granat-Struktur, ursprünglich von MENZER 1925 ermittelt, wurde in den letzten zehn Jahren wegen ihrer magnetischen Eigenschaften für die Festkörper-Physik von steigender Bedeutung. Während dieser Zeit wurden mehrere Vertreter der Granat-Struktur bezüglich ihrer Atomkoordinaten verfeinert; Resultate dieser Arbeiten und deren Konsequenzen werden diskutiert. Eine Übersicht über Kationen, welche Granat-Strukturen bilden können, wird im Hinblick auf ihr Koordinationsverhalten gegeben. Die Diskussion beschränkt sich nicht auf bereits Publiziertes, sondern wird ergänzt durch neues, bisher nicht veröffentlichtes Material.

Obwohl die Ionen*größe* für den Eintritt der Kationen in die verschiedenen Punktlagen der Granat-Struktur von großer Bedeutung ist, spielt deren *elektronischer Aufbau* eine wesentliche Rolle, z.B. im Falle von Cr^{3+} und Mn^{3+}. In diesem Sinne wird das Verhalten von Co^{2+} speziell untersucht, welches oktaedrische Sauerstoff-Umgebung gegenüber tetraedrischer bevorzugt. Co^{3+} konnte sowohl mit oktaedrischer wie auch mit tetraedrischer Umgebung hergestellt werden. Die Ionenverteilung im System $Y_3Fe_{5-x}Ga_xO_{12}$ wird auf Grund verschiedener Untersuchungsmethoden speziell diskutiert.

Abstract

The garnet structure, originally solved by MENZER, has become increasingly important in the last ten years. During this period a number of garnet-structure refinements have been carried out; these are reviewed and some of the consequences of the results are discussed. A survey has been made of all the cations

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* Im Hinblick darauf, daß Herr MENZER der Erste war, der eine Silikatstruktur — die des Granates — aufklärte (1925), erschien es den Editoren der Zeitschrift für Kristallographie wünschenswert, zu seinem 70. Geburtstag einen Artikel zu erbitten, der die Kristallchemie von Granatstrukturen behandeln würde. Herr GELLER hat sich freundlicherweise dazu bereit erklärt, und die Zeitschrift für Kristallographie bringt diesen Artikel am Anfang des sonst alphabetisch geordneten Festbandes.

Für die Redaktion (außer Menzer): gez. F. LAVES

which enter the garnet structure and their site preferences are given. Numerous examples of garnets and garnet systems that have been investigated are listed. Some are reported here for the first time.

The ionic site preference in the garnets is discussed; it appears that relative ionic size is of primary importance, but for certain ions like Cr^{3+} and Mn^{3+}, the electronic configuration also plays an important role. Considerable discussion is given to the Co^{2+} ion for which the evidence maintains that the Co^{2+} ion prefers, by far, the octahedral sites to the tetrahedral. Garnets have been prepared with Co^{3+} ion in the tetrahedral and in the octahedral sites. The determination of the distribution of ions in the system $Y_3Fe_{5-x}Ga_xO_{12}$ by different techniques is reviewed.

Introduction

Time has shown that the mineral world itself contains not only important materials but also clues to others which do not occur naturally. Sometimes these clues are quite subtle; in the garnet case, considerable time elapsed before they were recognized. While for many years the garnet structure, originally solved by MENZER[1,2], has been important to the mineralogist, it has been important to the physicist for only a little over ten years. Its greatest importance to the physicist is in the existence of the ferrimagnetic garnets[3,4], and the garnet structure first elucidated by MENZER played no small role in their discovery. The Néel theory[5] of ferrimagnetism must also be given tribute because it points to those crystal structures in which ferrimagnetism might exist.

The technological importance of the naturally occurring garnets has been limited to that of mild abrasives. An example is the garnet paper, obtained in a hardware store, used to smooth wood. Even this use is limited, because there are better abrasives for this application. Some silicate garnets are semi-precious and are used in jewelry. But the ferrimagnetic garnets have important technological uses in modern electronic devices. More recently neodymium doped yttrium aluminum and gallium garnets have been found to be good laser

[1] G. MENZER, Die Kristallstruktur von Granat. Centralbl. Min. [A] **1925**, 344—345; Z. Kristallogr. **63** (1926) 157—158.

[2] G. MENZER, Die Kristallstruktur der Granate. Z. Kristallogr. **69** (1928) 300—396.

[3] F. BERTAUT et F. FORRAT, Structure des ferrites ferrimagnétiques des terres rare. Compt. Rend. Acad. Sci. [Paris] **243** (1956) 382—384.

[4] S. GELLER and M. A. GILLEO, Structure and ferrimagnetism of yttrium and rare earth iron garnets, Acta Crystallogr. **10** (1957) 239.

[5] L. NÉEL, Propriétes magnétiques des ferrites; ferrimagnétisme et anti-ferromagnétisme, Annales Physique [Paris] **3** (1948) 137—198.

materials[6]. Thus the synthetic garnets have become a rich field for both scientific and technological exploration. The scientific literature of recent years abounds with papers on various studies of the garnets.

My own work in this field dates from the discovery of the ferrimagnetic garnets by GILLEO and me[4] in the Bell Telephone Laboratories. (As indicated earlier, the discovery had also been made independently and in a different manner from ours by BERTAUT and FORRAT[3] at Grenoble.) Since the discovery, I have been directly interested in the static magnetic behavior and in the crystal chemistry of the garnets. As a result of intensive work in these fields with the collaboration of several colleagues, we have developed a model[7] which accounts well for the magnetic behavior of the substituted ferrimagnetic garnets. This model enables one to make certain predictions concerning the behavior of as yet unmade garnets and to determine ion distributions in substituted yttrium iron garnets from a knowledge of the $0\,°K$ moments.

This paper will give mainly a survey of the crystal chemistry of the garnets including a discussion of the garnet structure refinements that have been reported and of the site preferences of various ions in the garnets. References to the magnetic behavior of the garnets will be made mainly as elucidation to the site preference determinations. In a few instances some heretofore unreported work will be included.

I do not intend this to be an *exhaustive* review in which I set myself the task of discussing every paper of any relevance whatever to the subject. But I hope that I shall not have missed any which cause me to omit a point of importance. I should point out that only once before have I written a paper[8] which included a review of the overall crystal chemistry of the garnets; that paper was written about eight years ago.

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[6] J. E. GEUSIC, H. M. MARCOS and L. G. VAN UITERT, Laser oscillations in Nd-doped yttrium aluminum, yttrium gallium and gadolinium garnets. Appl. Physics Letters **4** (1964) 182—184. See also T. H. MAIMAN, Laser applications. Physics Today **20** (1967) 24—28.

[7] S. GELLER, H. J. WILLIAMS, G. P. ESPINOSA and R. C. SHERWOOD, Importance of intrasublattice magnetic interactions and of substitutional ion type in the behavior of substituted yttrium iron garnets. Bell System Tech. Jour. **43** (1964) 565—623.

[8] S. GELLER, Magnetic interactions and distribution of ions in the garnets. J. Appl. Physics Suppl. **31** (1960) 30S—37S.

Garnet structure refinements

For almost thirty years after the publication of MENZER's papers[1,2], no garnet structure refinement was made. However, the recognized potential importance of the iron garnets led us to carry out the structure refinement of yttrium iron garnet[9] as soon as a single crystal, grown by NIELSEN and DEARBORN[10], became available. Since then, at least two other refinements of the yttrium iron garnet structure have been made[11,12]. Some early work was done on powders by x-ray diffraction[3] and neutron diffraction[13] techniques by the French investigators.

MENZER's original paper[2] gave the mathematical details of the equipoint positions of the space group $Ia3d$ to which the garnet structure belongs. The cations are all in special positions with no positional degrees of freedom, while the oxygen atoms are in the general positions (see Table 1). It is possible to refine the oxygen parameters by choosing to measure those intensities to which only oxygen atoms contribute; these are hkl with two indices odd and the third divisible by 4 and $hk0$ with h, $(k) = 8n$ and (h), $k = 2m$ $(n, m$ odd). There are others, e.g. $hk2$: 12, 4, 2 and 14, 6, 2; $hk4$: 12, 6, 4. There is also a large number of structure amplitudes which have

Table 1. *Description of garnet structure*

Point symmetry	222	$\bar{3}$	$\bar{4}$	$\bar{1}$
Space group position	$24c$	$16a$	$24d$	$96h$
Typical ideal formula	$\{Ca_3\}$	$[Al_2]$	(Si_3)	O_{12}
Coordination to oxygen	8	6	4	
Type polyhedron	Dodecahedron (distorted cube)	octahedron	tetrahedron	

[9] S. GELLER and M. A. GILLEO, Crystal structure and ferrimagnetism of yttrium iron garnet, $Y_3Fe_2(FeO_4)_3$. J. Physics Chem. Solids **3** (1957) 30—36. See also S. GELLER and M. A. GILLEO, The effect of dispersion corrections on the refinement of the yttrium-iron garnet structure. J. Physics Chem. Solids **9** (1959) 235—237.

[10] J. W. NIELSEN and E. F. DEARBORN, The growth of single crystals of magnetic garnets. J. Physics Chem. Solids **5** (1958) 202—207.

[11] A. BATT and B. POST, A procedure for parameter refinement in simple structures. Acta Crystallogr. **15** (1962) 1268—1270.

[12] F. EULER and J. A. BRUCE, Oxygen coordinates of compounds with garnet structure. Acta Crystallogr. **19** (1965) 971—978.

[13] F. BERTAUT, F. FORRAT, A. HERPIN et P. MÉRIEL, Étude par diffraction de neutrons die grenat ferrimagnétique $Y_3Fe_5O_{12}$. Compt. Rend. Acad. Sci. [Paris] **243** (1956) 898—901.

total cation contributions of the form $\pm 8(f_c^T - f_d^T) \sin\frac{1}{4}\pi h$, where f_c^T, f_d^T are the room temperature scattering factors of atoms in the c and d sites, respectively. The reflections involved have h, k, odd, $l = 2n$, n odd $(h, k, l$ permutable).

I have mentioned the intensities which should be most sensitive to the oxygen parameters, as an aid to those who might wish to determine only the oxygen positions of garnets. I have already shown[14] that it is necessary to use a more nearly complete set of data if one wishes to obtain thermal parameters of all the ions involved.

Good drawings of the garnet structure may be found in References[2,15,16]. The greatest appreciation of the structure can be obtained from a three-dimensional model now purchasable from at least two different sources. A word description of the structure is given in Table 1.

Because of the importance to the magnetic properties and the crystal chemistry of the different coordination polyhedra in the garnet, Fig. 1 gives the surroundings of an oxygen ion in grossularite, the figure being taken from the Abrahams-Geller paper[17].

Silicate garnets

Since the first refinement of a garnet structure, that of yttrium iron garnet[9], there have been several others. Five refinements have been made of silicate garnets: a grossularite from Chihuahua, Mexico by ABRAHAMS and GELLER[17], synthetic pyropes by ZEMANN and ZEMANN[18], and by GIBBS and SMITH[15], a natural pyrope by EULER and BRUCE[12] and a grossularite from Xalostoc, Mexico by PRANDL[16]. The last is the most recent one reported; it was based on both x-ray and neutron data.

The results obtained by PRANDL[16] indicate that if there are any differences in positional parameters resulting from the neutron vs the

[14] S. GELLER, Parameter interaction in least squares structure refinement Acta Crystallogr. 14 (1961) 1026—1035.

[15] G. V. GIBBS and J. V. SMITH, Refinement of the crystal structure of synthetic pyrope. Amer. Mineral. 50 (1965) 2023—2039.

[16] W. PRANDL, Verfeinerung der Kristallstruktur des Grossulars mit Neutronen- und Röntgenstrahlbeugung. Z. Kristallogr. 123 (1966) 81—116.

[17] S. C. ABRAHAMS and S. GELLER, Refinement of the structutre of a grossularite garnet. Acta Crystallogr. 11 (1958) 437—441.

[18] A. ZEMANN und J. ZEMANN, Verfeinerung der Kristallstruktur von synthetischem Pyrop, $Mg_3Al_2(SiO_4)_3$. Acta Crystallogr. 14 (1961) 835—837.

x-ray diffraction investigations, they are very small. Prandl's work includes the determination of anisotropic thermal parameters. However, while there are *apparent* differences in results between the neutron and x-ray investigations, the limits of error in each preclude any conclusion as to their reality. Prandl also made $77\,^\circ$K measurements of the neutron-diffraction intensities of reflections in the [111] zone. Positional and isotropic thermal parameters were deter-
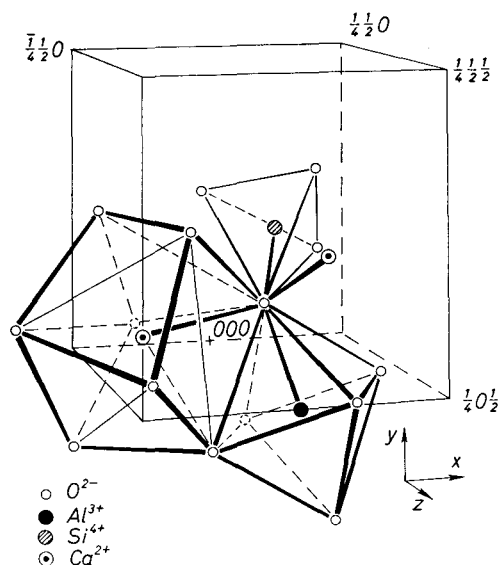

Fig. 1. Coordination about an oxygen ion in grossularite (after Abrahams and Geller[17])

mined from these and showed no significant difference from those determined from the [111] zone data taken at room temperature.

The x-ray data with which Prandl's refinement was made were obtained with a Buerger precession camera; intensities were measured with a photodensitometer. The neutron data were also obtained from a single crystal. Our data[17] were obtained from Weissenberg photographs and the intensities were estimated visually. Further, the origins and compositions of the specimens are different. Yet the differences in positional parameters of the oxygen ions are not large. If the averages of the four values for each parameter given in Prandl's Table 10 are compared with the final set of parameters of the Abrahams-Geller paper, we obtain:

	x	y	z
ABRAHAMS-GELLER	-0.0389	0.0456	0.1524
PRANDL	-0.0382	0.0456	0.1513

The standard errors for the Abrahams-Geller parameters were calculated to be 0.0005 and for the Prandl set 0.0001.

The interionic distances and angles in grossularite are given in the Abrahams-Geller[17] and Prandl[16] papers. The actual values are not strictly those for single cation-oxygen distances because the minerals do not have ideal formulas. In fact, if the chemical analysis given for the grossularite we investigated may be taken as that for the particular spherical specimen from which the x-ray data were collected, the formula may be written:

$$\{Ca_{2.84}Mg_{0.18}\}[Al_{1.63}Fe_{0.25}Mg_{0.11}Ti_{0.02}](Si_{2.96}Al_{0.06})O_{12} \, .$$
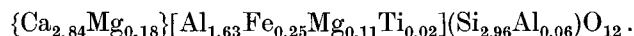
(The formula does not quite balance, there being an excess of 0.05 cations, but this is probably within the error of the chemical analysis.) If the $Fe^{3+}-O^{2-}$ and $Ti^{4+}-O^{2-}$ distances are assumed to be 2.01 Å and the $Mg^{2+}-O^{2-}$ distances 2.10 Å, the octahedral $Al^{3+}-O^{2-}$ distance in this grossularite would be 1.92 Å. The composition of the garnet investigated by PRANDL is much closer to that of pure $Ca_3Al_2Si_3O_{12}$ and therefore the octahedral cation-oxygen distance in his specimen should be closer to 1.92 Å than to 1.95 Å found[17] in the Chihuahua garnet. Thus there *should* actually be some difference between the two sets of oxygen coordinates. The distance found by PRANDL is 1.927 ± 0.004 Å. Of course, the error limits on our value are not as good, but these results appear to make sense anyway. However, the Si—O distances do not: PRANDL's value, 1.65 Å, is higher than ours, 1.64 Å, and probably the situation should be reversed; thus, perhaps we cannot draw any firm conclusions regarding the small differences, especially since our error limits are about four times as large as PRANDL's.

ZEMANN and ZEMANN[18] found a value of 1.89 Å for the $Al^{3+}-O^{2-}$ distance in the synthetic pyrope. Some years ago, I used the Busing-Levy least-squares program on their data and found the standard errors in the oxygen positional parameters to be 0.0005, 0.0004, and 0.0005, respectively. Thus the limits of error on the distances are the same as those in our grossularite investigation. The difference of the $Al^{3+}-O^{2-}$ distances in the two garnets (PRANDL's grossularite and ZEMANN's pyrope) therefore appears to be significant. The $Si^{4+}-O^{2-}$

distance given by ZEMANN and ZEMANN is 1.62 Å; my calculations gave 1.63 ± 0.02 Å, so that from these determinations, it is not possible to say unequivocally that the Si—O distances in the two garnets are significantly different.

GIBBS and SMITH[15] have also carried out a careful and detailed study on a synthetic pyrope. They did a least-squares refinement on the data of ZEMANN and ZEMANN to ascertain that the synthetic pyrope prepared by COES[19] had essentially the same detailed structure as the crystal they used, prepared by BOYD. The data for the Gibbs-Smith refinement were obtained from a polyhedral crystal of 0.32 mm and 0.41 mm minimum and maximum dimensions, respectively. Intensities of 374 independent reflections were measured with a scintillation-counter equi-inclination Weissenberg diffractometer using monochromatized MoKα radiation. Corrections for absorption and polarization of the beam by the monochromator were found to be negligible and therefore, were not needed. The oxygen positional parameters obtained from the refinement are −0.0328, 0.0501, 0.1533 (all ± 0.0006) (as compared with the values: 0.034, 0.050, 0.154 obtained by ZEMANN and ZEMANN).

The Si—O and Al—O distances obtained by GIBBS and SMITH are 1.635 Å and 1.886 Å, respectively. EULER and BRUCE found a value of 1.64 ± 0.02 and 1.90 ± 0.02 Å for these distances in a natural pyrope with formula $\{Mg_{1.6}Fe_{1.2}Ca_{0.2}\}[Al_2](Si_3)O_{12}$. Thus one is tempted to conclude (at present, more on intuition than on the basis of the calculated error limits) that in these silicate garnets, the Si—O distances are less affected by a change in the size of the divalent cation than are the Al—O distances. But if we compare PRANDL's result with that of GIBBS and SMITH on the Si—O distances in grossularite vs pyrope, 1.651 ± 0.005 vs 1.635 ± 0.006 Å, respectively, we see that there does appear to be some effect on the Si—O distance, which could be larger than the 0.005 Å proposed by GIBBS and SMITH[15].

ZEMANN and ZEMANN[18] had noticed anisotropy of the electron density about the Mg^{2+} ions and attributed this tentatively to statistical disorder of the arrangement of these ions about the special positions. However, these ions are in rather low symmetry positions, 222, and the results of GIBBS and SMITH show that the anisotropy of thermal vibrations of the Mg^{2+} ions accounts for the electron-density anisotropy observed by ZEMANN and ZEMANN.

[19] L. COES, High pressure minerals. J. Amer. Ceram. Soc. 38 (1955) 298.

In a paper[20] on the crystal chemistry of the garnets, ZEMANN discusses the question of the distortion of the coordination polyhedra. ZEMANN shows that if regular octahedra and tetrahedra are assumed with reasonable distances, 1.90 or 1.95 Å for Al—O and 1.62 Å for Si—O, a very short O—O distance of 2.44 Å is obtained for an unshared edge of the distorted cube, i.e. about 0.31 Å shorter than its minimum probable value of 2.75 Å. I should point out, however, that it seems possible that a garnet could be made in which at least the octahedron could be very nearly regular. In synthetic pyrope, the six O—O distances in the plane perpendicular to the threefold axis are longer than the six others by 0.08 Å, while in grossularite the exact reverse is true (see Table 1 of ZEMANN's paper).

Rare-earth and yttrium garnets

Structural refinements based on single-crystal data have been made on a substantial number of rare-earth and yttrium aluminum, gallium and iron garnets. Most of these have been reported recently by EULER and BRUCE[12]. As indicated earlier, the first was made on yttrium iron garnet by GELLER and GILLEO[9]; BATT and POST[11] reported a refinement in 1962 and EULER and BRUCE[12] also worked on yttrium iron garnet. The structure of gadolinium iron garnet was refined by WEIDENBORNER[21] and EULER and BRUCE[12] refined the structures of Lu, Yb, Y and Gd aluminum, Lu, Yb and Y gallium and Lu, Yb, Y, Dy and Sm iron garnets.

Our work and that of WEIDENBORNER were based on visually estimated intensities on Weissenberg photographs; the work of EULER and BRUCE and of BATT and POST was based on counter data. The last was based essentially on ten observational equations for refining the three positional parameters of the oxygen ion. That is, intensity ratios of reflections, with equal $h^2 + k^2 + l^2$, to which only oxygen ions contributed, were used, on the assumption that the oxygen thermal motions in the garnet are truly isotropic. This was hardly to be expected and as results of PRANDL[16] and of GIBBS and SMITH[15] show, they are anisotropic in the grossularite and in the synthetic pyrope. Further, although the discrepancy factor for the ten ratios is 7.7%, three of the ten have discrepancies of over 18%.

[20] J. ZEMANN, Zur Kristallchemie der Granate. Beitr. Mineralogie und Petrographie 8 (1962) 180—188.

[21] J. WEIDENBORNER, Least squares refinement of the structure of gadolinium-iron garnet, $Gd_3Fe_2Fe_3O_{12}$. Acta Crystallogr. 14 (1961) 1051—1056.

The calculated standard errors may therefore be unrealistically low. (BATT and POST did not report standard errors on the cation-oxygen distances which I have calculated [see below]. In the course of my calculations, I found that the average values of these distances, that they calculated from their parameters, were in error by about one standard deviation. The corrected values are listed in a subsequent table.)

The standard errors given by BATT and POST may not even be physically reasonable. At room temperature, yttrium iron garnet is not really cubic even though no significant deviation from cubicity has as yet been observed with x-rays. This means only that the x-ray diffraction technique, as others, has a limit on its "resolving power". Any crystal that has a spontaneous polarization, either magnetic or electric, cannot be cubic. The "easy" direction of magnetization of yttrium iron garnet below its Curie temperature is the [111] direction, therefore indicating that it actually belongs to a rhombohedral space group. This is not of great importance to the determination of the positional parameters inasmuch as it is unlikely that deviations from the cubic space-group positions are quantitatively measurable by known techniques. But that such deviations *may* exist should be recognized.

There is no question that physical measurement techniques other than those of x-ray diffraction "see" the non-cubicity: for example, the existence of the spontaneous magnetization alone (which only requires a small permanent magnet to observe), the optical birefringence observed by DILLON[22], the Mössbauer spectroscopic investigation of $Tm_3Fe_2Fe_3O_{12}$ by COHEN[23]. Of course, no *cubic* Shubnikov group describes a ferroelectric, ferrimagnetic, or ferromagnetic structure[24].

The three sets of oxygen positional parameters obtained in the three independent investigations of yttrium iron garnet are:

	x	σ	y	σ	z	σ
GELLER and GILLEO	−0.0274	0.0009	0.0572	0.0009	0.1495	0.0009
BATT and POST	−0.0269	0.0001	0.0581	0.0003	0.1495	0.0001
EULER and BRUCE	−0.0270	0.0004	0.0569	0.0005	0.1505	0.0005

[22] J. F. DILLON, JR., Optical properties of several ferrimagnetic garnets. J. Appl. Physics **29** (1958) 539—541; 1286—1291.

[23] R. L. COHEN, Mössbauer effect in Tm^{169} in thulium iron garnet. Physics Letters **5** (1963) 177—178.

[24] N. N. NERONOVA and N. V. BELOV, Ferromagnetic and ferroelectric space groups. Kristallografiya **4** (1959) 807—812; Soviet Physics—Crystallography **4** (1960) 769—774.

These are really all rather close, although because of the large lattice
constant, small differences in parameter values may cause substantial
differences in interionic distances:

	$Fe^{3+}(a)$—O^{2-}	σ	$Fe^{3+}(d)$—O^{2-}	σ	Y^{3+}—O^{2-}	σ
GELLER and GILLEO	2.01	0.01	1.88	0.01	2.43	0.01
					2.37	0.01
BATT and POST	2.013	0.002	1.881	0.001	2.417	0.003
					2.365	0.001
EULER and BRUCE	2.019	0.006	1.866	0.005	2.434	0.006
					2.356	0.005

The analogous Fe^{3+}—O^{2-} distances found in gadolinium iron garnet
are 2.00 (0.01) and 1.89 (0.01) Å. These, together with the values found
for yttrium iron garnet by GELLER and GILLEO and by BATT and POST
seem to favor the larger tetrahedral Fe^{3+}—O^{2-} distance, that is 1.88 Å
rather than 1.87 Å. Yet four out of five $Fe^{3+}(d)$—O^{2-} values obtained
by EULER and BRUCE for the iron garnets are lower: Lu, 1.87 Å;
Yb, 1.86 Å; Y, 1.87 Å; Dy, 1.86 Å; and Sm, 1.88 Å. The $Fe^{3+}(a)$—O^{2-}
distances for the same garnets were found to be 2.03 and 2.02 (for
two different LuFe garnet specimens), 2.01, 2.02, 2.03, and 2.04 Å,
respectively. It would seem that the value in GdFe garnet should lie
between those in DyFe and SmFe garnet, but this has not been found
to be the case (see Table 2).

Table 2. *Cation-oxygen distances in garnets as determined by* EULER *and* BRUCE

	Lu	Yb	Y	Gd	Dy	Sm
$Al^{3+}(a)$—O^{2-}	1.94 Å	1.94 Å	1.94 Å	1.94 Å		
$Ga^{3+}(a)$—O^{2-}	1.99	2.00	2.00			
$Fe^{3+}(a)$—O^{2-}	2.02	2.01	2.02		2.03 Å	2.04 Å
$Al^{3+}(d)$—O^{2-}	1.76	1.76	1.76	1.78		
$Ga^{3+}(d)$—O^{2-}	1.85	1.84	1.85			
$Fe^{3+}(d)$—O^{2-}	1.86	1.87	1.87		1.86	1.88

The d—h and a—h distances in the garnets refined by EULER and
BRUCE are realistically rounded off to two decimal places in Table 2.
These distances do not show a trend, e.g. $Fe^{3+}(d)$—O^{2-} = 1.86 Å in
Lu and DyFe garnet while in YbFe garnet it is larger, 1.87 Å. Thus,

it seems that no greater reliability of the distances in these iron garnets has been established by having done several structure refinements than as given by the individual error limits.

The results of EULER and BRUCE on the gallium garnets do not bear out my earlier reasoning[25] as to why the Ga^{3+} ions should have a preference at least equal to that of Al^{3+} ions for tetrahedral sites when substituted for Fe^{3+} ions in yttrium iron garnet. In my paper[25] on β Ga_2O_3, I had shown that the ratio of the average tetrahedral to average octahedral $Ga^{3+}—O^{2-}$ distance in β Ga_2O_3 was equal to the analogous ratio in yttrium aluminum garnet, the values in the latter having been taken from the results of PRINCE's neutron-diffraction investigation[26] of YAl garnet powder. However, according to the results of EULER and BRUCE, this ratio of the $Ga^{3+}—O^{2-}$ distances is greater than that for the $Al^{3+}—O^{2-}$ distances in the garnets. A recent investigation[27] of the site distribution of Ga^{3+} ions in $Y_3Fe_{5-x}Ga_xO_{12}$ confirms the *greater* preference of Ga^{3+} than Al^{3+} ions for the tetrahedral sites, at least to $x = 2.75$. However, it appears that for $x > 2.75$, the situation could be reversed. According to the results of EULER and BRUCE the ratios, referred to above, are the same in both YFe and YGa garnet and smaller in YAl garnet. If the results obtained by other investigators on YFe and GdFe garnet are compared with those of EULER and BRUCE on the gallium garnets, the ratio in the Ga garnets is smaller than that in the two iron garnets. Thus the relative site preference of the Al^{3+} and Ga^{3+} ions in the systems $Y_3Fe_{5-x}Al_xO_{12}$ and $Y_3Fe_{5-x}Ga_xO_{12}$ cannot now be explained on simple structural grounds. It might still be possible, however, if the distances were determined more accurately.

Garnet survey and ionic site preference

In the present paper, I hope not only to bring the previous survey[8] up to date, but also give more detail on the garnets and garnet systems that have been made.

In subsequent tables, I shall give lists of simple end-member garnets, namely the silicates, the germanates and the yttrium and

[25] S. GELLER, Crystal structure of β-Ga_2O_3. J. Chem. Physics **33** (1960) 676—684.

[26] E. PRINCE, Neutron diffraction measurements on yttrium-iron and yttrium-aluminum garnets. Acta Crystallogr. **10** (1957) 787—788.

[27] S. GELLER, J. A. CAPE, G. P. ESPINOSA and D. H. LESLIE, Gallium substituted yttrium iron garnet. Physic. Rev. **148** (1966) 522—524.

rare earth aluminum, iron and gallium garnets. Then I shall give a list of garnets and garnet systems to exemplify the ions which enter garnets and, when known, the sites they occupy. I also intend to discuss various aspects that have arisen in connection with these garnets.

Table 3. *End-member silicate garnets*

A^{2+}	B^{3+}	a [Å]	A^{2+}	B^{3+}	a [Å]
Mg	Al	11.459 [18,19,28]	Mn	Al	11.621 [28,36]
	Cr	Not reported [19]		Fe	11.82 [19,37]
	Fe	Not reported [19]	Fe	Al	11.526 [28]
Ca	Al	11.851 [28]	Co	Al	11.471 [38]
	Sc	12.27 [29]	Cd	Al	11.82 [39]
	V	12.09 [29], 12.070 [30], 12.068 [31]		V	12.09 [29]
	Cr	12.00 [32], 11.999 [33]			
	Fe	12.048 [28], 12.059 [34], 12.067 [7]			
	Ga	12.00 [35]			
	In	12.35 [29]			

[28] B. J. SKINNER, Physical properties of end-members of the garnet group. Amer. Mineral. **41** (1956) 428—436.

[29] B. V. MILL', Hydrothermal synthesis of garnets containing V^{3+}, In^{3+}, and Sc^{3+}. Dokl. Akad. Nauk. [USSR] **156** (1964) 814—816.

[30] R. G. STRENS, Synthesis and properties of calcium vanadium garnet (goldmanite). Amer. Mineral. **50** (1965) 260.

[31] S. GELLER and G. P. ESPINOSA, data not published previously. The specimen was prepared at 900°C and 20 kbar from constituent oxides mixed with $CaCl_2$.

[32] S. GELLER and C. E. MILLER, The synthesis of uvarovite. Amer. Mineral. **44** (1959) 445—446.

[33] H. E. SWANSON, M. I. COOK, E. H. EVANS and J. H. DE GROOT, Standard x-ray diffraction powder patterns. NBS Circular 539, Vol. **10** (1960) pp. 17—18.

[34] H. E. SWANSON, M. I. COOK, T. ISAACS, and E. H. EVANS, NBS Circular 539, Vol. **9** (1960) pp. 22—23.

[35] B. V. MILL', Hydrothermal synthesis of silicates and germanates with garnet structure type. Zhur. Neorg. Khim. (1966) 1533—1538.

[36] S. GELLER and C. E. MILLER, Silicate garnet—yttrium iron garnet solid solutions. Amer. Mineral. **44** (1959) 1115—1120.

[37] S. GELLER and C. E. MILLER, Substitution of Fe^{3+} for Al^{3+} in synthetic spessartite. Amer. Mineral. **44** (1959) 665—667.

[38] J. A. KOHN and D. W. ECKART, X-ray study of synthetic diamond and associated phases. Amer. Mineral. **47** (1962) 1422—1430. The authors stated incorrectly, however, that this garnet represented the first successful introduction of the Co^{2+} cation into a garnet.

[39] A. L. GENTILE and R. ROY, Isomorphism and crystalline solubility in the garnet family. Amer. Mineral. **45** (1960) 701—711.

Silicate garnets

The silicate garnets are listed in Table 3. These have been made mostly by hydrothermal techniques. (Even the higher pressure syntheses of COES[19] and our own[31] of $Ca_3V_2Si_3O_{12}$ may be so considered.) Spessartite $(Mn_3Al_2Si_3O_{12})$ is synthesized[40] by melting a mixture of the appropriate amounts of reactant oxides at a temperature of 1200—1250 °C. When cooled, a glass is obtained which is then annealed at 1080° for 18 hours. Synthetic uvarovite $(Ca_3Cr_2Si_3O_{12})$ may be obtained by solid-state reaction, but the conditions for attaining a good yield are given in a note published by GELLER and MILLER[32]. The synthesis of uvarovite is usually credited to HUMMEL[41]. However, according to the evidence he gives, he did not succeed in synthesizing a garnet. The spacings from his x-ray powder pattern are not indexable on a cubic cell, and it is inconceivable that this can be accounted for by measurement error. Because it is really mainly of importance that this garnet can be synthesized by solid-state reaction, I shall not carry the discussion to the point of comparing HUMMEL's data with ours here. However, SWANSON et al.[33] have prepared uvarovite and carefully measured the powder pattern with a diffractometer. As is their custom, they list all previous data by other authors. I therefore refer the reader to this more recent work for confirmation.

In Table 3, there are three values listed for the lattice constant of $Ca_3Fe_2Si_3O_{12}$. The first two were obtained for specimens synthesized hydrothermally, the third specimen was grown from a lithium molybdate flux. It now appears that the 12.048 Å value may be low; no analysis was given for this specimen. The second specimen was said to contain 0.01% Al and the third was not analyzed. It is probable that the lattice constant for a specimen with ideal composition lies between 12.059 and 12.067 Å.

The relative ionic sizes of the B^{3+} ions which fill the octahedral sites in $\{Ca_3\}[B_2^{3+}](Si_3)O_{12}$ have been derived from the rare-earth perovskite-like compounds[42] and these have been appropriate to the garnets. The actual values obtained are:

[40] H. S. YODER and M. L. KEITH, Complete substitution of aluminum for silicon: The system $3MnO \cdot Al_2O_3 \cdot 3SiO_2$—$3Y_2O_3 \cdot 5Al_2O_3$. Amer. Mineral. 36 (1951) 519—533.

[41] F. A. HUMMEL, Synthesis of uvarovite. Amer. Mineral. 35 (1950) 324—325.

[42] S. GELLER, Crystallographic studies of perovskite-like compounds. V. Relative ionic sizes. Acta Crystallogr. 10 (1957) 248—251. See also Structure Reports 21 (1957) p. 315.

In^{3+}	0.714	Fe^{3+}	0.628	Ga^{3+}	0.613
Sc^{3+}	0.686	Mn^{3+}	0.625	Cr^{3+}	0.608
Ti^{3+}	0.633	V^{3+}	0.625	Al^{3+}	0.558

I would thus expect the lattice constant of $Ca_3V_2Si_3O_{12}$ to be slightly smaller than that of $Ca_3Fe_2Si_3O_{12}$. MILL's value of 12.09 Å is too large,

Table 4. *End-member germanate garnets*

A^{2+}	B^{3+}	a [Å]	A^{2+}	B^{3+}	a [Å]
Ca	Al	12.12[43], 12.120[44]	Mn	Al	11.902[43], 11.901[44],
	Sc	12.504[44]			11.895[46]
	V	12.35[29], 12.320[45]		V	12.125[29], 12.099[45]
	Cr	12.265[44], 12.275[46]		Cr	12.027[43,44]
	Mn	12.325[47]		Fe	12.087[43,44]
	Fe	12.320[43], 12.312[44]		Ga	12.043[46]
	Ga	12.251[48]	Cd	Al	12.077[46]
	In	12.62[47], 12.59[49]		Sc	12.447[46]
	Rh	12.35[47]		V	12.29[29]
	Y	12.805[49]		Cr	12.213[46]
	Dy	12.83[49]		Mn	12.27[47]
	Ho	12.81[49]		Fe	12.261[46]
	Er	12.785[49]		Ga	12.191[46]
	Tm	12.765[49]		In	12.515[29]
	Yb	12.74[49]		Rh	12.285[47]
	Lu	12.73[49]			
Sr	Sc	12.785[49]			
	In	12.87[49], 12.88[49]			
	Y	13.085[49], 13.091[45]			
	Ho	13.09[49]			
	Er	13.065[49]			
	Tm	13.04[49]			
	Yb	13.03[49]			
	Lu	13.01[49]			

[43] S. GELLER, C. E. MILLER and R. G. TREUTING, New synthetic garnets. Acta Crystallogr. 13 (1960) 179—186.

[44] A. TAUBER, C. G. WHINFREY and E. BANKS, The crystal chemistry of some germanium garnets. J. Physics Chem. Solids 21 (1961) 25—32.

[45] S. GELLER and G. P. ESPINOSA, data not previously published.

[46] A. TAUBER, E. BANKS and H. KEDESDY, Synthesis of germanate garnets. Acta Crystallogr. 11 (1958) 893—894.

[47] B. V. MILL', Synthesis of garnets containing Mn^{3+} and Rh^{3+}. Zhur. Strukt. Khim. 6 (1965) 471—473.

[48] H. E. SWANSON, M. I. COOK, E. H. EVANS and J. H. DE GROOT, Standard x-ray diffraction powder patterns. NBS Circular 539, Vol. 9 (1960) pp. 15—20.

[49] B. V. MILL', Synthesis of garnets with large cations. Dokl. Akad. Nauk [USSR] 165 (1965) 555—558.

possibly an indication that small amounts of Ti^{4+} ion, from his titanium vessels, are in his garnet. (This is also indicated by the large value for the $Cd_3V_2Si_3O_{12}$; it should be smaller than for the Ca compound, in line with the relative values for the analogous Al compounds.) The value of 12.070 Å obtained by STRENS[30] seems better in relation to 12.067 for the $Ca_3Fe_2Si_3O_{12}$. The value, 12.068 Å, for the $Ca_3V_2Si_3O_{12}$ garnet that we synthesized is in very good agreement with STRENS' value.

I would also have expected the lattice constant of $Ca_3Ga_2Si_3O_{12}$ to be larger than that of $Ca_3Cr_2Si_3O_{12}$.

Germanate garnets

There are many new garnets among the simple end-member germanates (Table 4). Fifteen are listed in Table 4 which involve trivalent yttrium or a rare-earth ion in the a sites and the Ca^{2+} or Sr^{2+} ion in the c sites. Those with the Sr^{2+} ion all have lattice constants greater than 13.00 Å, the largest garnet unit cells known to date. All were made by solid-state reaction[49]. MILL' has synthesized some germanates hydrothermally[29,47,49] but all the germanate garnets can be made by solid-state reaction including $Mn_3V_2Ge_3O_{12}$.

The lattice constant, 12.35 Å, given by MILL for $Ca_3V_2Ge_3O_{12}$ is again high with respect to either of the values for the Fe compound. For a specimen of $Ca_3V_2Ge_3O_{12}$ which we prepared, we obtained a value of 12.320 Å. This was synthesized by firing an appropriate compacted mixture of $CaGeO_3$ and V_2O_3 in an evacuated sealed fused silica ampule at 960 °C for 1 hour. The specimen was reground, recompacted and fired in the same manner for an additional hour at 960 °C. The powder photograph showed a faint extra line indicating the presence of an extra phase, possibly $Ca_2Ge_3O_8$. It is not impossible that some V^{5+} ion is incorporated in our specimen, tending to give too large a value for the lattice constant.

We have similarly synthesized a specimen of $Mn_3V_2Ge_3O_{12}$. An appropriate mixture of Mn_2GeO_4, V_2O_3 and GeO_2 was compacted into a pellet, sealed in an evacuated fused silica tube and brought from 400° to 950 °C in 1 hour, then allowed to remain at 950 °C for 2 hours. A garnet with sharp back-reflection lines in the powder photograph (CrK radiation) was obtained having $a = 12.099$ Å as opposed to the value 12.125 Å found by MILL' for his specimen. On the basis of the reasoning given earlier, we suspected that MILL's lattice constant for this garnet, which he prepared hydrothermally,

was too high (as is the case for all his other vanadium garnets so prepared). Our value is 0.026 Å less than his, but is, nevertheless, still somewhat higher than that for the analogous iron compound.

There are actually at least three possible reasons for this: 1) In view of the closeness of lattice-constant values for the analogous V^{3+} and Fe^{3+} garnets, the sizes of the V^{3+} and Fe^{3+} ions may be equal or the V^{3+} ion may even be slightly larger than the Fe^{3+} ion. 2) Some pentavalent V^{5+} ions may be in the tetrahedral sites. 3) Some of the germanate garnets are difficult to obtain as decidedly single phases. There is some evidence[43,44] that it is possible that they have vacancies of some sort, which probably would affect the lattice-constant values.

I do not believe that any of these possibilities can be ruled out at this time. The weight of the evidence from the lattice constants alone favors the conclusion that the size of the V^{3+} ion is equal to or slightly greater than that of the Fe^{3+} ion. Actually this does not affect results of theory[50,51]; the list of radii given above cannot be considered to be perfect. Further, the surroundings of the ions in the perovskite-like[52] and garnet structures may be just sufficiently different to give slight size differences. Another example is that of Mn^{3+} ion which also appears to be slightly smaller than the Fe^{3+} ion in perovskites[42] but the same size as the Fe^{3+} ion in the bixbyite structure, in which case no significant change in lattice constant is observed[53] for $(Mn_{1-x}Fe_x)_2O_3$ for $0.01 \leq x \leq 0.50$. (We have found[54] that α Mn_2O_3 itself does not have the bixbyite structure.)

With regard to the Mn^{3+} ion, we had managed[55], apparently, to substitute this ion for 2% of the Fe^{3+} ion in yttrium iron garnet, but

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[50] J. H. VAN SANTEN and J. S. VAN WIERINGEN, Ionic radii of iron-group elements. The influence of crystalline field. Rec. trav. chim. Pays-Bas 71 (1952) 420—430.

[51] A. D. LIEHR, Ionic radii, spin-orbit coupling and the geometrical stability of inorganic complexes. Bell Syst. Tech. Jour. 39 (1960) 1617—1626.

[52] S. GELLER, Crystal structure of gadolinium orthoferrite. J. Chem. Physics. 24 (1956) 1236—1243; P. COPPENS and M. EIBSCHÜTZ, Determination of the crystal structure of yttrium orthoferrite and refinement of gadolinium orthoferrite. Acta Crystallogr. 19 (1965) 524—531.

[53] S. GELLER, R. W. GRANT, J. A. CAPE and G. P. ESPINOSA, Magnetic behavior of the system Mn_2O_3—Fe_2O_3. J. Appl. Physics 38 (1967) 1457—1458.

[54] S. GELLER, J. A. CAPE, R. W. GRANT and G. P. ESPINOSA, Distortion in the crystal structure of α-Mn_2O_3. Physics Letters 24A (1967) 369—371.

[55] S. GELLER, H. J. WILLIAMS, R. C. SHERWOOD and G. P. ESPINOSA, Substitutions of divalent manganese, iron and nickel in yttrium iron garnet. J. Physics Chem. Solids 23 (1962) 1525—1540.

MILL' has succeeded in making the garnets $Ca_3Mn_2^{3+}Ge_3O_{12}$ and $Cd_3Mn_2^{3+}Ge_3O_{12}$ [47]. MILL' has also succeeded in making two germanate garnets with Rh^{3+} ions in the a sites[47], namely those of Ca^{2+} and Cd^{2+}.

It should be mentioned here that KEITH and ROY[56] and SCHNEIDER, ROTH and WARING[57] have also had indication that rare earths or yttrium replaced Ga^{3+} or Al^{3+} in the gallium and aluminum garnets. I shall leave this, however, for later discussion.

The lattice constant, 12.251 Å, for $Ca_3Ga_2Ge_3O_{12}$ given by SWANSON et al.[48] seems small relative to either one given for the Cr garnet. The order seems more nearly correct for the Mn group of germanate garnets. For the In garnet, MILL' gives two different values 12.62 and 12.59 Å. The first was obtained for a hydrothermally synthesized garnet, the second for one prepared by solid state reaction. Inasmuch as the values MILL' obtained for his hydrothermally synthesized garnets are generally high by about 0.03 Å, I would speculate that the lower one is the more nearly correct one for the pure garnet.

Among the cadmium garnets, again the value for the V compound looks high, while the value for the Ga compound seems low.

I think it worth emphasizing that in the case of some of the germanates, there may be a question regarding ideal stoichiometry and some of the differences in lattice constant may be reflections of difficulties in this regard. Even when there is no difference between investigators, the garnet phase could still not be of the ideal stoichiometry.

Rare-earth aluminum, iron and gallium garnets

Lattice constants for these garnets are listed in Table 5. The lattice constant value given by YODER and KEITH[40] for the first known aluminum garnet is 12.01 ± 0.02 Å, BERTAUT and FORRAT[58] give 12.02 Å, GILLEO and GELLER[59], 12.003 Å, and EULER and BRUCE[12],

[56] M. L. KEITH and R. ROY, Structural relations among double oxides of trivalent elements. Amer. Mineral. 39 (1954) 1—23.

[57] S. J. SCHNEIDER, R. S. ROTH and J. L. WARING, Solid state reactions involving oxides of trivalent cations. J. Res. Nat. Bur. Standards 65A (1961) 345—374.

[58] F. BERTAUT et F. FORRAT, Étude des combinaisons des terres rares avec l'alumine et la galline. Compt. Rend. Acad. Sci. [Paris] 243 (1956) 1219—1222.

[59] M. A. GILLEO and S. GELLER, Magnetic and crystallographic properties of substituted yttrium-iron garnet $3Y_2O_3 \cdot xM_2O_3 \cdot (5-x)Fe_2O_3$. Physic. Rev. 10 (1958) 73—78.

Table 5. *Rare earth aluminum, iron and gallium garnets*

A^{3+}	B^{3+},C^{3+}	a [Å]
Y	Al	$12.01^{40,56}$, 12.02^{58}, 12.000^{12}, 12.003^{59}
Gd		12.11^{58}, 12.113^{12}, 12.111^{60}
Tb		12.074^{61}
Dy		12.06^{58}, 12.042^{61}
Ho		12.011^{61}
Er		11.98^{58}, 11.981^{61}
Tm		11.957^{60}
Yb		11.929^{60}
Lu		11.912^{60}
Y	Fe	$12.376^{4,62}$
La*		12.767^{63}
Pr*		12.646^{63}
Nd*		12.60^{62}, 12.596^{64}, 12.600^{63}
Pm*		12.57^{62}, 12.561^{63}
Sm		12.524^{62}, 12.530^{64}, 12.528^{65}, 12.529^{63}
Eu		12.518^{62}, 12.498^{63}
Gd		12.479^{62}, 12.472^{64}, 12.471^{63}
Tb		12.447^{62}, 12.436^{63}
Dy		12.414^{62}, 12.405^{63}
Ho		12.380^{62}, 12.375^{63}
Er		12.349^{62}, 12.347^{64}
Tm		12.325^{62}, 12.323^{63}
Yb		12.291^{62}, 12.302^{63}
Lu		12.277^{62}, 12.283^{63}
Y	Ga	12.30^{58}, 12.273^{59}, 12.280^{12}, 12.275^{57}, 12.274^{66}
Pr		12.57^{58}, 12.545^{45}

* Hypothetical.

[60] C. B. RUBENSTEIN and R. L. BARNS, Crystallographic data for rare-earth aluminum garnets: Part II. Amer. Mineral. 50 (1965) 782—785.

[61] C. B. RUBENSTEIN and R. L. BARNS, Crystallographic data for rare-earth aluminum garnets. Amer. Mineral. 49 (1964) 1489—1490.

[62] F. BERTAUT et F. FORRAT, Étude des paramètres des grenats. Compt. Rend. Acad. Sci. [Paris] 244 (1957) 96—99.

[63] G. P. ESPINOSA, Crystal chemical study of the rare-earth iron garnets. J. Chem. Physics 37 (1962) 2344—2347.

[64] S. GELLER, H. J. WILLIAMS and R. C. SHERWOOD, Magnetic and crystallographic study of neodymium substituted yttrium and gadolinium iron garnets. Physic. Rev. 123 (1961) 1692—1699.

[65] S. GELLER and D. W. MITCHELL, Rare earth ion radii in the iron garnets. Acta Crystallogr. 12 (1959) 936.

[66] G. P. ESPINOSA, A crystal chemical study of titanium (IV) and chromium (III) substituted yttrium iron and gallium garnets. Inorg. Chem. 3 (1964) 848—850.

Table 5. (Continued)

A³⁺	B³⁺,C³⁺	a [Å]
Nd	Ga	12.50^{58}, $12.506^{57,67}$
Sm		12.355^{56}, 12.42^{58}, $12.433^{57,67}$
Eu		$12.402^{57,68}$
Gd		12.39^{58}, $12.376^{57,68}$
Tb		Not reported
Dy		12.32^{58}, $12.307^{57,68}$
Ho		12.282^{57}
Er		12.25^{58}, $12.255^{57,67}$
Tm		Not reported
Yb		12.204^{12}, $12.200^{57,67}$
Lu		12.188^{12}, $12.183^{57,63}$

12.000 Å. The most accurate value for a stoichiometric $Y_3Al_2Al_3O_{12}$ is probably 12.002 ± 0.002 Å. For non-stoichiometric yttrium aluminum garnets, the lattice constants are generally higher; they contain excess yttrium[56]. RUBENSTEIN and BARNS[60,61] have carefully determined the lattice constants of single crystals of the rare earth aluminum garnets. These are plotted vs atomic number in Fig. 2. If all other points are correct, then the value for YbAl garnet is about 0.003 Å low. The authors have tacitly assumed that the crystals grew with ideal stoichiometry.

ESPINOSA[63] extended studies made by GELLER and coworkers[64,65] to cover all the rare earth iron garnets including hypothetical ones; that is, he determined the lattice constants that the large rare earth iron garnets would have if they existed. GELLER, WILLIAMS and SHERWOOD[64] had done this for Nd, and BERTAUT and FORRAT[62] had done so by extrapolation from two points; namely from $Y_3Fe_2Fe_3O_{12}$ and ${Y_{1.5}Nd_{1.5}}Fe_2Fe_3O_{12}$. ESPINOSA[63] found a value of 12.600 Å as compared with our earlier value of 12.596 Å for hypothetical NdFe garnet. GELLER et al.[64] found for ${Y_{3-x}Nd_x}Fe_2Fe_3O_{12}$, a maximum for x of 1.88. RAMSEY, STEINFINK and WEISS[69] studying this

[67] H. E. SWANSON, M. C. MORRIS, R. P. STINCHFIELD and E. H. EVANS, Standard x-ray diffraction powder patterns. NBS Monograph 25, Section 1 (1962) p. 34.

[68] H. E. SWANSON, M. C. MORRIS, R. P. STINCHFIELD and E. H. EVANS, Standard x-ray diffraction powder patterns. NBS Monograph 25, Section 2 (1963) p. 22.

[69] T. H. RAMSEY, JR., H. S. STEINFINK and E. J. WEISS, A study of neodymium substituted yttrium iron garnet. J. Physics Chem. Solids 23 (1962) 1105—1110.

system later found a maximum x of 1.95, claiming also that they obtained a single-phase garnet with $x = 1.95$ and $a = 12.524$ Å, the maximum they observed, and 0.011 Å larger than our maximum a. We had reported[64] that single-phase garnets were not obtained
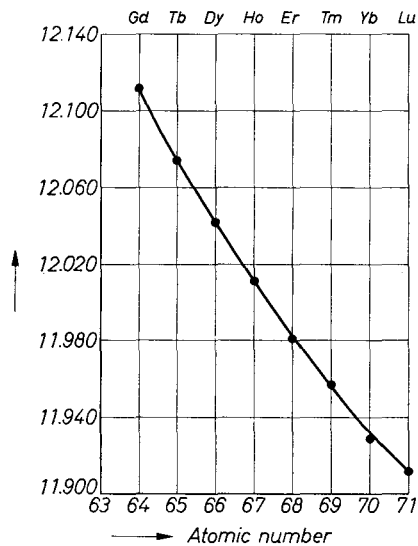

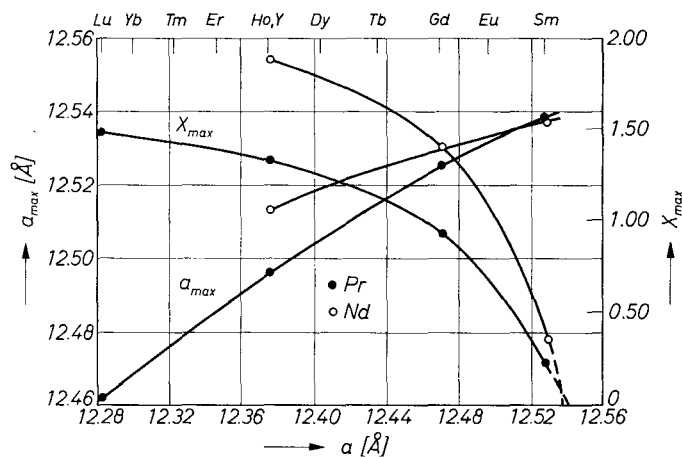Fig. 2. Lattice constant vs atomic number for rare-earth aluminum garnets. (Data from Refs. [60] and [61])

Fig. 3. Maximum lattice constant and maximum x in $\{R_{3-x}Pr_x\}Fe_2Fe_3O_{12}$ and $\{R_{3-x}Nd_x\}Fe_2Fe_3O_{12}$ where R = rare earth or yttrium vs end-member rare earth or yttrium iron garnet lattice constant. (The data for Nd are from Ref.[64], those for Pr from Ref.[63])

for values of $x \geq 1.80$. In a recent attempt to make the garnet with $x = 1.95$, the specimen obtained was clearly not single phase and the garnet phase present had $a = 12.517$ Å, 0.004 Å higher than our previous value. ESPINOSA's work[63], indicated that the Nd_2O_3 we had used must have contained an impurity ion smaller than Nd^{3+}. He obtained a value of 12.488 as opposed to 12.485 Å for the $x = 1.5$ specimen. The new maximum a value is in line with this difference and still indicates maximum $x = 1.88$.
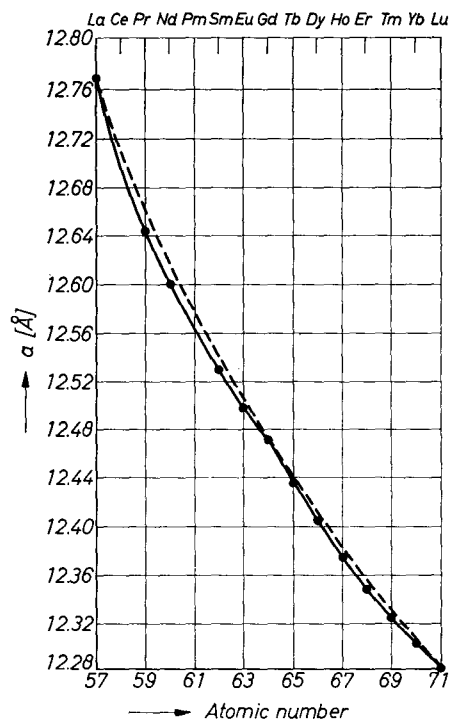
Fig. 4. Lattice constant vs atomic number for rare-earth iron garnets. Dashed curve passes through values for the trivalent rare earths with spherical electronic configuration (after ESPINOSA[63])

ESPINOSA also determined maximum x for M $=$ Pr and La in the systems $\{Y_{3-x}M_x\}Fe_2Fe_3O_{12}$ to be 1.33 and 0.45, respectively. He also determined the maximum substitution of Pr for Lu, Gd and Sm in their iron garnets. The results are shown in Fig. 3 taken from ESPINOSA's paper. It is seen that a maximum lattice constant for any iron garnet, obtained by extrapolation is 12.538 Å in good agreement with 12.540 Å obtained by GELLER et al.[64] who first determined this

value from their work with Nd substituted iron garnets. This value is just about 0.02 Å too small to allow the existence of $Pm_3Fe_2Fe_3O_{12}$. It is just about realized by the garnet $\{Pr_{0.25}Sm_{2.75}\}Fe_2Fe_3O_{12}$ [63].

A plot of a vs atomic number taken from ESPINOSA's paper is given in Fig. 4. It shows the small crystal-field effects on the rare-earth ions not having spherical electronic configurations and the expected cusp at the Gd^{3+} ion.

BERTAUT and FORRAT [62] predicted a value of 12.57 Å for a PmFe garnet, we obtained [64] 12.561 Å. The latter value is also obtained from the curve in ESPINOSA's paper. For a hypothetical $\{Ce_3\}Fe_2Fe_3O_{12}$, a value of 12.699 Å would be obtained from the same curve.

In the case of the gallium garnets, while there have been numerous investigations involving Tb and Tm garnets, I have not been able to find a report of the lattice constants of these with ideal stoichiometry. The lattice constants of the others have been mainly determined first by BERTAUT and FORRAT [58] and then by SCHNEIDER et al. [57] and by SWANSON et al. [67,68] on the materials made by SCHNEIDER et al. Because those of SWANSON et al. are insignificantly different from those of SCHNEIDER et al., only the averages of the two (which in no case differ by more than 0.002 Å) are listed. For YGa garnet, there are several values, the best seeming to be 12.274 ± 0.001 Å.

In the early work on a few of the gallium and aluminum garnets done by KEITH and ROY [56], it was found that excess yttrium or rare-earth oxide was soluble in the garnet. No proof was given, but it was postulated that the large ions were replacing the Ga^{3+} or Al^{3+} ions in octahedral sites. Some of the gallium-garnet crystals grown by REMEIKA (see Ref. [4]) showed solid-solution ranges within the same batch. Subsequently, SCHNEIDER et al. [57] explored these solid solutions in the rare earth and yttrium gallium garnet systems. They found that the "solubility" and lattice constant increase with decreasing rare earth ion radius until Tm^{3+} is reached, then both decrease. For Y^{3+}, both the range of solid solution and lattice-constant difference were substantially larger than those for Ho^{3+} with the same size.

SCHNEIDER et al. [57] also believe that in these solid solutions, the Ga^{3+} ions in a sites are replaced by the excess rare-earth ions. They mention that I said, in private communication, that the solid solution may be of the "interstitial and/or vacancy types instead of substitutional and thus results in a defect structure". I cannot remember exactly what I said but surely there are no interstitial sites in the garnet structure to be occupied. However, I did think it probable

that there might be a vacancy or *combination* vacancy-interstitial
situation. It is somewhat difficult to believe that the large ions of
the same species are going into both c and a sites simultaneously even
though there is little evidence to the contrary. Perhaps the most
substantial evidence is given by the germanate garnets, with rare-
earth ions in a sites, made by MILL', which seem to require larger
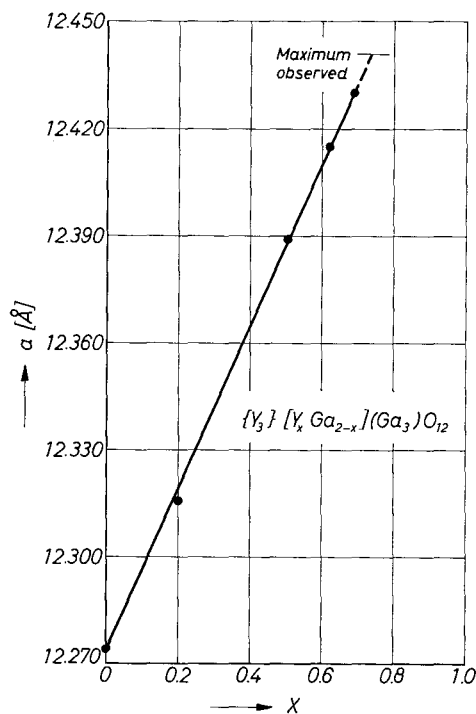c-site and smaller a-site ions. But there is evidence to support, at least

Fig. 5. Lattice constant vs x

tentatively, the substitutional or combined vacancy-interstitial hypo-
thesis, and this evidence is our own[45]. We have made several specimens
with increasing Y_2O_3:Ga_2O_3 ratios. A plot of the lattice constant vs
composition is given in Fig. 5. The lattice constant of the ideally
stoichiometric garnet is 12.274 Å while that obtained for the "garnet"
in the 3:3.25 specimen, which was not single phase, was 12.438 Å,
a very large increase indeed. The maximum lattice constant, 12.441 Å,
in the system was reported by SCHNEIDER *et al.*[57] for the 1:1 ratio.
The maximum solid solution probably has the ratio 3:3.42 or the
formula $Y_{3.74}Ga_{4.26}O_{12}$. The specimen with Y_2O_3:Ga_2O_3 of 3:3.50,

i.e. $Y_{3.69}Ga_{4.31}O_{12}$, was also not quite single phase. On the powder-diffractometer pattern taken with $CuK\alpha$ radiation, there are some extra lines with very low intensity at spacings: 4.17, 3.05, 2.88 Å. Nevertheless, the density of the specimen was measured pycnometrically and found to be 5.73 g/cm³. Now if the formula of the specimen is written $\{Y_3\}[Y_{0.69}Ga_{1.31}](Ga_3)O_{12}$, assuming eight of these per unit cell with lattice constant 12.430 Å, the theoretical x-ray density would be 5.67 g/cm³ in good agreement with the measured value. Any other formula requires oxygen as well as Ga vacancies and would result in lower density. The x-ray density, 5.80 g/cm³, of ideally stoichiometric yttrium gallium garnet is higher than that of $\{Y_3\}[Y_{0.69}Ga_{1.31}](Ga_3)O_{12}$, but this is actually to be expected.

I think that it would still be very interesting to examine the structure of a single crystal of this compound. It must, of course, have uniform composition if such an investigation is to be worthwhile. But obtaining such a crystal does not appear to be a simple task.

In the Tables 3—5 inclusive, I have not put down all values by all investigators. In some cases, I have shown more than one to indicate priority for the particular investigators even though I may believe their value is poorer than a later one. In some few cases, I have seen no point in adding a later one if it appears to be poorer than an earlier one.

Survey of the ions which enter garnets

While I shall try to cite most references, I do not expect this survey to be exhaustive of the references. I hope, however, to succeed in covering all the ions known to enter the garnets. But for a few cases, I shall not be considering slight amounts of ions that by fine spectroscopic measurements are found in a site.

Group IA

1. Li$^+$: a and d sites

$\{Ca_3\}[LiM^{2+}](V_3)O_{12}$ [70], M $\equiv$ Mg	$a = 12.412$ Å
Co	12.404
Ni	12.340
Cu	12.398
Zn	12.420

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[70] G. BAYER, Vanadates $A_3B_2V_3O_{12}$ with garnet structure. J. Amer. Ceramic Soc. 48 (1965) 600.

$\{Na_3\}[Al_2](Li_3)F_{12}$, $a = 12.121$ Å, cryolithionite. According to Menzer[71], the ionic distribution is in accordance with this formula.

2. Na^+: A number of garnets other than cryolithionite contain Na^+ ions in c sites.

$\{NaCa_2\}[Mn_2](As_3)O_{12}$ [72] (berzeliite)	$a = 12.49$ Å
$\{Na_3\}[Al_2](P_3)O_{12}$ [73]	a, not reported

See also 1, 3, 4, 8, 25, 27

Group IB

3. Cu^{2+}: a and c sites

$\{NaCa_2\}[Cu_2](V_3)O_{12}$ [74]	$a = 12.423$ Å
$\{CuGd_2\}[Mn_2](Ge_3)O_{12}$ [43] (tentative)	12.475

See also 1.

Group IIA

4. Mg^{2+}: c and a sites

$\{Mg_3\}[Al_2](Si_3)O_{12}$ [16,28]	$a = 11.459$ Å
$\{Gd_3\}[Mg_2](GaGe_2)O_{12}$ [43]	12.425
$\{MgGd_2\}[Mg_2](Ge_3)O_{12}$ [43]	12.31
$\{MnGd_2\}[MgMn](Ge_3)O_{12}$[43] (probable distribution)	12.395
$\{Ca_3\}[TiMg](Ge_3)O_{12}$ [43]	12.35
$\{Ca_3\}[ZrMg](Ge_3)O_{12}$ [43]	12.514
$\{NaCa_2\}[Mg_2](V_3)O_{12}$ [74]	12.446
$\{Y_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ [7]	
$\{Gd_3\}[Mg_xFe_{2-x}](Fe_{3-x}Si_x)O_{12}$ [75]	

See also 1, 17, 25, 33a.

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[71] G. Menzer, Die Kristallstruktur von Kryolithionit. Z. Kristallogr. **75** (1930) 265—287.

[72] F. Machatschki, Berzeliit, ein Arsenat vom Formel- und Strukturtypus Granat $(X_3Y_2z_3O_{12})$. Z. Kristallogr. **73** (1930) 123—140.

[73] E. Thilo, Über die Isotypie zwischen Phosphaten der allgemeinen Zusammensetzung $(Me_1)_3(Me_2)_2[PO_4]_3$ und den Silikaten der Granatgruppe. Naturwiss. **29** (1941) 239.

[74] A. Durif, Sur quelques composés non silicates isomorphes des granats. Int. Conf. on Physics of the Solid State and Application to Electronics and Telecommunications. Brussels, Belgium (1958) pp. 500—502.

[75] S. Geller, H. J. Williams, R. C. Sherwood and G. P. Espinosa, Magnetic and crystallographic studies of substituted gadolinium iron garnets. J. Appl. Physics **36** (1965) 88—100.

5. Ca^{2+}: thus far, all evidence points to preference for c sites.

There is some indication that Ca^{2+} ions may enter a sites: RING-WOOD and SEABROOK[76] have reported a pressure induced $CaGeO_3$ with garnet structure, i.e. $\{Ca_3\}[CaGe](Ge_3)O_{12}$. We have performed high-pressure experiments on this system and have not obtained a cubic material in any case. The powder photograph of one of the specimens appears to be indexable on a tetragonal cell with $a = 12.51$, $c = 12.36$ Å. The structure does appear to be closely related to that of the garnet. Thus far, we have not obtained single crystals which are required for a structure determination. For examples of Ca^{2+} ion in the garnets, see Tables 3—5 and the many other examples in this survey.

6. Sr^{2+}: c sites

In the earlier survey[8], I had said, "enters c sites but there is no known garnet in which Sr^{2+} ions *fill* the c sites". This was misinterpreted by MILL'[49] to mean that I had said that "Sr^{2+} is too large to fill all the dodecahedral positions and can only replace other cations partially...". He then counters this by giving examples of hydrogarnets, which he writes $3SrO \cdot Ga_2O_3 \cdot 6H_2O$ and $3SrO \cdot Al_2O_3 \cdot 6H_2O$. Leaving aside the misinterpretation of my remark, I do not consider the hydro-garnets to be *isostructural* with the garnets. *Thus* at the time I wrote the earlier paper, the statement was correct. Since then MILL' has produced a number of interesting garnets with Sr^{2+} ions filling the c sites; these are listed in Table 4. Nevertheless, the first indications that substantial amounts of Sr^{2+} ion would enter c sites were given in 1960:

$\{Sr_{0.5}Y_{2.5}\}[Fe_2](Fe_{2.5}Ge_{0.5})O_{12}$ [43] $a = 12.414$ Å

$\{Sr_{0.5}Y_{2.5}\}Sn_{0.5}Fe_{4.5}O_{12}$ [77] 12.49

$\{SrY_2\}SnFe_4O_{12}$ [77] 12.61

7. Ba^{2+}: small amounts are known to enter c sites[77]

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[76] A. E. RINGWOOD and M. SEABROOK, High pressure phase transformations in germanate pyroxenes and related compounds. J. Geophys. Res. 68 (1963) 4601—4609.

[77] S. GELLER, R. M. BOZORTH, M. A. GILLEO and C. E. MILLER, Crystal chemical and magnetic studies of garnet systems $M_3^{2+}Fe_2Sn_3O_{12}$—$Y_3Fe_2Fe_3O_{12}$. J. Physics Chem. Solids 12 (1959) 111—118.

Group IIB

8. Zn^{2+}: a sites and possibly c sites

$\{Gd_3\}[Zn_2](GaGe_2)O_{12}$ [43] $a = 12.464$ Å

$\{MnGd_2\}[ZnMn](Ge_3)O_{12}$ [45] (probable distribution)   12.427

$\{NaCa_2\}[Zn_2](V_3)O_{12}$ [74]   12.439

See also 1.

9. Cd^{2+}: c sites

$\{CdGd_2\}[Mn_2](Ge_3)O_{12}$ [43] $a = 12.473$ Å

See also Tables 3 and 4.

Group IIIB

10. Sc^{3+}: a sites

Examples of end-member garnets containing Sc^{3+} ions are given in Tables 3 and 4. However, the earliest published report of substitution of Sc^{3+} ion in the iron garnets is given in Ref. [78]. Some systems studied involving Sc^{3+} ion are:

$\{Y_3\}[Fe_{2-x}Sc_x](Fe_3)O_{12}$ [7,59,78]

$\{Gd_3\}[Fe_{2-x}Sc_x](Fe_3)O_{12}$ [75]

$\{Y_{3-y}Ca_y\}[Sc_xFe_{2-x}](Si_yFe_{3-y})O_{12}$ [7]

$\{Gd_2Y\}[Fe_{2-x}Sc_x](Fe_3)O_{12}$ [75]

11. Y^{3+}: c and a sites

See Tables 4 and 5 and the various other examples given in this survey. Also see previous discussion of solid solutions in the Y_2O_3–Ga_2O_3 and Y_2O_3–Al_2O_3 systems.

12. Rare earths: all the trivalent rare-earth ions except that of Pm are *known* to enter c sites in the garnets. Pm^{3+} should also, but as far as I know the rarity of Pm has precluded its being tried. Replacement of at least 1 $^0/_0$ of the yttrium by Ce^{3+} in YFe garnet has been recently proved [79]. (Actually, it should be possible to replace 30$^0/_0$ of the Y^{3+} by Ce^{3+} ion.) The smaller trivalent ions of Lu, Yb, Tm, Er, Ho, and Dy also enter a sites as shown in Table 4. Substitution of Yb^{3+} (in small amount) for Fe^{3+} in

[78] M. A. GILLEO and S. GELLER, Substitution for iron in yttrium iron garnet. J. Appl. Physics **29** (1958) 380—381.
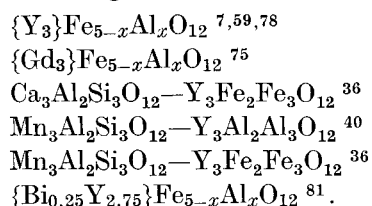
[79] K. A. WICKERSHEIM and R. A. BUCHANAN, Optical studies of exchange in substituted garnets. J. Appl. Physics **38** (1967) 1048—1049.

YFe garnet has been indicated by microwave resonance absorption measurement[80]. Various mixed rare earth iron garnet systems have also been studied.

Group IIIA

13. Al^{3+}: a and d sites

Many examples of end-member garnets containing Al^{3+} ion are given in Tables 3—5. In addition, several solid-solution systems including the Al^{3+} ion have been studied; some examples are:

$\{Y_3\}Fe_{5-x}Al_xO_{12}$ [7,59,78]

$\{Gd_3\}Fe_{5-x}Al_xO_{12}$ [75]

$Ca_3Al_2Si_3O_{12}$—$Y_3Fe_2Fe_3O_{12}$ [36]

$Mn_3Al_2Si_3O_{12}$—$Y_3Al_2Al_3O_{12}$ [40]

$Mn_3Al_2Si_3O_{12}$—$Y_3Fe_2Fe_3O_{12}$ [36]

$\{Bi_{0.25}Y_{2.75}\}Fe_{5-x}Al_xO_{12}$ [81].

14. Ga^{3+}: a and d sites

Many examples are given in Tables 3—5 and elsewhere in this survey. One of the most extensively studied systems is $Y_3Fe_{5-x}Ga_xO_{12}$ [27], a detailed discussion of which will be given elsewhere in this paper.

15. In^{3+}: a sites

The first introduction of In^{3+} ion into YFe garnet was reported in 1958[78]. Examples of complete a site occupation are given in Tables 3 and 4. There is a possibility that In^{3+} ions will enter c sites.
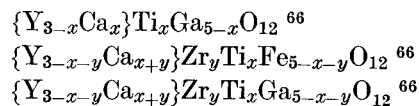
Group IVB

16. Ti^{4+}: prefers a sites but enters d sites

$\{Ca_3\}[TiNi](Ge_3)O_{12}$	$a = 12.341$[74], 12.32[43] Å
$\{Ca_3\}[TiCo](Ge_3)O_{12}$	12.356[74], 12.35[43]
$\{Y_{3-x}Ca_x\}Ti_xFe_{5-x}O_{12}$ [66,82]	

[80] J. F. Dillon, Jr., J. P. Remeika and L. R. Walker, Yb^{3+} on octahedral sites in YIG. Bull. Amer. Physic. Soc. [2] 11 (1966) 378.

[81] S. Geller, H. J. Williams, R. C. Sherwood and G. P. Espinosa, Bismuth substitution in yttrium iron aluminum garnets. J. Appl. Physics 35 (1964) 1754—1756.

[82] S. Geller, R. C. Sherwood, G. P. Espinosa and H. J. Williams, Substitution of Ti^{4+}, Cr^{3+} and Ru^{4+} ions in yttrium iron garnet. J. Appl. Physics 36 (1965) 321.
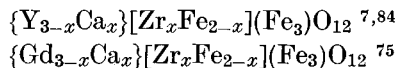
$\{Y_{3-x}Ca_x\}Ti_xGa_{5-x}O_{12}$ [66]
$\{Y_{3-x-y}Ca_{x+y}\}Zr_yTi_xFe_{5-x-y}O_{12}$ [66]
$\{Y_{3-x-y}Ca_{x+y}\}Zr_yTi_xGa_{5-x-y}O_{12}$ [66]

See also 4, 23, 24.

17. Zr^{4+}: a and c sites

$\{Ca_3\}[ZrMg](Ge_3)O_{12}$ [43] $a = 12.514$ Å
$\{Ca_3\}[Zr_2](V_{0.5}Ga_{2.5})O_{12}$ [83]   12.676
$\{Ca_3\}[Zr_2](V_{0.5}Fe_{2.5})O_{12}$ [83]   12.704
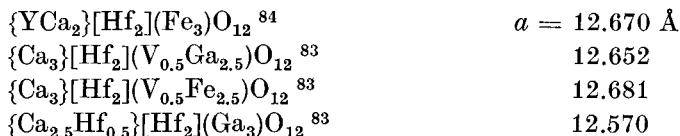$\{Ca_{2.5}Zr_{0.5}\}[Zr_2](Ga_3)O_{12}$ 12.600[84], 12.599[45] Å

(In this case, our powder photograph had some faint extra lines, indicating that the formula of the garnet is not precisely as written.)

$\{Y_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ [7,84]
$\{Gd_{3-x}Ca_x\}[Zr_xFe_{2-x}](Fe_3)O_{12}$ [75]

See also 4, 23, 24, 33a, 35.

18. Hf^{4+}: a and c sites

$\{YCa_2\}[Hf_2](Fe_3)O_{12}$ [84] $a = 12.670$ Å
$\{Ca_3\}[Hf_2](V_{0.5}Ga_{2.5})O_{12}$ [83]   12.652
$\{Ca_3\}[Hf_2](V_{0.5}Fe_{2.5})O_{12}$ [83]   12.681
$\{Ca_{2.5}Hf_{0.5}\}[Hf_2](Ga_3)O_{12}$ [83]   12.570

See also 23 and 24.

Group IVA

19. Si^{4+}: d sites only

Many examples are given in Table 3 and elsewhere in this survey. Comments under Si^{4+} in the earlier survey[8] have been corrected[7].

20. Ge^{4+}: prefers d sites but will enter a sites

Many examples are given in Table 4 and elsewhere in this survey. Comments under Ge^{4+} in the earlier survey[8] have been corrected[7].

See also Refs.[7] and [97].

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[83] B. V. Mill', G. M. Zadneprovskii and V. V. Bakakin, New compounds with garnet-type structure. Izv. Akad. Nauk SSSR, Neorg. Mater. 2 (1966) 1861—1864.

[84] S. Geller, R. M. Bozorth, C. E. Miller and D. D. Davis, Crystal chemical and magnetic studies of garnet systems $\{YCa_2\}[M_2^{4+}](Fe_3)O_{12}$—$\{Y_3\}[Fe_2](Fe_3)O_{12}$; M = Zr or Hf. J. Physics Chem. Solids 13 (1960) 28—32.

21. Sn^{4+}: prefers a sites but enters d sites

In the earlier survey[8], we gave as an example the distribution of Sn^{4+} ion in $Ca_3Fe_2Sn_3O_{12}$. In our first paper on the tin-substituted yttrium iron garnets, we indicated that we did not obtain a single-phase garnet with this composition. In later work[85], we were still unable to do so and we believe tentatively that defect structures are indicated. In addition to our studies[77,85] of the system, $\{Y_{3-x}Ca_x\}Fe_{5-x}Sn_xO_{12}$, some studies[86] have been made on the analogous Gd system; lattice constants are not reported, however. Other Sn-containing garnets reported are:

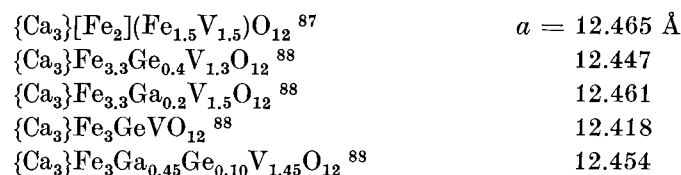|	
$\{Ca_3\}Sn_2V_{0.5}Ga_{2.5}O_{12}$ [83]	$a = 12.589$ Å
$\{Ca_3\}Sn_3Ga_2O_{12}$	12.69[49], 12.685[45]

(In this case, our powder photographs contained some faint unidentifiable extra lines, indicating that the formula of this garnet is not precisely as written.)

See also 6, 23, 24.

Group VB

22a. V^{3+}: a sites only (probably)
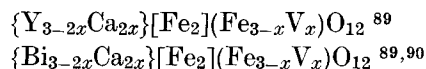
See Tables 3 and 4.

b. V^{5+}: d sites

$\{Ca_3\}[Fe_2](Fe_{1.5}V_{1.5})O_{12}$ [87]	$a = 12.465$ Å
$\{Ca_3\}Fe_{3.3}Ge_{0.4}V_{1.3}O_{12}$ [88]	12.447
$\{Ca_3\}Fe_{3.3}Ga_{0.2}V_{1.5}O_{12}$ [88]	12.461
$\{Ca_3\}Fe_3GeVO_{12}$ [88]	12.418
$\{Ca_3\}Fe_3Ga_{0.45}Ge_{0.10}V_{1.45}O_{12}$ [88]	12.454

[85] S. GELLER, H. J. WILLIAMS, R. C. SHERWOOD and G. P. ESPINOSA, On the tin-substituted yttrium iron garnets. J. Physics Chem. Solids 26 (1965) 443—445.

[86] K. P. BELOV and I. C. LYUBUTIN, Magnetic properties of the substituted garnet ferrites of gadolinium and yttrium. Kristallografiya 10 (1965) 351—356; Soviet Physics—Crystallography 10 (1966) 282—286.
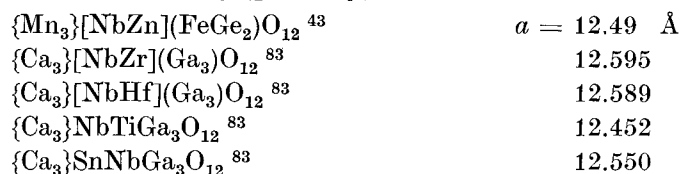
[87] S. GELLER, G. P. ESPINOSA, H. J. WILLIAMS, R. C. SHERWOOD and E. A. NESBITT, Rare-earth and yttrium-free ferrimagnetic garnet with 493°K Curie temperature. Appl. Physics Letters 3 (1963) 60—61.

[88] S. GELLER, G. P. ESPINOSA, R. C. SHERWOOD and H. J. WILLIAMS, Additional yttrium-free ferrimagnetic garnets. J. Appl. Physics 36 (1965) 321—322.

$\{Y_{3-2x}Ca_{2x}\}[Fe_2](Fe_{3-x}V_x)O_{12}$ [89]

$\{Bi_{3-2x}Ca_{2x}\}[Fe_2](Fe_{3-x}V_x)O_{12}$ [89,90]

See also 1, 3, 4, 8, 21, 27.

23. Nb^{5+}: a sites only (probably)

$\{Mn_3\}[NbZn](FeGe_2)O_{12}$ [43]	$a = 12.49$ Å
$\{Ca_3\}[NbZr](Ga_3)O_{12}$ [83]	12.595
$\{Ca_3\}[NbHf](Ga_3)O_{12}$ [83]	12.589
$\{Ca_3\}NbTiGa_3O_{12}$ [83]	12.452
$\{Ca_3\}SnNbGa_3O_{12}$ [83]	12.550

24. Ta^{5+}: a sites only (probably)

As indicated in my earlier survey[8], it is to be expected that Ta^{5+} with a size only slightly smaller than that of Nb^{5+} would replace Nb^{5+} in like compounds. This has been shown to be the case by MILL'[83]:

$\{Ca_3\}[TaZr](Ga_3)O_{12}$	$a = 12.591$ Å
$\{Ca_3\}[TaHf](Ga_3)O_{12}$	12.584
$\{Ca_3\}TaTiGa_3O_{12}$	12.455
$\{Ca_3\}TaSnGa_3O_{12}$	12.554

Group VA

25. P^{5+}: d sites only

$\{NaCa_2\}[Mg_2](P_3)O_{12}$ [73]	a, not reported

See 2.

26. As^{5+}: d sites only

See 2.

27. Sb^{5+}: a sites only

$\{Ca_3\}[Sb_{1.5}Fe_{0.5}](Fe_3)O_{12}$ [91]	$a = 12.580$ Å
$\{Ca_3\}[Sb_{1.5}Ga_{0.5}](Ga_3)O_{12}$ [45]	12.472
$\{NaCa_2\}[Sb_2](Fe_3)O_{12}$ [45]	12.600
$\{NaCa_2\}[Sb_2](Ga_3)O_{12}$ [45]	12.480
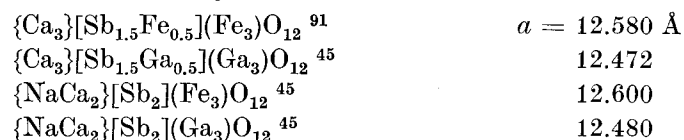
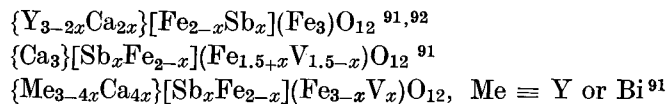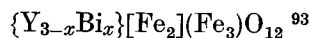[89] S. GELLER, G. P. ESPINOSA, H. J. WILLIAMS, R. C. SHERWOOD and E. A. NESBITT, Ferrimagnetic garnets containing pentavalent vanadium. J. Appl. Physics **35** (1964) 570—572.

[90] G. P. ESPINOSA and S. GELLER, Growth of single-crystal garnets of the system $\{Bi_{3-2x}Ca_{2x}\}[Fe_2](Fe_{3-x}V_x)O_{12}$. J. Appl. Physics **35** (1964) 2551—2552.

[91] S. GELLER, H. J. WILLIAMS, G. P. ESPINOSA and R. C. SHERWOOD, Ferrimagnetic garnets containing pentavalent antimony. J. Appl. Physics **35** (1964) 542—547.
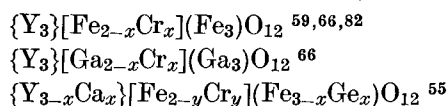
$\{Y_{3-2x}Ca_{2x}\}[Fe_{2-x}Sb_x](Fe_3)O_{12}$ [91,92]
$\{Ca_3\}[Sb_xFe_{2-x}](Fe_{1.5+x}V_{1.5-x})O_{12}$ [91]
$\{Me_{3-4x}Ca_{4x}\}[Sb_xFe_{2-x}](Fe_{3-x}V_x)O_{12}$, Me $\equiv$ Y or Bi [91]

28. Bi^{3+}: c sites only

$\{Y_{3-x}Bi_x\}[Fe_2](Fe_3)O_{12}$ [93]

See 13, 22b, 27.

Group VIB

29. Cr^{3+}: a sites only

See Tables 3 and 4 for examples of end-members.

$\{Y_3\}[Fe_{2-x}Cr_x](Fe_3)O_{12}$ [59,66,82]
$\{Y_3\}[Ga_{2-x}Cr_x](Ga_3)O_{12}$ [66]
$\{Y_{3-x}Ca_x\}[Fe_{2-y}Cr_y](Fe_{3-x}Ge_x)O_{12}$ [55]

Group VIIB

30a. Mn^{2+}: c and a sites

$\{CaGd_2\}[Mn_2](Ge_3)O_{12}$ [43]	$a = 12.55$ Å
$\{MnGd_2\}[Mn_2](Ge_3)O_{12}$ [43]	12.482
$\{CaY_2\}[Mn_2](Ge_3)O_{12}$ [43]	12.475
$\{MnY_2\}[Mn_2](Ge_3)O_{12}$ [43]	12.392
$\{Gd_3\}[Mn_2](GaGe_2)O_{12}$ [43]	12.550
$\{Y_3\}[Fe_{1.6}Mn_{0.4}](Fe_{2.6}Si_{0.4})O_{12}$ [55]	12.359
$\{Y_{2.9}Mn_{0.1}\}[Fe_2](Fe_{2.9}Si_{0.1})O_{12}$ [55]	12.368
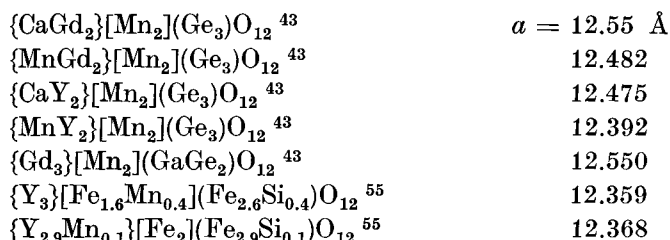
See Tables 3 and 4 and also 2, 4, 8, 9, 33a, 35.

b. Mn^{3+}: a sites

$\{Y_3\}[Mn_{0.1}Fe_{1.9}](Fe_3)O_{12}$ [55] $a = 12.375$ Å
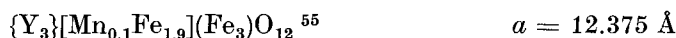
See Table 4 for end-members.

Group VIII

31a. Fe^{2+}: c and a sites

|	
$\{Fe_3\}[Al_2](Si_3)O_{12}$ [28]	$a = 11.526$ Å
$\{Y_{2.9}Fe_{0.1}\}[Fe_{0.3}^{2+}Fe_{1.7}^{3+}](Fe_{2.6}^{3+}Si_{0.4})O_{12}$ [55]	12.340
$\{Y_3\}[Fe_{2-x}^{3+}Fe_x^{2+}](Fe_{3-x}^{3+}Si_x)O_{12}$ [55]	
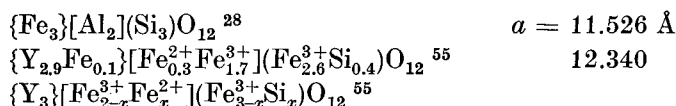
[92] G. BLASSE, Magnetic-garnet phases containing pentavalent antimony. Philips Res. Reports **19** (1964) 68—72.
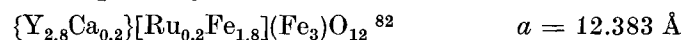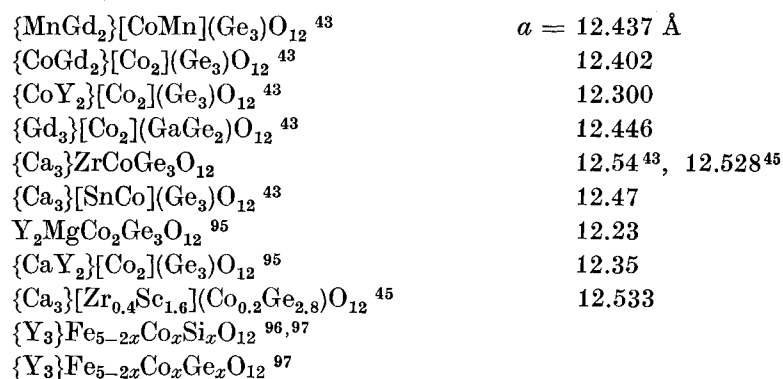
[93] S. GELLER, H. J. WILLIAMS, G. P. ESPINOSA, R. C. SHERWOOD and M. A. GILLEO, The reduction of the preparation temperature of garnets by bismuth substitution. Appl. Physics Letters **3** (1963) 21—22.

b. Fe^{3+}: a and d sites

See the numerous examples in Tables 3—5 and throughout this survey.

c. Fe^{4+}: d sites [94]

$\{Y_{2.9}Ca_{0.1}\}[Fe_2](Fe^{3+}_{2.9}Fe^{4+}_{0.1})O_{12}$ [45] $a = 12.378$ Å
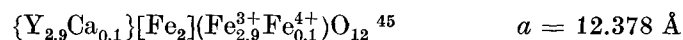
Magnetic measurements have not as yet been made on this material. The formula is written in accord with the Tchernev[94] paper.

32. Ru^{4+}: probably a sites

$\{Y_{2.8}Ca_{0.2}\}[Ru_{0.2}Fe_{1.8}](Fe_3)O_{12}$ [82] $a = 12.383$ Å

33a. Co^{2+}: c, a and d sites

$\{MnGd_2\}[CoMn](Ge_3)O_{12}$ [43]	$a = 12.437$ Å
$\{CoGd_2\}[Co_2](Ge_3)O_{12}$ [43]	12.402
$\{CoY_2\}[Co_2](Ge_3)O_{12}$ [43]	12.300
$\{Gd_3\}[Co_2](GaGe_2)O_{12}$ [43]	12.446
$\{Ca_3\}ZrCoGe_3O_{12}$	12.54[43], 12.528[45]
$\{Ca_3\}[SnCo](Ge_3)O_{12}$ [43]	12.47
$Y_2MgCo_2Ge_3O_{12}$ [95]	12.23
$\{CaY_2\}[Co_2](Ge_3)O_{12}$ [95]	12.35
$\{Ca_3\}[Zr_{0.4}Sc_{1.6}](Co_{0.2}Ge_{2.8})O_{12}$ [45]	12.533
$\{Y_3\}Fe_{5-2x}Co_xSi_xO_{12}$ [96,97]	
$\{Y_3\}Fe_{5-2x}Co_xGe_xO_{12}$ [97]	

See also 1, 16, Table 3, and discussion section on ionic-site preference.

b. Co^{3+} a and d sites

$\{Ca_3\}[Sc_{1.8}Co_{0.2}](Ge_3)O_{12}$ [45]	$a = 12.501$ Å
$\{Ca_3\}[Sc_{1.8}Zr_{0.2}](Co_{0.2}Ge_{2.8})O_{12}$ [45]	12.518
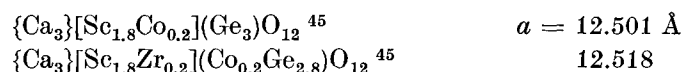
[94] D. I. TCHERNEV, Frequency-dependent anisotropy in Si- and Co-doped YIG and LuIG. J. Appl. Physics **37** (1966) 1318—1320. See also D. L. WOOD and J. P. REMEIKA, Optical transparency of rare-earth iron garnets. J. Appl. Physics **37** (1966) 1232—1233.

[95] D. REINEN, Die Lichtabsorption des Co^{2+} und Ni^{2+} in oxidischen Festkörpern mit Granatstruktur I. Z. anorg. allg. Chem. **327** (1964) 238—252.

[96] S. GELLER, H. J. WILLIAMS, R. C. SHERWOOD and G. P. ESPINOSA, Substitutions of divalent transition metal ions in yttrium iron garnet. J. Appl. Physics **33** (1962) 1195—1196.

[97] S. GELLER, H. J. WILLIAMS, G. P. ESPINOSA and R. C. SHERWOOD, Substitution of divalent cobalt in yttrium iron garnet. Physic. Rev. **136** (1964) A1650—A1656.

After calcining these specimens for half an hour at 1215 °C in oxygen, the first was fired at 1200 °C for 24 hours in O_2 then quenched. The second was fired at 1220 °C for 2 hours in O_2, then reground, recompacted and refired at 1225 °C for 16 hours in O_2. The first specimen, i.e. with the Co^{3+} ions presumably in octahedral sites is canary yellow; the second is yellow-green.

34. Rh^{3+}: a sites

See Table 4 for end-members.

35. Ni^2: a sites

$\{MnGd_2\}[MnNi](Ge_2)O_{12}$ [43]	$a = 12.413$ Å
$\{Gd_3\}[Ni_2](GaGe_2)O_{12}$ [43]	12.401
$\{Ca_3\}[ZrNi](Ge_3)O_{12}$ [43,45]	12.50
$\{Y_3\}[Fe_{2-x}Ni_x](Fe_{3-x}Si_x)O_{12}$ [55]	
$\{Y_3\}[Fe_{2-x}Ni_x](Fe_{3-x}Ge_x)O_{12}$ [55]	

See also 1 and 16.

Note: Wherever a system is given in the above survey, lattice constants for various compositions are given in the references.

Ionic site preference

In our earlier work on the garnets, it *appeared* that the octahedral and tetrahedral sites preferred cations with spherical or pseudospherical ground-state electronic configurations. I should emphasize that we did not assert this rule; rather we indicated that experiments designed to synthesize garnets with ions not satisfying this rule were unsuccessful. However, even though we were aware of the paper (see Ref. [8]), we somehow missed the synthesis by DURIF [74] of the garnet $\{NaCa_2\}[Cu_2](V_3)O_{12}$ in 1958. This alone would be enough to negate this rule because the Cu^{2+} ion has one of the largest Jahn-Teller distortions. But subsequently [55] we managed to replace a small amount of Fe^{3+} by Mn^{3+} ion in YFe garnet. Because it was only about 2% replacement, we could not be *absolutely* sure of it, even though the powder photograph indicated a single-phase material and the moment per formula unit was significantly higher than that of pure YFe garnet as it should have been.

More recently, garnets in which Mn^{3+} ions fill the a sites have been synthesized [47]. The Mn^{3+} ion, of course, is the other $3d$ ion with a very large Jahn-Teller distortion. Further, a silicate garnet (goldmanite)

was discovered[98] in which the V^{3+} ion very nearly filled the a sites, and in fact $Ca_3V_2Si_3O_{12}$ and the analogous germanate have been synthesized by others and also by us (see Table 3).

It still appears, however, that in the *garnets*, site preferences depend mostly on relative ionic sizes with the largest ions tending to occupy the dodecahedral or 8-coordination sites. Usually, but not always the smallest ions prefer the tetrahedral sites. There is no doubt that the Cr^{3+} ion in both the perovskite-like and garnet compounds is smaller than the Fe^{3+} ion. In fact, according to crystal field theory it should be[50,51]. Still the Cr^{3+} ion prefers cubic or octahedral symmetry; in the garnets it appears to go exclusively into the a sites even when other ions present are larger, for example, when substituted for Fe^{3+} or Ga^{3+} ions in YFe or YGa garnet, respectively. Much more Cr^{3+} replaces the Ga^{3+} than it does the Fe^{3+} ion indicating how sensitive this replacement is to the relative ionic sizes of the Fe^{3+} and Ga^{3+} in the tetrahedral coordination[66].

As pointed out earlier, the behavior of Ga^{3+} vs Al^{3+} ion when substituted for Fe^{3+} ion is still not understood on the ionic size basis. Also it is not entirely clear why so large an ion as Co^{2+}, while preferring the octahedral sites also goes into tetrahedral sites in substantial amount. [However, Co^{2+} does have a pseudospherical ground state ($4A_2$) in tetrahedral coordination; this may yet have some bearing on the matter.]

In a 1964 paper[95], REINEN has made certain claims regarding the site preference of the Co^{3+} ion. In particular he states: "Die von GELLER vertretene Ansicht, daß das Co^{2+}-Ion in Granaten die oktaedrische Koordination der tetraedrischen vorzieht, ist sicherlich nicht korrekt". The reference REINEN gives is to the present reference[43]. REINEN goes on to point out "... daß wie in Spinellen das Co^{2+}-Ion auch in Granaten eine starke Tendenz zu tetraedrischer Koordination besitzt." Further he says that the presence of the small Ge^{4+} ions, however, blocks the tetrahedral sites and therefore weakens this tendency. I shall show that all the evidence, including even that of REINEN, supports the original conclusion that in the garnets, the Co^{2+} ions prefer octahedral sites even though some Co^{2+} ions may go into tetrahedral sites.

The situation in the case of the spinels is not at all straightforward. In $CoAl_2O_4$ the Co^{2+} ions are in tetrahedral sites; on this basis alone

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[98] R. H. MOENCH and R. MEYROWITZ, Goldmanite, a vanadium garnet from Laguna, New Mexico. Amer. Mineral. **49** (1964) 644—655.

one might say that Co^{2+} ions appear to prefer tetrahedral sites, else $CoAl_2O_4$ would be an inverse spinel. Contrary to REINEN's arguments, however, very little, if any, germanium seems to exchange with Co in Co_2GeO_4, even though this should be easier in the spinel than in the garnet structure. So this already moves toward refutation of REINEN's thinking even on the spinels. But the really important point is that $CoFe_2O_4$ *is* an *inverse* spinel. Magnetic measurements have shown that all the Co^{2+} ions are in octahedral sites*. There is no germanium doing any blocking in $CoFe_2O_4$; the Fe^{3+} ions could be in either site. In fact, $MnFe_2O_4$ tends to be a normal spinel so it would seem that Co^{2+} does not actually show much desire for tetrahedral sites in $CoFe_2O_4$. But the situation with the garnets is much clearer: REINEN's remarks notwithstanding, the Co^{2+} ions *prefer* the octahedral coordination even though they will go into tetrahedral sites.

Now one of REINEN's strongest arguments is his synthesis of $Ca_3Zr_2Ge_2CoO_{12}$ showing that he was able to force one cobalt per formula unit into tetrahedral sites. On the other hand, he says that the distribution in $\{Y_2Ca\}[Co_2](Ge_3)O_{12}$ is as here indicated, that is, all octahedral sites are *filled* with Co^{2+} ions.

In the earlier part of his paper, REINEN says that even in $Ca_3ZrCoGe_3O_{12}$, *much* cobalt is in tetrahedral sites with an amount of Ge^{4+} equal to it in octahedral sites. Then why does not just a little bit of Co exchange with Ge in the case of $\{Y_2Ca\}[Co_2](Ge_3)O_{12}$? Further, even though he found that $Y_2Co_3Ge_3O_{12}$ was blue when fired in N_2, he agreed with us that the distribution is as we suggested it is—that is, $\{Y_2Co\}[Co_2](Ge_3)O_{12}$. Thus logically, this implies only that even if one could make garnets in which the d sites must be *filled* with Co^{2+} ions, all one could say is that the Co^{2+} ions do not have a preference between a and d sites. Of course, no such garnet has been made.

Actually, it is not even possible to make the garnet $\{Ca_3\}[Zr_2](CoGe_2)O_{12}$ (claimed by REINEN) by solid-state reaction. We have investigated the following system: $\{Ca_3\}CoZr_yGe_{3-y}O_{12}$ to see how much Co^{2+} ion will be forced into the tetrahedral sites. We assume that little or no Ge^{4+} will be in octahedral sites and will show later why this is valid. Thus we may write the distribution formula

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* *Added in proof.* A paper (EC-1) presented at the recent International Congress on Magnetism by G. A. SAWATSKY, F. VAN DER WOUDE and A. H. MORRISH indicates that the distribution of Co^{2+} ion in $CoFe_2O_4$ is sensitive to heat treatment. Nevertheless, at most, about 20 % of the Co^{2+} ions enter tetrahedral sites.

$\{Ca_3\}[Zr_{1+x}Co_{1-x}](Co_xGe_{3-x})O_{12}$. The garnet Reinen claims to have made has $x = 1.00$ and has a lattice constant of 12.62 Å. Our specimen with an attempted $x = 1.00$ is *not* single phase; the garnet present has $a = 12.619 \pm 0.002$ Å. We have made several other specimens:

$$x = 0.00 \qquad a = 12.528 \text{ Å}$$
$$0.20 \qquad 12.557$$
$$0.40 \qquad 12.588$$
$$0.60 \qquad 12.619.$$

Note that with $x = 0.60$, that is for $\{Ca_3\}[Zr_{1.6}Co_{0.4}](Co_{0.6}Ge_{2.4})O_{12}$, the lattice constant is the *same* as for the garnet phase present in the specimen attempted with $x = 1.00$ and also equal to the value obtained by Reinen. Further, even the specimen with $x = 0.60$ is not quite single phase. However, maximum x in this system is very near 0.60. So that even in this system, Co^{2+} does *not* show a *preference* for tetrahedral sites. That is, it does not seem possible to force more than $60^0/_0$ of the Co^{2+} into these sites.

Reinen also bases some of his claim on the observation that in the $\{Ca_3\}Me^{4+}Co^{2+}Ge_3O_{12}$ garnets, *many* Ge^{4+} ions are in ocatahedral sites while many Co^{2+} ions are in tetrahedral sites. (This is required if Co^{2+} ions are to be in tetrahedral sites, else the crystals would be of a complex vacancy type.) Now in our 1960 paper[43] we did not, of course, rule out the possibility that some of the Co^{2+} ions did go into tetrahedral sites in the garnets discussed in that paper, but we said that they were few and I still think so.

In a paper, overlooked by Reinen, it was shown by Pappalardo, Wood and Linares[99] that the tetrahedrally coordinated Co^{2+} ion has *much* stronger absorption than the octahedral Co^{2+} ion. In fact, that paper points out the discussions that those authors had with me. Our differences were resolved by just the point mentioned[99]: it is possible by optical spectroscopy to observe *very* small amounts of tetrahedral Co^{2+} ion, but even large amounts of octahedral Co^{2+} ion in the presence of very small amounts of tetrahedral Co^{2+} ion are not observable by this technique. The oscillator strengths of tetrahedral Co^{2+} appear to be between about two and three orders of magnitude larger than those of octahedral Co^{2+}. This appears to be the case for

[99] R. Pappalardo, D. L. Wood and R. C. Linares, Jr., Optical absorption study of Co-doped oxide systems. II. J. Chem. Physics **35** (1961) 2041—2059.

Ni^{2+} also[100] and possibly accounts for REINEN's conclusions about Ni^{2+} ion in the garnets. In this case also, there is evidence[55,100] that very few Ni^{2+} ions enter tetrahedral sites in the garnets (see below). In the paper by PAPPALARDO, WOOD and LINARES[100], they show that Ni^{2+} doped yttrium gallium garnets contain *only* octahedrally coordinated Ni^{2+} ions.

With regard to REINEN's results concerning the effect of temperature on distribution, if the tetrahedral site occupancy by Co^{2+} ions is low, a small absolute change will result in a high-percentage change in the tetrahedral sites. It is this percentage change that is seen in REINEN's Fig. 12. Thus, REINEN's results on $Ca_3ZrCoGe_3O_{12}$ imply only a small amount of Co^{2+} ion in tetrahedral sites. We have also fired our specimen of $\{Ca_3\}ZrCoGe_3O_{12}$ at three different temperatures: 1320 °C (in air), 1190 and 1125 °C in N_2. Contrary to REINEN's findings, the lattice constant was unchanged by these heat treatments. Also we saw no reddish gray color; the specimen fired at 1125 °C has a light blue-gray color.

I may also point out that in a paramagnetic resonance study of Co^{2+} ion in yttrium gallium garnet by CHAMBERLAIN and COOPER[101], no spectrum was observed having the S_4 symmetry for the tetrahedral sites; only a spectrum with the C_{3i} symmetry of the a sites was observed. This does not mean that there were no Co^{2+} ions in the tetrahedral sites of their YGa garnet specimen, just as the observation that the optical spectrum comes only from the tetrahedral Co^{2+} ions does not mean that there are only tetrahedral Co^{2+} ions in YGa garnet.

In the magnetic studies of the $\{Y_3\}Co_xFe_{5-2x}Si_xO_{12}$ and $\{Y_3\}Co_xFe_{5-2x}Ge_xO_{12}$ systems[97], we arrived at a good accounting for the observed results through application of the model[7] mentioned earlier and results obtained[55] on other divalent ion substituted yttrium iron garnets. In the first system, that is, the one in which the Co^{2+} ion was compensated by Si^{4+}, samples with $0.10 \leq x \leq 1.00$ were prepared, while for the system with Ge^{4+} ion compensation, specimens with $0.20 \leq x \leq 2.50$ were prepared. Our conclusion was: when $0.20 \leq x \leq 2.20$, 20% of the Co^{2+} ions were in tetrahedral sites. This demonstrates further the preference of Co^{2+} ions for the octahedral

[100] R. PAPPALARDO, D. L. WOOD and R. C. LINARES, JR., Optical absorption spectra of Ni-doped oxide systems. I. J. Chem. Physics **35** (1961) 1460—1478.

[101] J. R. CHAMBERLAIN and R. W. COOPER, Paramagnetic resonance in yttrium gallium garnet: Co^{2+} and Mn^{2+}. Proc. Physic. Soc. [London] 87 (1966) 967—970.

sites in the *garnets*. In these garnets, more Fe^{3+} ion could be in the octahedral sites but apparently this does not occur.

The amounts of Ge^{4+} in octahedral sites in the $\{Y_3\}Co_xFe_{5-2x}Ge_xO_{12}$ system are quite small: according to our estimates[97], there is 0.01 atom per formula unit in octahedral sites when $x = 1.00$ and 0.16 when $x = 2.20$.

I wish to make it very clear that I do not argue that Co^{2+} ion prefers octahedral coordination in all crystals, but it surely does in the garnets. It also prefers it in its own monoxide, CoO; after all, it could have chosen the zinc blende structure as one form of ZnO does. There is also no question about Co^{2+} ions entering tetrahedral sites in some garnets; as we have said elsewhere[97], it is the only divalent ion known to enter these sites in substantial amount. It may be that, logically, one could accept the statement that Co^{2+} ion shows a strong affinity for tetrahedral sites in the garnets if such statement were not coupled with the one that Co^{2+} does not *prefer* the octahedral sites in the garnets. In other words, relative to other divalent ions, the Co^{2+} ion has by far a greater affinity for tetrahedral sites in the garnets; however, in the *garnets* it has a much *higher* affinity for octahedral sites than it does for tetrahedral sites.

If the Ni^{2+} ions do go into tetrahedral sites in the garnets, very little do so indeed. This is indicated not only by the work of Pap-palardo et al.[100] but also by some additional work that we have done. We have investigated the system $\{Ca_3\}[Zr_{1+x}Ni_{1-x}](Ni_xGe_{3-x})O_{12}$ analogous to the one for Co^{2+} ion described above. A specimen with $x = 0.10$ is not single phase. Even a new specimen with $x = 0.00$ is somewhat suspect, but it has the same lattice constant, 12.50 Å, as reported in our 1960 paper[43]. The garnet phase in the $x = 0.10$ specimen has precisely the same lattice constant. However, this is the case only if no GeO_2 is lost. When GeO_2 is lost, lattice constants do change, as one would expect. Contrary to results reported by Reinen, firings at different temperatures do not have any effect on the lattice constant of the specimens in this system provided that no GeO_2 is lost. Further, no marked change in color occurs when the firing is carried out in N_2 atmosphere—even when GeO_2 is lost. This, also, is contrary to Reinen's reported results which indicate a yellow-green associated with the lower temperature firing.

We believe that the reason for Reinen's observation of a change in lattice constant in $\{Ca_3\}ZrNiGe_3O_{12}$ is not a *simple* redistribution of ions. It results from a loss of GeO_2 at the higher temperatures. In

fact, when our specimen with $x = 0.00$ lost 3% by weight of the original GeO_2, the lattice constant of the garnet present was 12.515 Å; REINEN's 12.52 Å for his specimen fired at the higher temperature agrees with this value.

Thus, in view of the results of PAPPALARDO et al.[100] implying no tetrahedral Ni^{2+} and of our results, it may well be that the tetrahedral Ni^{2+} ion observed by REINEN is in an extraneous phase present with his garnet. On the other hand, a loss of GeO_2 would require Ni^{2+} ion in the tetrahedral sites if the specimen were single phase; however, our specimen which had this loss was definitely not single phase, and I therefore doubt that REINEN's was.

Distribution of ions in the $\{Y_3\}Fe_{5-x}Ga_xO_{12}$ system

My prime task in this paper was to survey the crystal chemistry of the garnets. So much work has now been done on the garnets, that several volumes could be written on them alone. A recent paper of mine[102] gives a review of our work on the static magnetic behavior of the substituted garnets, and I shall not repeat that here. But I do wish to point out that the model[7] proposed by me and my colleagues for this magnetic behavior, provides a basis for obtaining valuable information (and also for making predictions) on the crystal chemistry of the garnets. Aside from unifying the results of magnetic measurements on the substituted yttrium iron garnets when the site preferences are essentially known, it has helped us to understand the low-temperature behavior of the substituted gadolinium iron garnets[75] and the garnets in which other paramagnetic ions are substituted for the Fe^{3+} ion[55]. It has especially given us an understanding of the very complex $\{Y_3\}Co_xFe_{5-2x}Ge_xO_{12}$ and the analogous $\{Y_3\}Co_xFe_{5-2x}Si_xO_{12}$ systems[97]. It has also enabled us to determine the ionic distribution in the systems $Y_3Fe_{5-x}Al_xO_{12}$ [7], $Y_3Fe_{5-x}Ga_xO_{12}$ [27] and $\{Y_{3-x}Ca_x\}Fe_{5-x}Ti_xO_{12}$ [82].

As an example, we show the distributions obtained for the aluminum and gallium substituted YFe garnet systems in Fig. 6. The method for accomplishing this has been described elsewhere[7,27]. Shown also are the points obtained in a nuclear resonance study[103] of the gallium

[102] S. GELLER, Magnetic behavior of substituted ferrimagnetic garnets. J. Appl. Physics 37 (1966) 1408—1415.

[103] R. L. STREEVER and G. A. URIANO, Nuclear resonance study of gallium-substituted yttrium iron garnet. Physic. Rev. 139 (1965) A305—A313.

substituted YFe garnet system. The agreement between the two methods is quite good, but is actually even better than it looks if we take the $0\,°K$ moments that the other authors obtained for their specimens (see Ref.[27]).
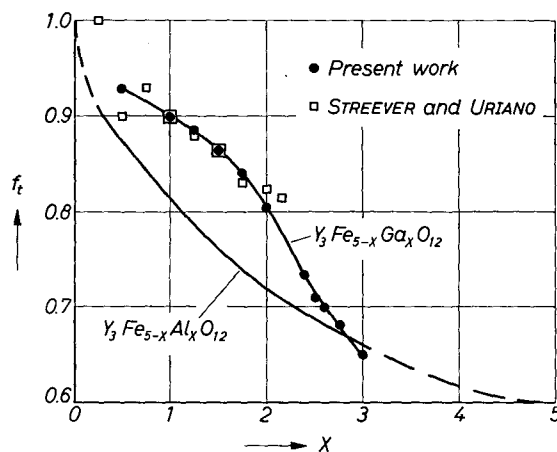

Fig.6. Fraction, f_t, of Ga^{3+} and Al^{3+} ions in tetrahedral sites in $Y_3Fe_{5-x}Ga_xO_{12}$ and $Y_3Fe_{5-x}Al_xO_{12}$, respectively (from Ref.[27])
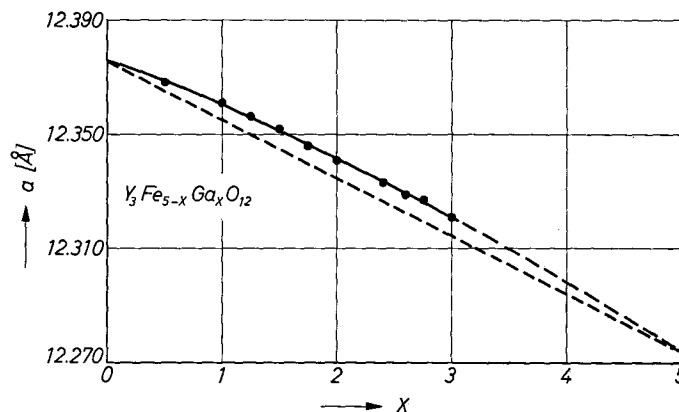
Fig.7. Lattice constant vs x (from Ref.[27])

For $x > 1.50$, the distribution appears to be sensitive to specimen heat treatment and this may be part of the reason for different $0\,°K$ moments obtained by different investigators. The importance of care in specimen preparation cannot be overestimated. In many systems the lattice-constant measurements can give an indication of the

specimen quality. Smooth curves should be obtained for lattice constant and moment, at a fixed temperature, vs composition. Examples from the $Y_3Fe_{5-x}Ga_xO_{12}$ system are given in Figs. 7 and 8.

Fig. 6 shows that for most of the composition range the Ga^{3+} ions have a greater preference for tetrahedral sites (f_t = fraction of Ga^{3+} or Al^{3+} ions in tetrahedral sites) than Al^{3+} ions to $x \approx 2.75$. For $x > 2.75$, the curves may coincide or cross. Unfortunately, we cannot
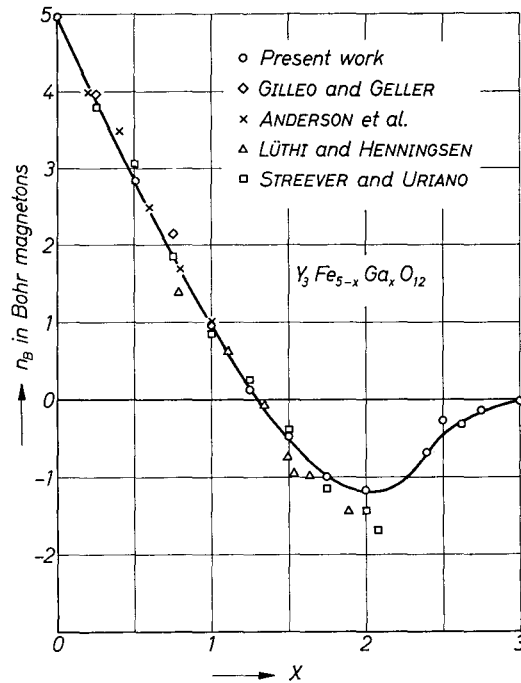

Fig. 8. Spontaneous moment at $0°K$ vs x (from Ref.[27]). (See Ref.[27] for pertinent references)

learn from static magnetic measurements anything about ionic distributions in specimens with x greater than 3.00. Furthermore, it is unlikely that the accuracy desired is attainable by diffraction techniques.

In regard to the diffraction techniques, a paper by FISCHER et al.[104] purports to give the distributions in the systems by both x-ray and

104 P. FISCHER, W. HÄLG, E. STOLL and A. SEGMÜLLER, X-ray and neutron diffraction study of substitutional disorder in yttrium-iron-gallium garnets. Acta Crystallogr. **21** (1966) 765—769.

neutron-diffraction techniques in the range $1.3 \leq x \leq 4.00$. The authors obtain a P (our f_t) (which is the fraction of Ga^{3+} ions in tetrahedral sites) with $a \pm \Delta$ where Δ is only a probable error. If they are using the proper terminology, their Δ is $0.6745\,\sigma$ which is at the 50% confidence level. Thus, all the probable errors should be multiplied by 4.5 to obtain limits of error (i.e. for a 99% confidence level). When this is done, the values ± 0.06 become ± 0.27; 0.03 becomes 0.14 and 0.02 becomes 0.09. This says that the methods give, at best, compatibility with our results.

Even if the probable errors were the actual limits of error, let us see what this would mean as far as the $0\,°K$ magnetic moment is concerned. Consider the garnet with the authors' c (our x) $= 2.0$. They get $f_t = 0.80 \pm 0.03$ (it should be 0.80 ± 0.14). For the lower value 0.77 the garnet formula is

$$\{Y_3\}[Fe_{1.54}Ga_{0.46}](Fe_{1.46}Ga_{1.54})O_{12}$$
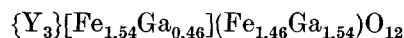
while for the upper limit 0.83, it is

$$\{Y_3\}[Fe_{1.66}Ga_{0.34}](Fe_{1.34}Ga_{1.66})O_{12}.$$
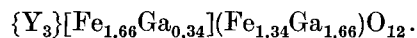
The $0\,°K$ moments for these, based on our model, would be -0.60 and $-1.58\,\mu_B$, respectively, per formula unit. The difference is *extremely* large. For our specimen, we obtained a (nominally) $0\,°K$ moment of $-1.17\,\mu_B$ from which we arrive at an f_t of 0.805. But while the agreement of the authors' average value, 0.80, with ours, 0.805, is very good, the confidence in their value is very low indeed. They have only a 50% probability that f_t will lie between 0.77 and 0.83 and that the expected $0\,°K$ moment per formula unit will be between -0.60 and $-1.58\,\mu_B$.

The average values of f_t obtained by Fischer *et al.* for $x = 2.5$ and 3.0 are not in agreement with our values. Because the limits of error on the Fischer *et al.* values are so high, there is no point in discussing these differences further. I will assert that powder-diffraction methods are unsuitable to make a physically significant determination of the distribution of cations in the system $Y_3Fe_{5-x}Ga_xO_{12}$. I am skeptical of the applicability to single crystals in this system, of the x-ray diffraction technique for ionic distribution determination, even if there were assurance that the composition were everywhere uniform.

We can look at this in the following way. Take the case of $x = 2$ again: using the *limits of error* on the value of $f_t = 0.80$ found by

FISCHER *et al.*, namely $\pm$ 0.14, we have for the low limit, average and high limit formulas, respectively:

1) ${Y_3}[Fe_{1.32}Ga_{0.68}](Fe_{1.68}Ga_{1.32})O_{12}$
2) ${Y_3}[Fe_{1.60}Ga_{0.40}](Fe_{1.40}Ga_{1.60})O_{12}$
3) ${Y_3}[Fe_{1.88}Ga_{0.12}](Fe_{1.12}Ga_{1.88})O_{12}$.

Then the average Z per atom in octahedral and tetrahedral sites, respectively, are:

	octahedral	tetrahedral
1)	25.04	25.64
2)	24.20	26.20
3)	23.36	26.76

The coherent x-rays "see" only these averages and these are fitted by the least-squares calculation. These values, incidentally, will give the largest differences; for higher $(\sin\theta)/\lambda$, the differences (neglecting thermal motions) are smaller. Also, it should be kept in mind that the first and third cases are for the *limits* of error not the probable error.

We must find the cases for which we would expect the largest percentage differences in intensity. For the reflection 800, for example, there would be no difference at all because all cations contribute constructively to it. If the standard errors in the measurements were uniform from specimen to specimen, then the authors' Table 3 indicates a standard error of 15.5°/$_0$ in the intensity of this reflection and a calculated difference from the observed intensity of 7.1°/$_0$.

There are reflections to which $16a$, $8c$ and $8d$ site atoms contribute. (The Y^{3+} ions in c sites make the same contribution to each of the sums.) The sums are:

1)   894,   2)   885,   3)   876.

The *largest* difference corresponding to the range of 0.28 (not 0.06) is only 18 electrons, about 2°/$_0$. The oxygen contribution, if any, could reduce or increase this value but probably not by much; so the difference in intensity in this range is about 4°/$_0$. There is no measured value in Table 3 which has so small a standard error.

There are reflections to which the contributions are $+ 16f_a - 8f_d - 8f_c$. These give

1)   93,   2)   111,   3)   128.

This time the difference for the 0.28 range is 35 electrons, about 32% and the difference in intensities would be about 74%, if oxygen contributions are neglected. Some of the reflections for which this situation occurs are: 220, 620, (10, 2, 0; 862), (660, 822), (10, 6, 0; 866), etc. Let us again look at Table 3 of the authors' paper and again assuming the measurements to be of the same quality and intensity distribution as for $x = 2$, we find

hkl	I_{calc}	I_{obs}	$\sigma(I_{obs})$
220	0.15	0.16	0.10
620	0.01	0.00	0.10
10, 2, 0 862	5.43	3.83	3.50
660 822	0.78	1.25	1.30
10, 6, 0 866	2.87	3.09	2.00

It is seen that for just this group which would be sensitive to the differences, the standard errors are very large indeed.

There is little point in further analysis of the x-ray powder method. I hope I have made the point that most of the reflections are insensitive to a wide difference in the distribution, and the few that are sensitive have large standard errors. It is probable that even the calculated large limits of error are conservative estimates because of the inclusion in the calculation of the many reflections which are not sensitive to the distribution.

In fact, one may ask why, when the difference in neutron scattering lengths of Ga and Fe is so much more favorable than that of the atomic scattering factors of Ga^{3+} and Fe^{3+}, are the error limits for the neutron and x-ray investigation the same. Yet the R values for the neutron intensities were 1/4 to less than 1/2 those for the x-ray intensities and the average measurement error appears to be lower. In the case of the neutron investigation the authors used only data which were not from coincident nonequivalent reflections. Even with the more favorable difference, the sensitivity is, on the average, small or nonexistent. Of 25 reflections in their Table 4, there are six which have contributions only from oxygen atoms: 431, 541, 543, 741, 820, 860. The 800 reflection, the strongest listed, is insensitive to the distribution because *all* the cations present in the crystal contribute constructively to the intensity. (The agreement between the calculated

and observed values for the 800 is very good too.) The 640 is another strong reflection. It has contributions to the structure amplitude: $16f_c + 16f_d$. For $x = 2.5$ and the limiting compositions (0.77 ± 0.14) 0.63 and 0.91, we would have:

	Y	tetr	sum
$\{Y_3\}[Fe_{1.08}Ga_{0.92}](Fe_{1.42}Ga_{1.58})O_{12}$	12.00	13.28	25.28
$\{Y_3\}[Fe_{1.78}Ga_{0.22}](Fe_{0.72}Ga_{2.28})O_{12}$	12.00	12.48	24.48

The contribution from oxygen will be about 9.5 so the structure amplitudes, neglecting thermal motions, are 34.8 and 34.0, a difference of about $2^0/_0$, or $4^0/_0$ in intensity. This is one-half the standard error of the measurement, and I emphasize again that this is for the range 0.28 (limits of error) not 0.06 (probable error). Needless to say, if we had done *all* the above on the basis of the 0.06 range, the results would appear to be even less significant.

Concluding remarks

I have included in this paper many pieces of work that we have done over the last five years or so and have not published previously. Some work has been done to check on results of others and to refute some conclusions by others with which I did not agree.

Now that I have finished, it seems that this paper could make a small book, but there are two reasons why it will not be one. First, the more important one is my having been privileged by the invitation to write this paper in honor of Professor G. MENZER, who solved the very important garnet structure. Second, I have been critical (I hope not too harshly) of several papers, and I think that it is infinitely simpler for those criticized to reply, if they so desire, to a journal article than to a book. But I should say that I shall not become engaged in any polemic as a result of this. For those who have been criticized, I should point out that I have also criticized myself in a few places—possibly with greater kindness.