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New Synthetic Garnets

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Twenty-three new synthetic garnets of types:

$$M^{2+}R^{3+}_2\mathrm{Mn_2Ge_3O_{12}},\; M^{2+}R^{3+}_2M^{2+}_2\mathrm{Ge_3O_{12}},\; R^{3+}_3M^{2+}_2\mathrm{GaGe_2O_{12}} \text{ and } \mathrm{Ca_3}M^{4+}M^{2+}\mathrm{Ge_3O_{12}}$$

are reported. In these formulae, M^{4+} is a tetravalent metal ion of Zr, Sn or Ti; R^{3+} is an yttrium or gadolinium ion; M^{2+} is one of a variety of divalent metal ions, not all of which go into all the types. It is probable that R^{3+} could be almost any trivalent rare earth ion. Three other garnets are reported: $\mathrm{Mn_3NbZnFeGe_2O_{12}}$; one of probable formula $\mathrm{Ca_3ZrFeGe_{2\cdot8}O_{12}}$, in which Fe has an average valence of 2·9 and $\mathrm{Y_2Mn_2FeGe_{2\cdot8}O_{12}}$ in which Fe has an average valence of 2·8. The latter two are defect structures. It is shown quantitatively that two-thirds of the $\mathrm{Co^{2+}}$ ions in $\mathrm{CoGd_2Co_2Ge_3O_{12}}$ and in $\mathrm{CoY_2Co_2Ge_3O_{12}}$ occupy octahedral positions, the remaining third occupying the dodecahedral positions. The distributions of ions in the other new garnets is discussed. To date, the $\mathrm{Co^{2+}}$ ion is the only one with non-spherical electronic configuration which is definitely known to occupy octahedral positions in the garnets. There are still no known garnets in which ions with non-spherical electronic configuration occupy tetrahedral positions.

The programming of the calculation of powder intensities including both real and imaginary parts of the dispersion corrections on the IBM 704 computer is briefly described in an appendix.

Introduction

The garnet structure belongs to space group O_h^{10}–$Ia3d$ with metal ions in 16*a*, 24*c* and 24*d* and oxygen (or fluorine) ions in 96*h*. It is convenient to write the chemical formula of one unit (see Gilleo & Geller, 1958*a*) $\{A_3\}[B_2](C_3)\mathrm{O}_{12}$, where $\{\,\}$ represent a *c* or dodecahedral site, [ ] an *a* or octahedral site and ( ) a *d* or tetrahedral site. The three sites are accessible to both magnetic and non-magnetic ions of a great variety, but conditions of electronic configuration and size determine the extent to which ions go into the different sites.

Yttrium–iron garnet, $\{\mathrm{Y_3}\}[\mathrm{Fe_2}](\mathrm{Fe_3})\mathrm{O_{12}}$, has been studied very thoroughly and from various points of view. An accurate structure determination (Geller & Gilleo, 1957*a*) shows that the geometry of the $[\mathrm{Fe^{3+}}]$–O–$(\mathrm{Fe^{3+}})$ linkages is conducive to the strong magnetic interaction which is observed (Aleonard, Barbier & Pauthenet, 1956; Geller & Gilleo, 1957*b*). The results of the structure determination indicated also that if a magnetic rare earth ion were substituted for $\mathrm{Y^{3+}}$, the magnetic interaction between it and a magnetic ion in a tetrahedral site would be stronger than that with a like magnetic ion in an octahedral site. Until recently no *direct* *c*–*a* or *c*–*d* interactions had been observed. Some of the compounds reported herein, having magnetic ions in *c* and *a* sites only, have been shown to have antiferromagnetic ordering with a resultant spontaneous magnetization at very low temperatures (Gilleo & Geller, 1958*a*). Garnets in which magnetic ions *fill* only the *c* and *d* sites are yet to be made.

The crystal chemical aspects of the garnets are also of importance. It has been shown that when non-magnetic ions are substituted for Fe^{3+} in

$$\{Y_3\}[Fe_2](Fe_3)O_{12}\ ,$$

the larger ion prefers the site which allows it most space (Gilleo & Geller, 1958*b*; Geller, Bozorth, Gilleo & Miller, 1959; Bozorth, Geller & Miller, 1959). This is not necessarily true of magnetic ions. For example, it is known that Cr^{3+} ion is smaller than Fe^{3+} ion (Geller, 1957*a*), but prefers only octahedral sites in the garnets (Gilleo & Geller, 1958*b*). We have already mentioned (Gilleo & Geller, 1958*b*) that the octahedral and tetrahedral sites of the garnets seem to prefer occupation by ions with spherical electronic configurations.* Actually, in an octahedral crystal field, the Cr^{3+} ion satisfies this criterion with a crystal ground state: $^4A_{2g}$. On the other hand, the tetrahedral crystal field ground state of Cr^{3+} is $^4T_1$ which is not spherical. This would appear to be a plausible explanation of the preference by Cr^{3+} for the octahedral sites. In the present paper, we report the synthesis of garnets containing Co^{2+} ions in octahedral sites; for Co^{2+}, the octahedral crystal field ground state is non-spherical.

Because the garnets have become so interesting, it seemed worthwhile to explore possibilities of putting all kinds of ions into them and this paper establishes that a large number of ions will go into the garnets. However, in all cases but that of Co^{2+}, the ions going into the octahedral and tetrahedral sites in significant number do have spherical or 'pseudo-spherical' ground states.

Attempts to put Fe^{2+} ions into the garnets have led to some interesting results, including the establishment of the existence of defect structures in some garnet systems.

Preparation of the compounds

Each of the polycrystalline garnets was prepared by mixing and grinding, in an agate mortar, the required amounts of pure oxides. A pellet, made of the reaction mixture, was heated in N_2 atmosphere to temperatures above 1000 °C. The pellet was reground and refired at increased temperature repeatedly until a sharp X-ray photograph was obtained. From one to seven firings were required depending on the compound. Optimum temperatures for preparing particular garnets are given in the last column of Table 1. Pellets heated above 1200 °C. were given short firing times to prevent loss of GeO_2. In some cases, small amounts of GeO_2 were probably lost; also in some cases excess GeO_2 was added and firing carried to the point of correct stoichiometry.

In the case of garnets with general formula $M_3^{2+}M_2^{3+}Ge_3O_{12}$, only one purely garnet phase was obtained by direct solid-state synthesis, namely $Ca_3Fe_2Ge_3O_{12}$. The others prepared by us always occurred with small to minute amounts of extraneous phases. However, it was possible to isolate single crystals of $Mn_3Fe_2Ge_3O_{12}$ from reaction mixtures which had been carried to the melting point, about 1235–1240 °C. These crystals had a vitreous appearance and did not have developed faces; however, a small crystal photographed with a precession camera gave ample confirmation.

Crystallographic data

Powder photographs were taken, with Cr *K* radiation, of all products using Norelco Straumanis type cameras with 114·6 mm. diameter. Lattice constants of the various garnets are listed in Table 1.

The existence of garnets of formula $Ca_3TiM^{2+}Ge_3O_{12}$ with M = Ni, Co and Mg was reported earlier by Durif (1958). Because of the work of Tauber, Banks & Kedesdy (1958), we have not attempted to exhaust the possibilities of the garnets of type $M_3^{2+}M_2^{3+}Ge_3O_{12}$. In Table 1(*F*), the lattice constants of those we have made are compared with some of those reported by Tauber *et al.* (1958). The compounds $Fe_3Al_2Ge_3O_{12}$ and $Sr_2Fe_2Ge_3O_{12}$ did not form under the conditions of our experiments. However, lower concentration solid solutions can be made of a nominal $Sr_3Fe_2Ge_3O_{12}$ with $Y_3Fe_2Fe_3O_{12}$.*

It is probable that most of the rare earths excluding possibly Nd, Pr, Ce and La may be substituted for Gd or Y in the garnets described above. The larger rare earths will probably enter these garnets if mixed with smaller rare earths in proportions depending on their relative sizes. It is very likely that all the divalent ions which go into the

$$\{R_3^{3+}\}[M_2^{2+}](GaGe_2)O_{12}$$

type garnets will also go into the

$$\{Ca_3\}[M^{4+}M^{2+}](Ge_3)O_{12}$$

types.

Distribution of ions in $Co^{2+}R_2^{3+}Co_2^{2+}Ge_3O_{12}$

The distribution of ions in the garnets

$$Co^{2+}R_2^{3+}Co_2^{2+}Ge_3O_{12},\quad R = \text{Gd and Y},$$

was determined by comparison of observed powder diffraction intensities with those calculated for the models

$$\{CoR_2\}[Ge_2](Co_2Ge)O_{12}\quad \text{and}\quad \{CoR_2\}[Co_2](Ge_3)O_{12}\ .$$

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* This is much unlike the octahedral sites of the perovskite-like structures (see, for example, Geller, 1957*b*).

* For example, the lattice constant of the solid solution 1 $Sr_3Fe_2Ge_3O_{12}$:5 $Y_3Fe_2Fe_3O_{12}$ is 12·414 ± 0·003 Å. It is probable that somewhat more concentrated solutions, perhaps up to 1:1 can be made.

Table 1. *Lattice constants, colors, and optimum firing temperatures*

(*A*). $M^{2+}R^{3+}_2Mn_2Ge_3O_{12}$ type

M^{2+}, R^{3+}	a_0 (Å)	Color*	Optimum firing temp. (°C.)
Ca, Gd	12·555 ± 0·005	Lt. Brown	1350
Mn, Gd	12·482 ± 0·010	Brown	1200
Cu, Gd	12·475 ± 0·005	Lt. Brown	1200
Cd, Gd	12·473 ± 0·005	Lt. Brown	1250
Co, Gd	12·437 ± 0·005	Blue-gray	1380
Zn, Gd	12·427 ± 0·005	Brown	1060
Ni, Gd	12·413 ± 0·003	Brown	1350
Mg, Gd	12·395 ± 0·010	Gray-tan	1380
Ca, Y	12·475 ± 0·010	Lt. Brown	1250
Mn, Y	12·392 ± 0·010	Lt. Brown	1200

(*B*). $M^{2+}R^{3+}_2M^{2+}_2Ge_3O_{12}$ type ($M \neq$ Mn)

M^{2+}, R^{3+}	a_0 (Å)	Color	Optimum firing temp. (°C.)
Co, Gd	12·402 ± 0·005	Blue	1270
Mg, Gd	12·31 ± 0·01	White	1300
Co, Y	12·300 ± 0·003	Blue	1270

(*C*). $R^{3+}_3M^{2+}_2GaGe_2O_{12}$ type

R^{3+}, M^{2+}	a_0 (Å)	Color	Optimum firing temp. (°C.)
Gd, Mn	12·550 ± 0·003	Brown	1300
Gd, Co	12·446 ± 0·003†	Blue	1250
Gd, Co	12·460 ± 0·003‡	Blue	1250
Gd, Zn	12·464 ± 0·003	White	1300
Gd, Mg	12·425 ± 0·005	White	1350
Gd, Ni	12·401 ± 0·003	Green	1350

(*D*). $Ca_3M^{4+}M^{2+}Ge_3O_{12}$ type

M^{4+}, M^{2+}	a_0 (Å)	Color	Optimum firing temp. (°C.)
Ti, Co	12·35 ± 0·01	Dark blue-green	1350
Ti, Mg	12·35 ± 0·01	Yellow	1300
Ti, Ni	12·32 ± 0·01	Blue-green	1350
Sn, Co	12·47 ± 0·02	Blue-gray	1300
Zr, Co	12·54 ± 0·01	Blue	1350
Zr, Mg	12·514 ± 0·005	White	1400
Zr, Ni	12·50 ± 0·01	Green	1350

(*E*). $Mn_3NbZnFeGe_2O_{12}$

a_0 (Å)	Color	Optimum firing temp. (°C.)
12·49 ± 0·01	Black	1450§

(*F*). $M^{2+}_3M^{3+}_2Ge_3O_{12}$ type

	a_0 (Å)	
Garnet	This work	Tauber *et al.*
$\{Ca_3\}Al_2Ge_3O_{12}$	12·12 ± 0·01	—
$\{Ca_3\}Fe_2Ge_3O_{12}$	12·320 ± 0·004	12·312
$Mn_3Al_2Ge_3O_{12}$	11·902 ± 0·005	11·895
$Mn_3[Cr_2]Ge_3O_{12}$	12·027 ± 0·003	12·027
$Mn_3Fe_2Ge_3O_{12}$	12·087 ± 0·003	12·087

* It should be remembered that these are colors of finely divided powders.

† Made with excess GeO_2.

‡ Probably non-stoichiometric because of loss of GeO_2.

§ This garnet melts congruently at this temperature.

A Norelco diffractometer and Cu *Kα* radiation were used. In the calculations of intensities, corrections were made for dispersion (Dauben & Templeton, 1955) of Cu *Kα* radiation by the metal ion. Both the real and imaginary parts of the correction were included (see Appendix). The scattering factors of Co^{2+}, Gd^{3+}, Y^{3+} and Ge^{4+} were taken from the tables of Thomas & Umeda (1957). For O^{2-}, the scattering factors of Berghuis *et al.* (1955) for O arbitrarily modified such that $f_{O^{2-}} = 10·00$ at $(\sin\theta)/\lambda = 0$ and $f_{O^{2-}} = f_O$ for all values of $(\sin\theta)/\lambda \geq 0·20$. The temperature factors used were 0·6, 0·1, 0·3, 0·4 and 1·2 Å² for Co^{2+}, Gd^{3+}, Y^{3+}, Ge^{4+} and O^{2-} respectively. Because even sizeable changes in oxygen coordinates do not greatly affect the agreement between the calculated and observed powder intensities, initial calculations were made with the oxygen coordinates found for yttrium–iron garnet (Geller & Gilleo, 1957*a*).

The data for $CoGd_2Co_2Ge_3O_{12}$ are given in Table 2: The last column lists the calculated relative intensities for the distribution $\{CoGd_2\}[Ge_2](Co_2Ge)O_{12}$, the fourth column, those for the distribution

$$\{CoGd_2\}[Co_2](Ge_3)O_{12}\,.$$

The agreement between calculated and observed intensities is significantly better for the second distribution than for the first. This is particularly well seen by examining the *400*, *420*, *422*, *444*, *640*, and *642* reflections.

The garnet $CoY_2Co_2Ge_3O_{12}$ gave a much better diffraction pattern than that of the Gd compound,

Table 2. *Calculated and observed relative intensities of* $CoGd_2Co_2Ge_3O_{12}$

hkl	I_o	$I_c(1)$	$I_c(2)$	$I_c(3)$
211	23	20	30	37
220	22	19	12	6
321	17	13	14	17
400	117	124	119	132
420	444	452	444	403
422	168	181	178	204
431	12	9	8	8
521	24	20	21	26
440	12	7	9	4
532 611	33	23	20	25
444	69	61	61	45
640	145	127	136	123
633 721 552	8	7	8	10
642	138	143	141	162
800	53	52	58	58
840	33	32	33	38
842	83	88	83	73
664	23	26	26	30
10,4,0 864	60	74	74	66
10,4,2	35	32	32	37

(1) 2 Co^{2+} ions/formula unit in octahedral positions; final O^{2-} parameters.

(2) 2 Co^{2+} ions/formula unit in octahedral positions; YIG O^{2-} parameters.

(3) 2 Co^{2+} ions/formula unit in tetrahedral positions; YIG O^{2-} parameters.

In all cases one Co^{2+} ion/formula unit is in a dodecahedral position.

All lines not listed were either space group absences or were not observed with calculated values all less than 4.

presumably because of the much reduced fluorescence. The data for the Y compound are given in Table 3: Listed in column 5 of Table 3 are the intensities calculated for the distribution $\{CoY_2\}[Ge_2](Co_2Ge)O_{12}$ and in column 4, for $\{CoY_2\}[Co_2](Ge_3)O_{12}$, with the same oxygen parameters as before. Again the agreement between calculated and observed intensities for the latter model is better than for the former. It now appeared that some further improvement could be obtained by adjustment of oxygen coordinates.

In CoO with the NaCl-type structure, the Co^{2+}–O^{2-} distance is 2·125 Å (Ingersoll & Hanawalt, 1929). In the spinel-type $GeCo_2O_4$ (Romeijn, 1953), this distance calculated from the proposed oxygen parameter, 0·375, is 2·08 Å. Now the average octahedral Ge^{4+}–O^{2-} distance in the rutile type GeO_2 carefully determined by Baur (1956) is 1·88 Å. From the parameter given by Romeijn for $GeCo_2O_4$, one obtains 1·80 Å for the tetrahedral Ge^{4+}–O^{2-} distance in this spinel. If, however, this parameter is changed to 0·370 from 0·375 one obtains 2·12 Å for the Co^{2+}–O^{2-} distance and 1·73 Å for the Ge^{4+}–O^{2-} distance. This value for the tetrahedral Ge^{4+}–O^{2-} distance appears to be a more reasonable one when compared with the tetrahedral Si^{4+}–O^{2-} distance, 1·64 Å, in grossularite (Abrahams & Geller, 1958) and also when differences between octahedral and tetrahedral distances of other ions are examined.

Table 3. *Calculated and observed relative intensities of* $CoY_2Co_2Ge_3O_{12}$

hkl	I_o	$I_c(1)$	$I_c(2)$	$I_c(3)$
220	9	7	3	1
400	93	102	97	110
420	291	320	313	276
332	13	9	10	6
422	138	141	138	163
431	10	9	7	7
521	7	7	8	13
440	6	4	6	1
611 532	12	10	8	13
444	44	42	42	28
640	108	94	102	90
642	126	117	114	134
800	36	38	43	43
840	27	25	26	31
842	65	62	58	49
664	22	20	21	25
10,4,0 864	60	52	53	44
10,4,2	30	26	25	30
880	25	27	25	25
12,0,0 884	12	12	12	14
12,2,0	16	13	13	11
12,2,2 10,6,4	30	29	28	34
12,4,4	16	16	16	10
12,6,0 10,8,4	42	37	39	33
12,6,2	19	16	17	20
888	16	14	14	14
12,8,0	12	10	10	12
14,4,0 12,8,2	48	43	43	36
14,4,2 12,6,6 10,10,4	45	43	43	53
12,10,0 12,8,6	84	85	85	69

Notes of Table 2 apply to this table also.

Table 4. *Distances in cobalt garnets as given by the final calculated oxygen coordinates*

	$\{CoGd_2\}[Co_2](Ge_3)O_{12}$	$\{CoY_2\}[Co_2](Ge_3)O_{12}$
Ge^{4+}–O^{2-}	1·73 Å	1·72 Å
Co^{2+}–O^{2-}	2·11	2·10
$\left\{\frac{CoR_3^{2+}}{3}\right\}$–$O^{2-}$	2·50, 2·37	2·48, 2·36

Following the above considerations, a set of parameters was calculated and no further attempt made to refine them. These are (−0·034, 0·054, 0·158), yielding the distances shown in Table 4. It is seen, columns 3 of Tables 2 and 3, that the agreement between calculated and observed intensities is somewhat improved when these parameters* are used in the calculation of intensities. Unfortunately, the intensities of only the *211* and *220* reflections appear to have any significant sensitivity to the different sets of oxygen coordinates.

Defect structures and Fe^{2+} ion in the garnets

A number of attempts to prepare garnets containing substantial amounts of Fe^{2+} ion led to some interesting results. The garnet $Gd_3Fe_2^{2+}GaGe_2O_{12}$ could not be prepared under the conditions of our experiments. Starting materials were oxides except that for the source of Fe^{2+}, $Fe(C_2O_4)_2.2\,H_2O$ was used. Firing was carried out in either N_2 or Ar atmosphere. However, although in all cases a garnet phase was formed, almost all of the Fe ions present were in the trivalent state; an analysis of one sample showed that less than 4% were divalent. The garnet phase was undoubtedly a solid solution of $Gd_3Fe_2Fe_3O_{12}$ and $Gd_3Ga_2Ga_3O_{12}$. Also present in the powder photographs of the samples were the strongest lines of a gadolinium–germanium oxide phase.† The lattice constant of the garnet phase present was what might be predicted for a $Gd_3Fe_2^{2+}GaGe_2O_{12}$ garnet if it existed. However, this coincided with what would be obtained from the solid solution of gallium and iron garnets that could be formed, so that the chemical analysis for Fe^{2+} ion proved extremely useful.

Considering that perhaps two Fe^{2+} ions per formula unit were too many, we attempted to make the garnet $Ca_3ZrFeGe_3O_{12}$. The photograph taken after the first

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* These parameters should not be considered accurate enough for arguing refined theoretical or experimental points. Only a single crystal analysis can yield values for such purposes. Unfortunately, we do not have single crystals of these garnets at this time.

† A specimen of gadolinium–germanium oxide of reactant proportions Gd_2O_3–$2\,GeO_2$ fired at 1270 °C., gives a complex powder photograph with these lines.

firing indicated very great disorder, to an extent approaching the amorphous condition. Repeated firings narrowed the lines but after seven or eight firings, the garnet phase, though well established, still gave fairly broad lines in the back reflection region of the photographs.

In these cases, the results were similar whether the firings were carried out in N_2 or in Ar atmosphere. The lattice constant of the phase was 12·54 Å, close to that of $Ca_3ZrCoGe_3O_{12}$, indicating that there was indeed a good chance that the Fe^{2+} had gone into the structure. (It may be recalled that the lattice constant of $Ca_3Fe_2Ge_3O_{12}$ (Table 1(*F*)) is 12·312 Å.) A chemical analysis for total Fe and Fe^{2+} ion, however, proved differently: results were 8·8% total iron and 1·00% Fe^{2+} by weight. Theoretically, there should have been 8·3% total iron. However, some GeO_2 is lost in the firings thus raising the percentage of total iron. The results of the analysis lead to the conclusion that the garnet phase prepared has the probable formula $Ca_3ZrFe^{+2\cdot9}Ge_{2\cdot8}O_{12}$ with a defect structure.

In attempts to make the garnet $FeY_2Mn_2Ge_3O_{12}$ (see Table 1(*A*)), a result similar to the preceding one was obtained. Only 19% of the Fe remained divalent and it is probable that GeO_2 was lost. Thus the probable formula is $Y_2Mn_2Fe^{+2\cdot8}Ge_{2\cdot8}O12$; the Mn average valence may also be somewhat more than two. This garnet phase also gave a powder photograph having broad back reflection lines. The lattice constant is 12·33 ± 0·01 Å.

It appears that in at least the garnets containing Ge^{4+} ion, such defect structures exist and that the defects, perhaps tetrahedral site vacancies, in some cases cause an *increase* in lattice constant. There are apparently other cases of defect structure among the new garnets. For example, the $Gd_3Co_2GaGe_2O_{12}$ fired with excess GeO_2 to correct stoichiometry has a smaller lattice constant (Table 1(*C*)) than that from which some GeO_2 was undoubtedly lost. It was difficult to obtain sharp phases for the Mg^{2+} compounds; some of these also may have defect structures (see Table 1).

It should be kept in mind that small amounts of many of the ions in these new compounds may be present in valence states other than as formulated.

General discussion of ion distribution

It has been mentioned that the strongest interactions in a ferrimagnetic garnet would be expected to occur between magnetic ions in *a* and *d* sites (Geller & Gilleo, 1957*a*). Interactions between magnetic ions in *c* and *a* sites would be expected to be very weak. Attempts by us to produce garnets with magnetic ions only in the *c* and *a* sites began some time ago with investigations of silicates (Geller & Miller, 1958*a*, 1959*a*, *b*). However, the garnets $\{Mn_3\}[Cr_2](Si_3)O_{12}$ or $\{Mn_3\}[Fe_2](Si_3)O_{12}$* could not be made by means of direct high temperature synthesis at ordinary pressures (Geller & Miller, 1958*a*, 1959*a*). In a manner described earlier, we succeeded in isolating a sufficient amount of the single phase $Mn_3Fe_2Ge_3O_{12}$ for magnetic measurements down to He temperatures. These measurements showed that $Mn_3Fe_2Ge_3O_{12}$ does not have a spontaneous magnetization (Bozorth, Geller & Miller, 1959). There are several possible causes for this result: (1) expected weak interactions because of unfavorable geometry; (2) distribution of Fe^{3+} ions over the octahedral and tetrahedral sites (Tauber *et al.*, 1958; Bozorth, Geller & Miller, 1959) resulting in a marked weakening of interaction; (3) inherently weak interaction between Mn^{2+} and Fe^{3+} ions.

It is known that the Mn^{2+} ion ($3d^5$), despite its large size, will enter either the octahedral or dodecahedral sites in the garnets. From existing experimental knowledge of the garnets it would seem unlikely that very much Mn^{2+} would enter the tetrahedral sites when other smaller ions are present which favor occupation of the tetrahedral sites. Thus if one could make a garnet with Mn^{2+} in the octahedral and Ge^{4+} in the tetrahedral sites, a filling of the dodecahedral sites with magnetic ions might produce a ferrimagnetic garnet (with low Curie temperature, of course, because of the unfavorable geometry for interaction) which might also be iron free.

As shown above, such garnets have now been synthesized. The garnets $\{MnGd_2\}[Mn_2](Ge_3)O_{12}$ and $\{CaGd_2\}[Mn_2](Ge_3)O_{12}$ are ferrimagnetic and there appears to be weak antiferromagnetic interaction in $MnY_2Mn_2Ge_3O_{12}$ and in $CaY_2Mn_2Ge_3O_{12}$ (Gilleo & Geller, 1958*a*). Because the results of magnetic measurements on these compounds were somewhat inconclusive, the garnet $\{Gd_3\}[Mn_2](GaGe_2)O_{12}$ was prepared and found to be ferrimagnetic with a Curie temperature of about 8 °K. and a saturation magnetization extrapolated to 0 °K. of at least $9\cdot6\mu_B$, close to the expected value of $11\mu_B$ (Gilleo & Geller, 1958*a*).

Although it is known that Ge^{4+} ions will enter the octahedral sites in substantial amounts in some garnets (Tauber, Banks & Kedesdy, 1958; Bozorth, Geller & Miller, 1959) it is unlikely that there is much Ge^{4+} ion in octahedral sites in the manganese compounds. Any non-magnetic ion replacing the Mn^{2+} ion in the $\{Gd_3\}[Mn_2](GaGe_2)O_{12}$, for example, would raise the moment.

It is not too surprising to find Ni^{2+} going into octahedral sites in the garnets $Gd_3Ni_2GaGe_2O_{12}$ and $Co_3M^{4+}NiGe_3O_{12}$ type because the octahedral crystal field splitting of the *d*-levels would lead to a configuration of electrons (6 paired in $d\varepsilon$ and 2 unpaired in $d\gamma$) which would give Ni^{2+} a pseudospherical ground state. On the other hand, because it was felt that the octa-

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* This garnet has, however, been reported by Coes (1955) who has provided us with some. It has been found (Bozorth, Geller & Miller, 1959) that magnetic interactions between Mn^{2+} and Fe^{3+} ions in $\{Mn_3\}[Fe_2](Si_3)O_{12}$ are apparently very much weaker than those between Gd^{3+} and Mn^{2+} ions in $\{Gd_3\}[Mn_2](GaGe_2)O_{12}$ (Gilleo & Geller, 1958*a*).

hedral and tetrahedral sites would exclude non-spherical ions, the Co^{2+} ions not in dodecahedral sites in $Co^{2+}Gd_2Co_2Ge_3O_{12}$ were expected to be in the tetrahedral sites. There *were* two seemingly good reasons for this: the tetrahedral crystal field ground state of Co^{2+} is $^4A_2$, a pseudospherical state, whereas the octahedral field ground state is non-spherical and very complicated (see e.g. van Santen & van Wieringen, 1952); thus the Co^{2+} ions would prefer the tetrahedral and non-selective dodecahedral sites. The other reason is not as important as it is interesting. It is usually thought that the Co^{2+} ion is 'colored' blue in tetrahedral and red in octahedral complexes (see e.g. Grum-Grzhimailo & Pliusnina, 1958). In fact in the spinel-type compounds $CoAl_2O_4$ and $GeCo_2O_4$, this *is* the case: the former is blue, the latter red.* The garnets containing the Co^{2+} and any 'uncolored ion' are all blue (Table 1). Furthermore, when Co^{2+} ion occurs in a garnet containing another 'colored ion', the resultant color is what would be expected from combination of primary colors. For example $Ca_3ZrMgGe_3O_{12}$ is white indicating that all of its ions are 'white', $Ca_3ZrCoGe_3O_{12}$ is blue, $Ca_3TiMgGe_3O_{12}$ is yellow; $Ca_3TiCoGe_3O_{12}$ is green.

Despite all this, the above considerations did not lead to the correct prediction. The Co^{2+} ions which are not in the dodecahedral sites are apparently in the octahedral sites. Of course, the particular measurements made cannot tell us really just how many Co^{2+} ions do occupy tetrahedral positions, but there are probably few.

Because this result was really unexpected, corroborative experiments were carried out. There was good reason to suppose from earlier work (Geller & Miller, 1958*a*†, *b*) that tin and zirconium would occupy octahedral sites in the garnets. (A naturally occurring mineral garnet, Kimzeyite, containing a substantial amount of Zr^{4+} ion (Milton & Blade, 1958) has also recently been reported.) The garnets

$$\{Ca_3\}[ZrM^{2+}](Ge_3)O_{12}$$

(Table 1) most likely have the ion distribution indicated by the brackets. We attempted to substitute various amounts of Zr^{4+} for Ge^{4+} in the $CoGd_2Co_2Ge_3O_{12}$ garnet without success. This is not cited as conclusive, but rather as corroborative evidence. To be sure, it is possible that the experimental conditions were not favorable for this substitution. But because it is very probable that the Zr^{4+} ion would go only into octahedral sites, this gives some indication that the Co^{2+} could not be forced into the tetrahedral positions. Experiments were also carried out with Sn^{4+} with similar results.

Now a disturbing feature of the result is the color of the octahedral Co^{2+} ion in the garnets. It was felt that perhaps another example of blue octahedral Co^{2+} ion could be found. There has been some work at these Laboratories on tungstates (see e.g. Van Uitert & Soden, 1960; Peter, 1959). A recent structure determination of $NiWO_4$ (Keeling, 1957) indicates that both the Ni^{2+} and W^{4+} ions have octahedral coordination. Crystals of $CoWO_4$ were prepared by Van Uitert & Soden (1959). When pulverized, these had the same blue color as the cobalt garnets. A single crystal of $CoWO_4$ photographed with a Buerger precession camera indicated that it was isostructural with $NiWO_4$. Thus it appears that subtle distortions of the octahedral field about the Co^{2+} ion make extreme changes in its color.

With regard to the ion distribution in the other garnets, we have not done accurate intensity* or magnetic measurements. But some qualitative experiments and considerations of ionic size allow us to draw some tentative conclusions. For example, the garnets

$$CuGd_2Cu_2Ge_3O_{12},\quad Gd_3Cu_2GaGe_2O_{12},\quad CdGd_2Cd_2Ge_3O_{12}$$

did not form under the conditions of our experiments. Thus in $CuGd_2Mn_2Ge_3O_{12}$ and in $CdGd_2Mn_2Ge_3O_{12}$, the Cu^{2+} and Cd^{2+} ions are probably mostly, if not entirely, in dodecahedral sites. The Ca^{2+} ions in the various garnets are also almost surely entirely in the dodecahedral sites. In $CoGd_2Mn_2Ge_3O_{12}$, the Co^{2+} ions are probably mostly in octahedral sites as indicated by the blue color of the material, and because Co^{2+} ion is smaller than Mn^{2+}. The garnets $ZnGd_2Zn_2Ge_3O_{12}$ and $NiGd_2Ni_2Ge_3O_{12}$ would not form under the conditions of our experiments. However, the garnets $Gd_3Zn_2GaGe_2O_{12}$ and $Gd_3Ni_2GaGe_2O_{12}$ (Table 1(*C*)) formed readily, a strong indication that in the garnets $ZnGd_2Mn_2Ge_3O_{12}$ and $NiGd_2Mn_2Ge_3O_{12}$, the Zn^{2+} and Ni^{2+} ions are mostly in the octahedral sites. Because $MgGd_2Mg_2Ge_3O_{12}$ and $Gd_3Mg_2GaGe_2O_{12}$ both exist as in the case of the Co^{2+} compounds, Mg^{2+} may occupy either the dodecahedral† or octahedral sites. It is probable, however, that because Mg^{2+} is substantially smaller than Mn^{2+}, it will prefer the octahedral sites in $MgGd_2Mn_2Ge_3O_{12}$.

In garnets of the type $Ca_3M^{4+}M^{2+}Ge_3O_{12}$ it is probable that all the tetravalent atoms other than Ge^{4+} will prefer the octahedral sites because of relative size. The Zr^{4+} ions are very large and almost surely would not go into tetrahedral sites. The Sn^{4+} ions would strongly prefer the octahedral sites, but slight amounts could interchange with Ge^{4+}. In the case of Ti^{4+}, it is probable that although strongly preferring the octahedral sites as against Ge^{4+} more Ti^{4+} would interchange with Ge^{4+} than would Sn^{4+}. A cursory attempt to make the garnet $Ca_3NiTi_2Ge_2O_{12}$ did not produce

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* This has been reported by Romeijn (1953) and confirmed by us.

† See also Geller, Bozorth, Gilleo & Miller (1959).

* In some cases, it is possible to draw some conclusions regarding ion distribution from a qualitative comparison of powder photographs.

† The Mg^{2+} ions also occupy dodecahedral sites in the pyrope garnet.

a single phase but did produce a garnet phase with a substantially larger lattice constant than that of $Ca_3TiNiGe_3O_{12}$.

The garnet $\{Mn_3\}[NbZn](FeGe_2)O_{12}$ probably has the distribution indicated. It would not be surprising if the Ta^{5+} ion could be substituted for Nb^{5+} in this garnet. The V^{5+} ion, however, being much smaller than Nb^{5+} might be expected to show a preference for tetrahedral sites. Attempts to make garnets with more Fe^{3+} ion in the tetrahedral sites such as $\{Mn_3\}[NbSc](Fe_2Ge)O_{12}$ were not successful. The garnet $\{Mn_3\}[NbZn](FeGe_2)O_{12}$ does not appear to be ferrimagnetic down to liquid N_2 temperature. However, it is possible that it does become ferrimagnetic at lower temperatures.

We wish to thank T. Y. Kometani and E. Bloom for chemical analyses of some of the specimens and Mrs A. Werner for translating the Grum-Grzhimailo and Pliusnina article from the Russian.

APPENDIX

The program used to compute the powder intensities was written in Fortran for the IBM type 704 Data Processing System; it is an extension of an earlier program modified to include the imaginary part of the dispersion correction and to bring out significant internal details of the calculation. The logical flow is largely based on that of a structure factor program originally devised by J. N. Hobstetter.

The program treats any structure (centrosymmetric or otherwise) in any of the three orthogonal systems, the hexagonal, or the trigonal. A code number for the system is read in with the input data to route the internal flow appropriately. Reflection indices are internally generated and limited to those which are symmetrically non-equivalent in the particular system and which result in a value of $\sin^2\theta$ less than a value specified at object time. To maintain the generality of the program without incorporating a separate subroutine for each space group, the coordinates of all atoms in the cell are read in, however related by symmetry. In a structure of some complexity, this may be not only inconvenient but can result in error when manually handling a quantity of data. In the present case, a short separate program was written to generate the 96h equivalent positions of the oxygens from the one set of parameters and to punch these in the format required by the main program.

It is desirable in a structure factor or intensity program to distinguish between systematically absent reflections and those of negligible intensity. It is also desirable to avoid summation errors over terms which should be identically zero but for which the machine may in fact be retaining small residuals. The following two rather arbitrary devices have been evolved which seem to have met these problems satisfactorily in the structures we have treated to date: First, when the summation of the trigonometric terms for the jth set of i crystallographically equivalent atoms is formed, if

$$\{|\sum_i \cos 2\pi(hx_i+ky_i+lz_i)| + |\sum_i \sin 2\pi(hx_i+ky_i+lz_i)|\} \le 0{\cdot}00001\ ,$$

the respective cosine and sine terms are set identically equal to zero and the interpolation of the atomic scattering factor is evaded. Second, on having formed over the j non-equivalent crystallographic species the summations of the cosine and sine contributions to the structure factor, both real (A, B, where the respective atomic scattering factors include the real part of the dispersion correction and the isotropic temperature factor) and imaginary (A', B', including the imaginary part of the dispersion correction and the isotropic temperature factor), if the integer part of

$$1000(|A|+|B|+|A'|+|B'|)=0\ ,$$

the reflection is regarded as extinguished and further computations bypassed.

Output data are written on two tapes. One of these presents but one line of data per reflection and gives the indices, d, θ, the real part of the intensity $(A^2+B^2).LP$, and the total intensity

$$[(A-B')^2+(B+A')^2].LP.$$

This tape is punched onto cards which are sorted on θ and listed to give the reflections in order of their appearance. No absorption or multiplicity factors have been included. These may be applied manually where needed. A suitable way to treat multiplicity factors of complex patterns is also with small separate programs using the cards thus produced as input data.

The second tape prints the above results in order of the generation of reflections and provides the following additional data: the real and imaginary contributions to $|F^2|$, and, for each jth crystallographically non-equivalent atomic species, the number j of the species, A_j, B_j, A'_j, B'_j, and the atomic scattering factor including the real part of the dispersion correction, both with and without the isotropic temperature factor.

We have found this rather detailed exposure of the behavior of the various atomic species to be of substantial benefit. It reveals the sensitivity of critical reflections to adjustment of any of the parameters. This can be of particular value in the earlier stages of analysis for the examination of trial structures, generally prior to any contemplated refinement routines. The distribution of Co^{2+} ions described in the present paper is a case in point.

The program as presently constituted used approximately 5·4 sec. of computing time per reflection in summing over the total of 160 atoms per cell. The detailed print-out entailed an observable increase in writing time over previous programs. The program can, of course, be expedited for centrosymmetric structures by omission of sine terms. While this is easily done with octal correction cards, we have found it advantageous, particularly with rather complex centrosymmetric structures, to preserve these terms for at least the early computations, as errors in input data can be detected and isolated by spurious non-zero values of B-contributions.

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On the Taylor Series Approximation of ΔF

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One contributing factor for the necessity of damping factors to insure convergence in the least-squares analysis of crystal structure parameters is the neglect of higher order derivatives in the Taylor series approximation for ΔF. It is shown here how a second derivative term can be introduced into the general framework of the procedure without requiring a major change in existing computation programs.

On the Taylor series approximation of ΔF

It is a well established fact that the corrections $2\pi\Delta x$ of positional parameters calculated from the approximation

$$\Delta F = \sum_i (dF_{ci}/dx) 2\pi \Delta x_i$$

by least-squares procedures often do not result in convergence to a value $2\pi x_i$ when these corrections are used as successive approximations. This state of affairs can be remedied by the application of arbitrary damping factors to these calculated values of $2\pi\Delta x_i$. Usually, the damping factors used in the first cycles have values between 0·2 and 0·5. These values are adjusted upwards either arbitrarily, or according to a scheme such as that proposed by Vand & Pepinsky (1958) as convergence is approached. The use of damping factors is somewhat unsatisfactory, since there appears to be no theoretical basis for it. Since the best damping factor for a specific set of data is not known, convergence will be generally slower than the ideal rate and non-uniform for different atoms (unless individually adjustable damping factors are used).

Up to now, the feeling existed that the need for damping factors can solely be associated with the