

data depend only on the oxygen-ion parameters. (II) For hkl with two indices odd and the third equal $2n$, n odd, the total cation contribution is of the form $\pm 8 (f_{\text{Mn}^{2+}}^{\text{T}} - f_{\text{Ge}^{4+}}^{\text{T}}) \sin \frac{1}{4} \pi h$, where $f_{\text{Mn}^{2+}}^{\text{T}}$ and $f_{\text{Ge}^{4+}}^{\text{T}}$ are the room-temperature scattering factors of the Mn^{2+} and Ge^{4+} ions, respectively. A total of 96 independent data belong to these two classes. The remainder of the data, which in general have large contributions from the cations, were found to be substantially affected by extinction and were therefore omitted from the calculations.

Two series of least-squares calculations¹³, one using the data of both classes I and II and the other using only those of class I, were carried out. The two refinements converged quickly to final parameter values which differ slightly but not significantly. Because there seems to be no real basis for deciding between the two sets of final parameter values, both, together with the averages, are given in Table 1.

Table 1. *Oxygen-ion parameters*
(Standard deviations are in parentheses)

Parameter	(1) Based on data of Class I	(2) Based on data of Classes I and II	(3) Average
x	0.02997 (0.00025)	0.02982 (0.00038)	0.02990
y	0.05453 (0.00029)	0.05331 (0.00039)	0.05392
z	0.65305 (0.00034)	0.65317 (0.00037)	0.65311
β_{11}	0.00177 (0.00026)	0.00174 (0.00031)	0.00176
β_{22}	0.00054 (0.00026)	0.00143 (0.00035)	0.00099
β_{33}	0.00105 (0.00027)	0.00122 (0.00034)	0.00114
β_{12}	-0.00011 (0.00024)	0.00028 (0.00028)	0.00009
β_{13}	0.00007 (0.00027)	-0.00032 (0.00023)	-0.00012
β_{23}	-0.00075 (0.00021)	-0.00015 (0.00024)	-0.00045

The data used did not permit refinement of the cation thermal parameters¹⁴. Therefore, for the cations, isotropic thermal parameters, $B_{\text{Mn}} = 0.25 \text{ \AA}^2$ and $B_{\text{Ge}} = 0.19 \text{ \AA}^2$, were estimated from the oxygen-ion thermal parameters by assuming these parameters to be related inversely as the atomic weights. These were kept constant throughout

¹³ W. R. BUSING, K. O. MARTIN and H. A. LEVY, ORFLS, a FORTRAN crystallographic least-squares program. ORNL-TM-305 (1962), with modifications by J. A. IBERS, W. C. HAMILTON, C. K. JOHNSON, R. D. ELLISON and H. A. LEVY.

¹⁴ S. GELLER, Parameter interaction in least-squares structure refinement. Acta Crystallogr. **14** (1961) 1026-1035.

the calculations. It is unlikely that the oxygen-ion positional parameters are affected by this treatment because (1) the thermal parameters are small, (2) there are no large correlations¹⁴ between the thermal parameters and the oxygen-ion positional parameters, and (3) the results of the two refinements agree well.

After the refinement had converged, additional iterations were carried out with the Ge^{4+} multiplier as a variable; there was no indication of a distribution of the Fe^{3+} and Ge^{4+} ions over both the octahedral and tetrahedral sites. On the contrary, the multiplier increased by 3.20%, which indicates that the Ge^{4+} form factors are somewhat in error or, perhaps, that in this case, form factors for Ge^{3+} should be used. This was not pursued further, however.

Table 2. Observed and calculated structure amplitudes

h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $	h	k	l	$ F_o $	$ F_c $					
0	2	8	68	68	1	7	8	21	24	2	5	5	< 10	13	3	5	8	82	89	4	6	12	< 13	13
0	6	8	14	13	1	6	9	35	37	2	3	7	105	105	3	4	9	47	46	5	5	6	12	10
0	8	10	24	20	1	2	11	28	21	2	5	7	93	88	3	3	10	14	19	5	6	7	11	9
1	1	2	59	54	1	5	10	18	17	2	3	9	33	34	3	7	8	15	19	5	7	8	13	12
1	2	3	78	77	1	4	11	35	35	2	7	7	26	25	3	6	9	43	39	5	6	9	30	32
1	3	4	113	119	1	8	9	46	48	2	5	9	53	48	3	5	10	36	36	5	5	10	54	55
1	2	5	55	56	1	7	10	11	13	2	3	11	52	45	3	4	11	22	25	5	8	9	24	25
1	1	6	92	97	1	3	12	37	40	2	7	9	74	68	3	8	9	13	14	5	7	10	56	58
1	4	5	25	27	1	6	11	51	52	2	5	11	51	44	3	7	10	33	30	5	6	11	39	30
1	3	6	84	85	1	5	12	< 15	8	2	4	12	< 15	3	3	6	11	17	20	5	9	10	60	57
1	2	7	50	47	1	2	13	78	75	2	9	9	< 15	9	3	5	12	36	36	6	7	7	86	80
1	5	6	46	44	1	9	10	38	32	2	7	11	24	19	3	9	10	52	55	6	7	9	< 12	9
1	4	7	56	59	1	4	13	< 15	5	2	3	13	29	25	3	4	13	23	24	6	9	9	97	96
1	3	8	20	21	1	8	11	19	17	2	5	13	85	80	3	8	11	< 13	12	6	7	11	48	52
1	2	9	58	53	1	7	12	< 15	2	2	9	11	29	26	3	7	12	45	43	7	8	9	24	22
1	6	7	116	114	1	1	14	35	36	3	4	5	16	15	4	5	7	73	75	7	7	10	57	56
1	5	8	61	62	1	3	14	16	12	3	3	6	46	49	4	5	9	< 12	0					
1	4	9	69	73	1	6	15	45	44	3	5	6	102	100	4	7	9	16	15					
1	1	10	104	103	2	3	3	214	233	3	4	7	39	41	4	5	11	< 15	3					
1	3	10	48	52	2	3	5	27	31	3	6	7	47	47	4	7	11	47	50					

Table 2 compares the observed structure amplitudes with those calculated from the final average parameter values [column (3) of Table 1]. For the complete set of data in Table 2, the conventional $R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.070$. For the data of class I only, $R = 0.055$.

Interionic distances and angles

Interionic distances and angles, computed from the final average parameter values [column (3) of Table 1], are given in Table 3. The standard errors given in Table 3 are based on the larger standard deviations, those in column (2) of Table 1. The *limits of error* are taken as three times the standard errors.

Discussion

The refinement of the structure of $\text{Mn}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$ gives the first determination of the tetrahedral $\text{Ge}^{4+}-\text{O}^{2-}$ and 8-coordination $\text{Mn}^{2+}-\text{O}^{2-}$ distances in a garnet. The $\text{Ge}^{4+}-\text{O}^{2-}$ distance, 1.766 Å, is significantly longer than the $\text{Ge}^{4+}-\text{O}^{2-}$ distances, 1.737 and 1.741 Å, in quartz-type GeO_2 ¹⁵. The difference is about the same as occurs in the analogous $\text{Si}^{4+}-\text{O}^{2-}$ distances¹, indicating perhaps more ionicity in these bonds in the garnets than in the quartz-type structures. The two $\text{Mn}^{2+}-\text{O}^{2-}$ distances are 2.30 and 2.42 Å. These are rather close

Table 3. *Interatomic distances and angles*

GeO ₄ tetrahedron	Ge—O	(4) 1.766 Å (0.007 Å)*
	O—O	(2) 2.681 Å (0.013 Å), (4) 2.980 Å (0.013 Å)
	O—Ge—O	(2) 98.8° (0.5°), (4) 115.1° (0.3°)
FeO ₆ octahedron	Fe—O	(6) 1.995 Å (0.007 Å)
	O—O	(6) 2.712 Å (0.012 Å), (6) 2.926 Å (0.014 Å)
	O—Fe—O	(6) 85.7° (0.1°), (6) 94.3° (0.3°)
MnO ₈ dodecahedron (distorted cube)	Mn—O	(4) 2.303 Å (0.007 Å), (4) 2.421 Å (0.007 Å)
	O—O**	(2) 2.681 Å (0.013 Å), (4) 2.712 Å (0.012 Å),
		(4) 2.766 Å (0.017 Å), (2) 2.921 Å (0.016 Å),
		(4) 3.484 Å (0.004 Å), (1) 3.816 Å (0.012 Å),
		(1) 3.922 Å (0.015 Å),
	O—Mn—O	(4) 70.0° (0.4°), (2) 71.2° (0.4°),
		(4) 71.6° (0.4°), (2) 74.2° (0.3°)
	Mn—Fe	(4) 3.378 Å
	Mn—Ge	(2) 3.022 Å, (4) 3.701 Å
	Fe—Ge	(6) 3.378 Å
	Fe—O—Ge	(6) 127.8° (0.9°)
Fe—O—Mn	(6) 99.4° (0.4°), (6) 103.4° (0.5°)	
Ge—O—Mn	(4) 95.0° (0.4°), (4) 123.5° (0.7°)	
Mn—O—Mn	(8) 103.1° (0.5°)	

* (frequency of occurrence) distance or angle (standard error).

** These are the *edges* of the dodecahedron. The last three independent O—O distances are the diagonal *edges* of the "twisted cube". These are six other diagonals (not edges of the dodecahedron): (1) 3.816 Å (0.012 Å), (1) 3.922 Å (0.015 Å), (4) 4.185 Å (0.004 Å). In Ref.¹⁶, Table 3, the distance taken for the 4-multiple diagonal edge should have been 3.45 Å instead of 4.24 Å.

¹⁵ G. S. SMITH and P. B. ISAACS, The crystal structure of quartz-like GeO_2 , *Acta Crystallogr.* **17** (1964) 842–6.

¹⁶ S. C. ABRAHAMS and S. GELLER, Refinement of the structure of a grossularite garnet. *Acta Crystallogr.* **11** (1958) 437–441.

¹⁷ S. GELLER and M. A. GILLES, Crystal structure and ferrimagnetism of yttrium iron garnet. *J. Physics Chem. Solids* **3** (1957) 30–36. (See also *Structure Reports* **21**, pp. 294–297).

to the $\text{Y}^{3+}-\text{O}^{2-}$ distances, 2.37 and 2.43 Å in yttrium-iron garnet¹⁷. The averages are 2.36 and 2.40 Å, respectively. The $\text{Ca}^{2+}-\text{O}^{2-}$ distances in grossularite^{16,18} are 2.33 and 2.49 Å, average, 2.41 Å, again quite close to the value for the average $\text{Mn}^{2+}-\text{O}^{2-}$ distance. There appears to be an anomaly here, but it more likely involves the $\text{Ca}^{2+}-\text{O}^{2-}$ distances than the others. The coordination-number-6 distances from NaCl type structures of CaO^{19} and MnO^{20} are 2.40 and 2.22 Å, respectively, while the average CN6 $\text{Y}^{3+}-\text{O}^{2-}$ distance²¹ is 2.28 Å. Examination of the differences for CN6 distances indicates that the CN8 average distances of $\text{Mn}^{2+}-\text{O}^{2-}$ and $\text{Y}^{3+}-\text{O}^{2-}$ are nominally in *relative* agreement with the CN6 distances. On the other hand, the Ca^{2+} ion seems to be "contracted" in the grossularite garnet. Further structure refinements of garnets with *c* sites filled with Mn^{2+} or Ca^{2+} ions should be of interest in this regard.

The $\text{Fe}^{3+}-\text{O}^{2-}$ distance, 2.00 Å, agrees well with the octahedral $\text{Fe}^{3+}-\text{O}^{2-}$ distance found in yttrium-iron garnet by GELLER and GILLES¹⁷ and by BATT and POST²², in gadolinium-iron garnet by WEIDENBORNER²³, and in ytterbium-iron garnet by EULER and BRUCE²⁴. The octahedral $\text{Fe}^{3+}-\text{O}^{2-}$ distances reported for other iron garnets including that of yttrium by EULER and BRUCE²⁴ are higher, but do not show a trend with size of rare earth. While it might be argued that the error limits make the differences of questionable significance, the refinements of several different garnet structures with octahedral Fe^{3+} distances should show a trend of some reasonable sort. Because the agreement with a value of 2.00–2.01 Å found for such a variety of garnets (i.e., YFe, GdFe and YbFe garnets and

¹⁸ W. PRANDL, Verfeinerung der Kristallstruktur des Grossulars mit Neutronen- und Röntgenstrahlbeugung. *Z. Kristallogr.* **123** (1966) 81–116.

¹⁹ L. OFTEDAL, Die Gitterkonstanten von CaO, CaS, CaSe, CaTe. *Z. physik. Chem.* **128** (1927) 154–158.

²⁰ See J. D. H. DONNAY, G. DONNAY, E. G. COX, O. KENNARD and M. V. KING, *Crystal Data, Determinative Tables, Second Edition*, A.C.A. (1963) for the many references to MnO.

²¹ M. G. PATON and E. N. MASLEN, A refinement of the crystal structure of yttria. *Acta Crystallogr.* **19** (1965) 307–310. — A. FERT, Structure of some rare earths. *Bull. Soc. franç. Mineral. Cristallogr.* **85** (1962) 267–270.

²² A. BATT and B. POST, A procedure for parameter refinement in simple structures. *Acta Crystallogr.* **15** (1962) 1268–1270.

²³ J. WEIDENBORNER, Least-squares refinement of the structure of gadolinium-iron garnet, $\text{Gd}_3\text{Fe}_2\text{Fe}_3\text{O}_{12}$. *Acta Crystallogr.* **14** (1961) 1051–1056.

²⁴ F. EULER and J. A. BRUCE, Oxygen coordinates of compounds with garnet structure. *Acta Crystallogr.* **19** (1965) 971–978.

$\text{Mn}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$) is already so good, it would seem that some of the iron-garnet structures refined by EULER and BRUCE²⁴ warrant restudy.

The departures from regularity of the three coordination polyhedra in $\text{Mn}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$ are similar to those found in other garnets. The GeO_4 tetrahedra are elongated in the directions parallel to the $\bar{4}$ axes as are the corresponding tetrahedra in all other garnets for which accurate structural data are available^{1,8,16-18,22-25}. The FeO_6 octahedra are elongated in the directions parallel to the $\bar{3}$ axes as are the corresponding octahedra in all established cases except that of grossularite^{1,8,16-18,22-26}. The shorter edges of the tetrahedra and the octahedra (2.681 and 2.712 Å) are shared with the MnO_8 dodecahedra and are also the shortest edges of the latter. The next-longest edge of the dodecahedron (2.766 Å) is shared with another dodecahedron.

In an earlier paper⁵, it was indicated that there were several possible reasons for the absence of ferrimagnetism in $\text{Mn}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$: (1) weak interaction because of unfavorable geometry, (2) distribution of Fe^{3+} ions over the octahedral and tetrahedral sites resulting in a marked weakening of interaction, and (3) inherently weak interaction between Mn^{2+} and Fe^{3+} ions. Ferrimagnetism had been observed in $\{\text{Gd}_3\}[\text{Mn}_2](\text{GaGe}_2)\text{O}_{12}$ ²⁷ and since it was expected that a $\text{Gd}^{3+}-\text{O}^{2-}-\text{Mn}^{2+}$ interaction should be weaker than a $\text{Mn}^{2+}-\text{O}^{2-}-\text{Fe}^{3+}$ interaction, the third possibility was assumed to be unlikely. The second possibility is ruled out by the present analysis.

The $\text{Mn}^{2+}-\text{O}^{2-}-\text{Fe}^{3+}$ angles in $\text{Mn}_3\text{Fe}_2\text{Ge}_3\text{O}_{12}$ (Table 3) appear to be unfavorable²⁸ for interaction; for comparison the $\text{Me}(a)-\text{O}-\text{Me}(d)$ angle²⁹ in MnFe_2O_4 is 123°. Furthermore in this almost normal ferrosin, the $\text{Me}(a)-\text{O}$ distance is 1.95 Å, while in the garnet the $\text{Mn}-\text{O}$ distances 2.30 and 2.42 Å are considerably longer. (Of course, the longer distances in the garnet are to be expected because of the higher coordination of Mn^{2+} ions, i.e., eight in the garnet as against four in the spinel.) The first possibility would then appear to be the most likely.

²⁵ J. ZEMANN, Zur Kristalchemie der Granate. Beitr. Mineralogie Petrographie 8 (1962) 180-188.

²⁶ In Ref.¹ the word "longer" in the eleventh line of Page 9 should be replaced by the word "shorter".

²⁷ M. A. GILLES and S. GELLER, The interaction of magnetic ions in $\text{Gd}_3\text{Mn}_2\text{Ge}_2\text{GaO}_{12}$ and related garnets. J. Physics Chem. Solid 10 (1959) 187-190.

²⁸ P. W. ANDERSON in Magnetism, edited by G. T. RADO and H. SUHL, Vol. 1, pp. 25-83 (Academic Press, New York, 1963).

²⁹ J. M. HASTINGS and L. M. CORLISS, Neutron diffraction study of manganese ferrite. Physic. Rev. 104 (1956) 328-331.