Crystal Structure of β-Ga$_2$O$_3$

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The crystal structure of β-Ga$_2$O$_3$ has been determined from single-crystal three-dimensional x-ray diffraction data. The monoclinic crystal has cell dimensions $a = 12.23 \pm 0.02$, $b = 3.04 \pm 0.01$, $c = 5.80 \pm 0.01$ A and $\beta = 103.7 \pm 0.3°$ as originally reported by Kohn, Katz, and Broder [Am. Mineral. 42, 398 (1957)]. There are 4 Ga$_2$O$_3$ in the unit cell. The most probable space group to which the crystal belongs is C_{2h}^3–$C2/m$; the atoms are in five sets of special positions $4i$: $(000, \frac{1}{2}\frac{1}{2}0) \pm (x0z)$. There are two kinds of coordination for Ga^{3+} ions in this structure, namely tetrahedral and octahedral. Average interionic distances are: tetrahedral Ga—O, 1.83 A; octahedral Ga—O, 2.00 A; tetrahedron edge O—O, 3.02 A; and octahedron edge O—O, 2.84 A. Because of the reduced coordination of half of the metal ions, the density of β-Ga$_2$O$_3$ is lower than that of α-Ga$_2$O$_3$ which has the α-corundum structure. Also the closest approach of two Ga^{3+} ions in β-Ga$_2$O$_3$ is 3.04 A which is considerably larger than the closest approach of metal ions in the sesquioxides with the α-corundum-type structure and, in agreement with the results of thermodynamic meas-

urements, the β phase appears to be the structurally more stab one.

The average Ga—O distances in the structure seem to accou for the fact that although the Ga^{3+} ion is substantially larg than the Al^{3+} ion its quantitative preference for tetrahedrally c ordinated sites when substituted for Fe^{3+} ion in the iron garne is very nearly the same as that of the Al^{3+} ion.

The structure accounts for a recent result obtained by Pet and Schawlow from paramagnetic-resonance measurements Cr^{3+}-ion-doped β-Ga$_2$O$_3$, namely that the Cr^{3+} ion substitutes f the Ga^{3+} ions in a single set of equivalent octahedral sites.

The magnetic aspects of the β-Ga$_2$O$_3$ structure are discussed a it is shown that a possible Fe$_2$O$_3$ isomorph could be expected to at least antiferromagnetic with a Néel temperature of about 700° Furthermore, a knowledge of the β-Ga$_2$O$_3$ structure and of t nature of site preferences of the Ga^{3+} and Fe^{3+} ions in the garne lead to a prediction regarding the structure of the ferrimagnet crystals of formula Ga$_{2-x}$Fe$_x$O$_3$ recently discovered by Remeika

INTRODUCTION

MUCH attention has recently been given the sesquioxides of the $3d$ elements particularly in regard to their magnetic nature. Several of these have the α-Al$_2$O$_3$ (α-corundum) structure.[1] Crystals of α-Al$_2$O$_3$ doped with small amounts of magnetic ions are not only of scientific interest but have important application as MASER materials. Trivalent gallium with $3d^{10}$ configuration is nonmagnetic and therefore a Ga$_2$O$_3$ crystal doped with a magnetic ion is also of scientific and possibly technological interest.

In these Laboratories paramagnetic-resonance studies by Peter and Schawlow[2] on Cr^{3+}-ion-doped β-Ga$_2$O$_3$ crystals prepared by Remeika[3] indicated that the Cr^{3+} ions had replaced Ga^{3+} ions in crystallographically equivalent octahedral sites. If the Cr^{3+} ions had entered crystallographically nonequivalent octahedral sites, this certainly would have been detected. On the other hand, it would not have been simple to detect tetra- hedrally coordinated Cr^{3+} ions.

Since Kohn, Katz, and Broder had shown[4] that the unit cell of β-Ga$_2$O$_3$ contained 8 Ga^{3+} ions, then, as will be shown in detail later, these ions must be in at least two sets of crystallographically nonequivalent positions. Because there seemed little reason to expect the Cr^{3+}

ions to prefer one set of octahedral sites to another an because the Cr^{3+} ion shows an exclusive preference f octahedral coordination, (see, for example, footno references 5–7) it appeared reasonable to speculate tha the Ga^{3+} ions had two types of coordination in Ga$_2$O$_3$. If this speculation proved sound, we would ha the first clear-cut case in which a *pure* sesquioxi contained octahedrally and tetrahedrally coordinate metal ions in the same structure.

With the present interest in the $3d$ transition-met oxides, it would seem worthwhile to determine t structures of any of those yet unknown. (Indeed the now appears to be good reason to refine *known* structure of these oxides to provide needed accuracy for theoret cal considerations.) Such knowledge could be importar to our understanding of the crystal chemistry of t ions involved. For example, the Fe^{3+} and Ga^{3+} ions wit spherical electronic configurations $3d^5$ and $3d^{10}$, r spectively, have both octahedral and tetrahedr coordination in the garnets $\{Y_3\}[Fe_2](Fe_3)O_{12}$ an $\{Y_3\}[Ga_2](Ga_3)O_{12}$ and in solid solutions of one these in the other.[5] Both the Ga^{3+} and Al^{3+} ions a smaller than the Fe^{3+} ion, but the Ga^{3+} is substantiall larger than the Al^{3+} ion.[8] Yet when these ions are su stituted for the Fe^{3+} ion in the garnets they show ve nearly the same quantitative preference for tetrahedr sites.[5,9] The present investigation appears to clari this observation.

The structure of β-Ga$_2$O$_3$ also accounts for its beir

[1] R. W. G. Wyckoff, *Crystal Structures*, Vol. II (Interscience Publishers Inc., New York). See also Z. Krist., Strukturbericht 1, 240 (1931); L. Pauling and S. B. Hendricks, J. Am. Chem. Soc. 47, 781 (1925); W. H. Zachariasen, Z. Krist., Strukturbericht 2, 310 (1937).

[2] M. Peter and A. L. Schawlow, Bull. Am. Phys. Soc. Ser. II, 5, 158 (1960).

[3] J. P. Remeika, J. Appl. Phys. 31, 263S (1960); See also Con- ference on Magnetism and Magnetic Materials, Detroit, Michigan, November, 1959, Paper No. S4.

[4] J. A. Kohn, G. Katz, and J. D. Broder, Am. Mineral. 42, 398 (1957).

[5] M. A. Gilleo and S. Geller, Phys. Rev. 110, 73 (1958).

[6] S. Geller, J. Appl. Phys. 31, 30S (1960).

[7] S. Geller, C. E. Miller, and R. G. Treuting, Acta Cryst. 1 179 (1960).

[8] S. Geller, Acta Cryst. 10, 248 (1957).

[9] S. Geller, J. Phys. Chem. Solids (to be published).

the thermodynamically stable room-temperature phase,[10] for its having a lower density than that of the α phase, and allows us to make a speculation regarding the structure of the recently discovered ferrimagnetic (and piezoelectric) $Ga_{2-x}Fe_xO_3$.[3]

DETERMINATION OF THE STRUCTURE

The crystals used in this study were prepared by J. P. Remeika.[3] Powdered specimens gave photographs in agreement with the patterns reported by Kohn et al.[4] and by Foster and Stumpf[10] for the β-Ga_2O_3. Most of the crystals photographed were twinned, some multiply, but after some searching one was found from which a small single-crystal segment with long direction along the monoclinic b axis was cleaved. The cell constants[11] $a = 12.23 \pm 0.02$, $b = 3.04 \pm 0.01$, $c = 5.80 \pm 0.01$ A, $\beta = 103.7 \pm 0.3°$ given by Kohn et al.[4] are quite accurate for our purposes as established by the complete indexing of the powder pattern taken with $CuK\alpha$ radiation (see Appendix). The space group to which the crystal belongs was reported by Kohn et al. to be C_{2h}^3, which is indeed the *most probable* one and with which all our data are compatible. There are 4 Ga_2O_3 in the unit cell;[4] the x-ray density is therefore 5.94 g/cm.

The crystal photographed with the Weissenberg camera and both $CuK\alpha$ and $MoK\alpha$ radiation had the dimensions: length 1.3 mm and cross section 0.09×0.11 mm. The diffraction symmetry was C_{2h}-$2/m$, with systematic absences, hkl, $h+k \neq 2n$. Thus the possible space groups are C_{2h}^3-$C2/m$, C_s^3-Cm and C_2^3-$C2$. The space group Cm would require two equivalent atoms related by the symmetry plane to be at a maximum distance from each other of 1.52 A thus indicating that the crystal cannot possibly belong to this space group.

The corresponding intensities on the even-numbered (Weissenberg) layers about the b axis were very similar as were those on the odd-numbered layers. Thus the structure appeared to be layered at one-half the b axis. It was therefore unlikely that the heavy atoms would be at combinations of positions such that the y coordinates differed by other than multiples of $\frac{1}{2}b$, (although, of course very small deviations might occur). In such a case the positions of $C2$ with $y=0$ or $\frac{1}{2}$ become special positions of $C2/m$. Negative tests for piezo- and pyroelectricity supported the conclusion that the most probable space group for the crystal is $C2/m$.

In $C2/m$, the general positions and positions e-h would require two equivalent atoms related by the symmetry plane to be at 1.52 A from each other. Thus atoms could not be in any of these positions.

The intensities were estimated visually by comparison with a calibrated intensity scale and by cross comparison of intensities on various photographs. Intensities of zero-level data taken with $MoK\alpha$ radiation were

averaged with those taken with $CuK\alpha$ radiation when observable with both radiations. (The small dispersion corrections for Ga would not have a significant effect.) Because no really new information was obtainable from other than the zero and first layers, intensities on these were the only ones quantitatively estimated.

Because absorption of both radiations by the crystal was high ($\mu_{CuK\alpha} = 299$ cm^{-1}, $\mu_{MoK\alpha} = 255$ cm^{-1}), it was necessary to use a small crystal (see above). Thus maximum exposure times for the photographs taken with $MoK\alpha$ radiations were 102, 90, 70, and 90 hr for the zero through third layers, respectively. With $CuK\alpha$ radiation, the maximum exposure times were about 20 hr. Absorption corrections were applied assuming the crystal to be cylindrical with an average radius of 0.05 mm. The absorption correction tables used were those of Bond[12] and applied to the first layer in accordance with the formula given by Bond.[12] (see also footnote reference 13). Lorentz-polarization-Tunell rotation-factor corrections were also applied.[14]

A Patterson projection on (010) clearly showed the peaks resulting from Ga—Ga interactions, and it appeared that all atoms must lie in the symmetry planes, and occupy five sets of positions $4i$: (000, $\frac{1}{2}\frac{1}{2}0) \pm (x0z)$. It was also clear that the contributions from the Ga^{3+} ions would determine most of the phases. It was necessary to consider the first-layer data for the purpose of distinguishing the most probable among homomorphic (010) projections. A (010) Fourier synthesis, a generalized Patterson projection using the $h1l$ data, a generalized Fourier projection with the $h1l$ data, and a pseudo-three-dimensional difference synthesis aided in determining the oxygen-ion positions. The pseudo-three-dimensional synthesis was done as follows: The contributions of the Ga^{3+} ions were subtracted from the observed structure factors. These had been scaled on the basis that, as indicated, the contributions of oxygens were generally not large. Thus some intuition entered into this scaling and as will be seen appeared to be quite sound. The remainders assumed to be the oxygen contributions, but of course containing numerous error contributions, were used in the synthesis. Each such amplitude, $h0l$, and $h1l$ was counted once in the synthesis. As expected, some spurious peaks occurred. Nevertheless, having obtained fairly accurate positions of the Ga^{3+} ions, the results of this synthesis together with structural considerations led to a determination of the oxygen trial parameters.

The trial parameters (for refinement) are given in Table I. It should be mentioned that the oxygen-ion positions were expected to be quite inaccurate, the idea being to save the author time by allowing the IBM 704 computer to do *all* of the refining.

[10] L. M. Foster and H. C. Stumpf, J. Am. Chem. Soc. 73, 1590 (1951).

[11] Our designation of the axes is in keeping with the convention $c < a$ for the monoclinic cell.

[12] W. L. Bond, Acta Cryst. 12, 375 (1960).

[13] M. J. Buerger and N. Niizeki, Am. Mineral. 43, 726 (1958).

[14] I am indebted to Dr. R. G. Treuting for programing the calculation of the corrected relative squared structure amplitudes and relative structure amplitudes on the IBM 704 computer.

TABLE I. Trial parameters.

Atom	Coordinates		B, A^2
	x	z	
Ga_I	0.087	−0.204	0.2
Ga_{II}	0.341	−0.312	0.2
O_I	0.153	0.092	0.8
O_{II}	0.492	0.248	0.8
O_{III}	0.829	0.443	0.8

REFINEMENT OF THE STRUCTURE

Refinement of the structure was carried out with the Busing-Levy[15] least-squares program for the IBM 704 computer. Only $h0l$ and $h1l$ amplitudes were used. In the first refinement cycles 824 data were included. All observed amplitudes were weighted unity; all unobserved amplitudes included at one-half threshold value were weighted 0.01. Two scale factors corresponding to the two k values (zero and first layers about b) of the data were refined. Both of these were started at 1.000 and are the scale factors mentioned earlier. Atomic scattering factors used for the structure amplitude calculations were those of Thomas and Umeda[16] for Ga^{3+} and for O^{2-} those given by Berghuis *et al.*[17] for O arbitrarily modified such that $f_{O^{2-}} = 10$ at $\sin\theta/\lambda = 0$ and $f_{O^{2-}} = f_O$ at $\sin\theta/\lambda \geq 0.20$.

Convergence was attained within three cycles: in the final cycle, the largest change in any coordinate was 0.003 A by O_{II} in the a direction. The weighted R factor was 0.171 for the data calculated on the basis of the parameters of the second cycle. The final scale factors were 0.988 and 0.997 with σ's of 0.010, meaning that these are not significantly different from 1.000.

Examination of the calculated and observed data indicated some large discrepancies in the high-angle data taken with the Mo$K\alpha$ radiation. These data had been taken with Kodak type KK film, which unfortunately has rather large grain size. Small weak spots are difficult to see in this case; the difficulty is more pronounced when the α_1, α_2 doublet is resolved. Because the data were plentiful, it was decided to omit a large portion of the high-angle reflections. The total data were therefore reduced from 824 to 522. Two least-squares cycles were run. The largest difference in coordinates between the results so obtained and those obtained previously was 0.005 A for atom O_{III} in the a direction. The final parameters with their standard deviations are given in Table II.

The weighted R factor calculated by the Busing-Levy program was 0.166. However, if unobserved reflections are excluded; the R factor

$$\sum |F_{obs} - F_{calc}| / |\sum |F_{obs}|$$

[15] W. R. Busing and H. A. Levy, ORNL Central Files Memorandum 59–4–37 (April, 1959).
[16] L. H. Thomas and K. Umeda, J. Chem. Phys. **26**, 293 (1957).
[17] J. Berghuis, I. J. M. Haanappel, M. Potters, B. O. Loopstra: C. H. MacGillavry, and A. L. Veenendaal, Acta Cryst. **8**, 478 (1955).

for the $h0l$ reflections is 0.143 and for the $h1l$, 0.130. The comparison of calculated and observed structure amplitudes is given in Table III.

INTERATOMIC DISTANCES AND ANGLES

The estimated standard deviations of the positions of the atoms are 0.004, 0.004, 0.033, 0.028, and 0.028 A for Ga(I), Ga(II), O(I), O(II), and O(III), respectively. These standard deviations of position should be considered as radii of circles in the mirror planes. Standard deviations in bond lengths were computed taking into consideration the angle made between the bond direction and the symmetry planes. The interatomic distances and their standard deviations are given in Table IV.

The important angles are given in Table V. Individual standard deviations were not calculated for these, but an estimate of the standard deviation of an O—Ga—O angle is 1.3° and of a Ga—O—Ga angle, 0.9°.

DESCRIPTION OF THE STRUCTURE

The arrangement of the ions in the β-Ga_2O_3 structure is shown in Figs. 1 and 2. The oxygen ions are arranged in a "distorted cubic" close-packed array. There are two crystallographically nonequivalent gallium and three nonequivalent oxygen ions in the unit cell. Each Ga_I^{3+} ion is surrounded by a distorted tetrahedron of oxygen ions: one O_I^{2-} at 1.80 A, two O_{II}^{2-} ions at 1.83 A, and one O_{III}^{2-} ion at 1.85 A (average 1.83 A). Each Ga_{II}^{3+} ion is surrounded by a highly distorted octahedron of oxygen ions: two O_I^{2-} at 1.95 A, one O_{II}^{2-} ion at 1.95 A, one O_{III}^{2-} ion at 2.02 A, and two O_{III}^{2-} ions at 2.08 A (average 2.00 A). A tetrahedron shares *only* corners with other tetrahedra in the b-axis direction and with octahedra in other directions. An octahedron shares edges with adjacent octahedra in the b axis direction and in roughly the [102] direction: the shared edges are, respectively, O_I–O_{III} and O_{III}–O_{III}, each of length 2.67 (Table IV). The distance 2.67 A is the shortest O–O distance in the structure. This is

TABLE II. Final parameters.

	Scale factors		Standard deviations	
	1	0.984		0.013
	2	0.988		0.014

Atom	Coordinates		B, A^2	$\sigma(x)$	$\sigma(z)$	$\sigma(B)$
	x	z				
Ga_I	0.0904	−0.2052	0.33	0.0002	0.0005	0.05
Ga_{II}	0.3414	−0.3143	0.28	0.0002	0.0005	0.05
O_I	0.1674	0.1011	0.76	0.0019	0.0041	0.32
O_{II}	0.4957	0.2553	0.43	0.0016	0.0034	0.25
O_{III}	0.8279	0.4365	0.46	0.0015	0.0034	0.25

TABLE III. Calculated and observed amplitudes.

k=0

ℓ	h=0 Obs.	Calc.	h=2 Obs.	Calc.	h=4 Obs.	Calc.	h=6 Obs.	Calc.	h=8 Obs.	Calc.	h=10 Obs.	Calc.	h=12 Obs.	Calc.	h=14 Obs.	Calc.	h=16 Obs.	Calc.	h=18 Obs.	Calc.	h=20 Obs.	Calc.	h=22 Obs.	Calc.	h=24 Obs.	Calc.	h=26 Obs.	Calc.	h=28 Obs.	Calc.
0		440	<9	-1	93	-126	57	53	23	-26	<13	1	125	116	<19	2	84	-77	<20	9	19	24	<19	1	33	28	<20	2	35	-34
1̄	22	-18	47	33	97	-141	67	-66	112	145	30	36	82	-66	<14	-5	22	-23	25	-23	53	55	20	20	43	<46	18	-11		
2̄	117	-151	107	-123	45	45	48	46	<12	-2	<13	10	77	-62	83	-69	57	50	45	45	<19	29	<19	-11	<19	-9	30	-26		
3̄	<10	6	27	-27	76	62	122	111	69	-58	109	-93	38	31	42	34	<17	8	40	33	<19	-18	51	-49	<19	20	49	36		
4̄	24	30	136	178	17	-23	76	64	35	28	46	-39	15	15	100	100	<17	-13	48	-61	<19	14	<18	12	<19	3	24	31		
5̄	<13	-2	17	8	19	20	144	-109	26	-27	136	107	<13	4	50	-42	<14	5	41	-35	<19	-15	51	55	<19	6	41	-39		
6̄	23	28	107	-96	57	-49	52	40	<15	10	<13	13	19	16	78	-61	40	-42	49	47	<19	22	<19	-20	<19	-20				
7̄	16	-21	<12	-6	14	-23	63	52	63	59	65	-47	46	-46	<18	21	<18	14	<19	14	<19	27	<19	-22						
8̄	61	-64	26	34	81	81	<17	-21	17	-21	<18	7	40	-34	24	22	66	64	<18	-18	29	36	<19	11						
9̄	41	42	<18	-7	25	17	<18	5	78	-72	<19	-3	74	63	<18	-9	<19	-18	<19	5	27	-34	<18	-4						
1̄0	43	44	<19	12	54	-59	<19	-18	<19	22	<19	-2	22	17	<19	11	47	-47	<19	-20										
1̄1	<19	-23	<19	-2	<19	-11	<19	-15	43	40	22	29	33	-32	<18	-19	<19	12	<18	3										
1̄2	24	-15	30	-36	30	29	30	36	<19	-14	<19	-2	<18	-4																
1			53	30	145	145	70	-49	125	-130	34	31	61	51	<10	0	24	28	<18	-11	55	-53	<19	14	42	42				
2			43	38	88	75	19	-18	<13	-2	46	-41	83	-75	33	36	62	59	30	-29	22	-22	<19	-1	<18	-23				
3			82	-72	72	-65	108	105	73	62	79	-64	22	-21	<17	-2	<18	-21	38	39	25	31	38	-41						
4			113	-104	<20	16	<19	4	<16	-8	88	84	17	18	74	-69	<19	-3	38	30	<19	3	<18	18						
5			99	86	17	-18	123	-103	22	15	49	50	<18	-3	<19	15	<19	-3	43	-44	<19	5	39	39						
6			72	61	14	-17	<7	-7	30	-17	64	-56	<19	17	48	54	<19	-20	22	-27	<18	3								
7			44	-42	57	52	35	58	30	-42	22	-28	<19	10	<19	-13	<19	19	23	31										
8			<18	-7	<18	17	<18	-6	38	43	<19	23	39	-47	<19	-13	23	29												
9			<19	-13	64	-66	<19	1	39	39	<19	0	<19	3	<18	1														
10			<19	-10	<19	-11	<19	-5	38	-34	<19	4	39	40																
11			<19	21	42	43	<19	-22	29	-27																				
12			<18	18	<17	-1																								

k=1

ℓ	h=1 Obs.	Calc.	h=3 Obs.	Calc.	h=5 Obs.	Calc.	h=7 Obs.	Calc.	h=9 Obs.	Calc.	h=11 Obs.	Calc.	h=13 Obs.	Calc.	h=15 Obs.	Calc.	h=17 Obs.	Calc.	h=19 Obs.	Calc.	h=21 Obs.	Calc.	h=23 Obs.	Calc.	h=25 Obs.	Calc.
0			21	17	110	-101	132	-112	51	53	56	61	21	-27	<20	-9	28	-21	45	-45	30	28	46	41	22	-26
1̄			135	-136	29	33	23	24	25	20	69	69	18	-31	79	-79	<21	25	45	45	<23	-4	<23	8	<22	-4
2̄	63	55	88	-88	14	14	161	181	<15	-11	95	-86	<18	21	<20	1	<21	4	59	61	<23	-3	57	51	<23	6
3̄	55	-46	143	145	14	14	42	-40	16	13	67	-69	19	-30	96	87	<21	16	55	-52	<23	-4	<23	-7	<23	-11
4̄	<15	1	35	41	26	27	96	-96	72	-71	43	56	22	32	<20	-16	<21	3	22	-32	33	-37	33	36	<23	28
5̄	71	87	58	-59	65	-61	17	17	<18	3	22	31	46	54	24	-36	40	-56	<23	26	30	30	<23	-1	<22	13
6̄	<18	-12	<18	10	63	-64	24	28	121	105	<20	-22	55	-49	22	15	<22	-11	<23	10	38	51	<23	-11	45	-39
7̄	79	-94	<20	-11	68	79	<20	-6	<20	-11	<21	9	56	-62	<22	-11	59	67	<23	-2	38	-34	<23	3	<21	-15
8̄	<21	10	<21	-7	27	36	<21	19	68	-69	25	-32	26	40	<23	9	<23	-3	<23	8	32	-34	<22	34		
9̄	71	53	45	41	50	-39	<22	-22	<22	5	<23	-5	30	31	<23	33	<23	-31	<22	20	<21	14				
1̄0	<23	-11	<23	6	<23	-6	46	-41	33	29	70	55	<23	-19	<23	-20	<23	6	<22	-13						
1̄1	<23	-2	73	-57	<23	3	52	40	<23	-9	<23	3	<23	2	55	-45	<22	1	47	42						
1̄2	<22	-6	<22	2	<22	-6	29	28	<22	8	54	45	<22	-11												
1	209	162	79	61	80	-62	<14	-2	51	-47	38	-41	78	80	36	38	58	-57	<23	-16	<23	5	<23	-11	22	24
2	64	-57	14	-11	180	174	18	14	97	-98	<18	12	20	18	<20	-1	59	52	57	-50	<23	-1				
3	138	-143	31	30	40	35	<16	2	53	57	19	-16	80	-79	<22	15	47	49	<23	-3	<23	0	<22	-1		
4	15	20	47	-53	95	-96	31	35	58	67	20	-25	<21	-19	<22	-8	46	-39	<23	15	45	43				
5	58	66	38	-47	<18	-17	<19	-13	29	-33	38	49	36	46	37	-45	<23	-26	<23	14	<22	-6				
6	<19	-16	96	93	20	29	77	-74	<22	-5	26	26	<23	0	23	31	<23	14								
7	<20	10	27	35	<21	-4	22	31	<23	-3	42	-58	<23	3	30	42	<22	0								
8	<23	-20	40	-63	<22	15	42	53	<23	-16	<23	-22	<23	-2												
9	<23	-28	<23	-22	<23	3	<23	-19	<23	22	23	40														
10	42	43	30	29	50	-44	<23	-15	<23	25																
11	38	28	<23	-2	<22	12	<22	2																		

TABLE IV. Interatomic distances and standard deviations.

	Atom pair (No.)	Distance, A	σ, A		Atom pair (No.)	Distance, A	σ, A
Ga_IO_4 tetrahedron	$Ga-O_I$	1.80	0.03	$Ga_{II}O_6$ octahedron	$Ga-O_I(2)$	1.95	0.03
	$Ga-O_{II}(2)$	1.83	0.01		$Ga-O_{II}$	1.95	0.03
	$Ga-O_{III}$	1.85	0.03		$Ga-O_{III}$	2.02	0.03
	$O_I-O_{II}(2)$	2.93	0.04		$Ga-O_{III}(2)$	2.08	0.02
	O_I-O_{III}	3.13	0.04		O_I-O_I	3.04	0.01
	$O_{II}-O_{II}$	3.04	0.01		$O_I-O_{II}(2)$	2.90	0.04
	$O_{II}-O_{III}(2)$	3.02	0.03		$O_I-O_{III}(2)$	2.85	0.04
					$O_I-O_{III}(2)$	2.67	0.04
					$O_{II}-O_{III}(2)$	2.89	0.03
					$O_{III}-O_{III}(2)$	2.67	0.04
					$O_{III}-O_{III}$	3.04	0.01
Shortest Ga–Ga distances	$Ga_I-Ga_I(2)$	3.04	0.01	Averages	Ga_I-O	1.83	
	$Ga_{II}-Ga_{II}(2)$	3.04	0.01		$Ga_{II}-O$	2.00	
	$Ga_{II}-Ga_{II}(2)$	3.11	0.01		O—O, octahedron	2.84	
	Ga_I-Ga_{II}	3.28	0.01				
	$Ga_I-Ga_{II}(2)$	3.30	0.01		O—O, tetrahedron	3.02	
	$Ga_I-Ga_{II}(2)$	3.33	0.01				
	$Ga_I-Ga_{II}(2)$	3.45	0.01				

TABLE V. Bond angles.

Within a tetrahedron (involve only Ga_I)			Within an octahedron (involve only Ga_{II})	
$2\ O_I-Ga-O_I$	107.6°		O_I-Ga-O_I	102.7°
O_I-Ga-O_I	117.8		$2\ O_I-Ga-O_{II}$	96.1
$O_{II}-Ga-O_{II}$	112.0		$2\ O_I-Ga-O_{III}$	91.9
$2\ O_{II}-Ga-O_{III}$	110.2		$2\ O_I-Ga-O_{III}$	83.1
			$2\ O_{II}-Ga-O_{III}$	91.5
			$O_{III}-Ga-O_{III}$	94.1
			$2\ O_{III}-Ga-O_{III}$	81.4

Ga_I-O-Ga_{II} (tetrahedral-octahedral) angles

$2\ Ga-O_I-Ga$	123.3°	(2 different Ga_{II}'s)
$2\ Ga-O_{II}-Ga$	123.0	(2 different O_{II}'s)
$2\ Ga-O_{III}-Ga$	122.3	(2 different Ga_{II}'s)
$Ga-O_{III}-Ga^a$	115.4	

Ga_I-O-Ga_I (tetrahedral-tetrahedral) angles

$2\ Ga-O_{II}-Ga$	112.0°	(2 different O_{II}'s)

$Ga_{II}-O-Ga$ (octahedral-octahedral) angles

$2\ Ga-O_{III}-Ga$	98.4°	(2 different Ga_I's)
$2\ Ga-O_{III}-Ga$	98.4	(2 different O_{III}'s)
$Ga-O_I-Ga$	102.7	
$Ga-O_{III}-Ga$	94.1	

ª Ga_I and Ga_{II} in same plane.

in agreement with the observation[18] that in ionic structures, the mutual repulsion of the positive ions tends to reduce the length of shared edges of anion polyhedra.

Because of the short b axis, there are two $O_I{}^{2-}$ and two $O_{III}{}^{2-}$ ions (along the b axis) at corners of an octahedron. The structure cannot possibly then have two $O_{II}{}^{2-}$ ions at the remaining corners of the octahedron, since these must lie in the mirror plane containing the $Ga_{II}{}^{3+}$ ion within the octahedron. Thus there is only one $O_{II}{}^{2-}$ ion at a corner of the octahedron, the remaining corner being occupied by a third $O_{III}{}^{2-}$ ion.

At the corners of the tetrahedron, there are two $O_{II}{}^{2-}$ ions which are along the b axis, the other corners

[18] L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed., Chap. 13, Sec. 6.

being occupied by an $O_I{}^{2-}$ and an $O_{III}{}^{2-}$ ion each lying in the mirror plane containing the $Ga_I{}^{3+}$ ion within the tetrahedron.

Thus each $O_I{}^{2-}$ ion is at the corner of two octahedra and one tetrahedron; each $O_{II}{}^{2-}$ ion is at the corner of one octahedron and two tetrahedra; and each $O_{III}{}^{2-}$ ion is at the corner of three octahedra and one tetrahedron. *If* the octahedra and tetrahedra were regular, it would be doubtful that such a structure could exist, because the sums of the bond numbers of the bonds at all oxygen ions would not be 2 (see footnote reference 18). They would be: at $O_I{}^{2-}$, $1\frac{3}{4}$, at $O_{II}{}^{2-}$, 2; and at $O_{III}{}^{2-}$, $2\frac{1}{4}$. However, the polyhedra are probably not regular. In fact, the four bonds to $O_{III}{}^{2-}$ are the longest ones: $Ga_I-O_{III}=1.85$ A, $Ga_{II}-O_{III}=2.08(2)$ and 2.02

A, whereas those to O_I^{2-} are the shortest ones: Ga_I–O_I = 1.80 A and Ga_{II}–O_I = 1.95 A(2). The Ga_I–O_{II} distance 1.83 A is equal to the average Ga_I–O distance, but the Ga_{II}–O_{II} distance, 1.95 A, is 0.05 A shorter than the average Ga_{II}–O distance. Thus the sum of the bond numbers of the bonds to an O_{II}^{2-} ion is somewhat greater than two, but not importantly so (see footnote reference 20).

Actually, the statistical calculation tells us that: there are no significant differences in Ga_I–O distances, nor in the Ga_{II}–O_I and Ga_{II}–O_{II} distances, nor in the two Ga_{II}–O_{III} distances. The shorter Ga_{II}–O_{III} distance is only possibly significantly different from the Ga_{II}–O_I and Ga_{II}–O_{II} distances. However the long Ga_{II}–O_{III} distance is significantly larger than the shortest distances. Unfortunately, the oxygen ions contribute little to the intensities in comparison with gallium ions and it is unlikely that much greater reliability can be attained even from more accurate intensity data. Also it would appear to be quite difficult to obtain crystals of the aluminum isomorph designated as θ-Al$_2$O$_3$[19,20]; none have as yet been reported.

Nevertheless, the aforementioned criterion defined by Pauling[18] indicates that the oxygen polyhedra must be irregular and therefore that the calculated distances are perhaps better than indicated by the standard deviations.

DISCUSSION

1. Comparison with α-Corundum Structure

The β-Ga$_2$O$_3$ structure (Figs. 1 and 2) appears to be quite different from that of α-Ga$_2$O$_3$ which has the α-corundum structure. The latter has the oxygen ions in approximately hexagonal close-packed array with all the Ga^{3+} ions octahedrally coordinated to O^{2-} ions. Also in the α phase, octahedra share edges and faces
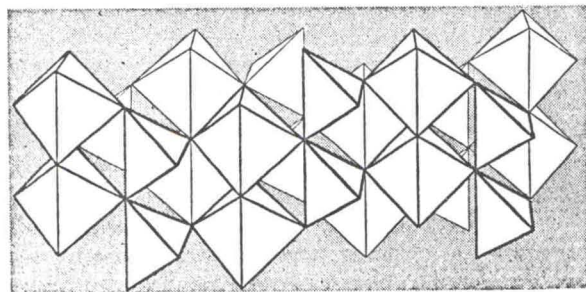

FIG. 1. Perspective view of the arrangement of the oxygen octahedra and tetrahedra in β-Ga$_2$O$_3$.

[19] H. C. Stumpf, A. S. Russell, J. W. Newsome, and C. M. Tucker, Ind. Eng. Chem. **42**, 1398 (1950).

[20] The lattice constants of this phase derived by the present author from the powder data given by Stumpf et al.[19] are a = 11.83±0.02, b = 2.92±0.01, c = 5.64±0.01 A, and β = 104.0±).5°. The powder data, however, are not completely correct, the most outstanding discrepancy being that of d_{001} which should be 5.47 A as against the reported 5.25 A. Also it is possible that some observable lines have been omitted; one of these is the [40$\bar{1}$] reflection.
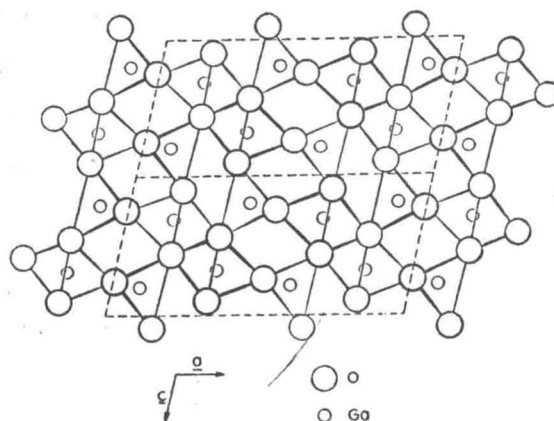
FIG. 2. Plan view of the β-Ga$_2$O$_3$ structure. Lines connecting atoms indicate the manner in which the octahedra and tetrahedra are constructed from and joined by the oxygen atoms in the three consecutive symmetry planes. Only the upper faces of the polyhedra are depicted. For increased clarity, this figure should be studied simultaneously with Fig. 1.

which brings the metal ions very near each other. Accurate atomic positional parameters for α-Ga$_2$O$_3$ have not been determined. However, in Fe$_2$O$_3$,[1] the closest approach of two Fe^{3+} ions through a shared octahedral face is 2.88 A and through a shared edge 2.96 A.[21] In β-Ga$_2$O$_3$ no faces are shared between polyhedra and the shortest Ga^{3+}–Ga^{3+} distance is 3.04 A.

Now it is recognized that usually structures in which faces of polyhedra are shared are less stable than those in which edges are shared, which in turn are less stable than structures in which only corners are shared.[18] Thus, one would expect the β phase to be more stable than the α phase. Foster and Stumpf have shown[10] that although the α-Ga$_2$O$_3$ forms at lower temperatures than does β-Ga$_2$O$_3$, the α phase is metastable. In the case of alumina, it appears that the α phase forms at higher temperatures than the θ (isostructural with β-Ga$_2$O$_3$) just the reverse of the gallia. Yet it appears that although seen rarely in comparison with the α phase, the θ-Al$_2$O$_3$ is the thermodynamically stable phase at room temperature[19] and that although α-Al$_2$O$_3$ is thermodynamically metastable at room temperature the $\alpha \rightarrow \theta$ transition of Al$_2$O$_3$ is "infinitely" sluggish at such temperature.

As one might expect, the lower average coordination in the β-Ga$_2$O$_3$ is accompanied by a lower density; the volumes per Ga$_2$O$_3$ in the α and β phases are 47.8 and 52.8 A^3, respectively.

[21] Recent accurate work on Ti$_2$O$_3$ and V$_2$O$_3$ by Nordmark[22] has led to the Me–Me distances: 2.55 and 2.64 A, respectively, across the shared face and 2.99 and 2.88 A, respectively, across the shared edge. In any case, the closest approach of Ga^{3+} ions in β-Ga$_2$O$_3$ is substantially greater than that of the metal ions in any of the α phases.

[22] C. Nordmark, in Final Technical Report, "Studies on the crystal chemistry of titanium, vanadium and molybdenum oxides at elevated temperatures" by A. Magnéli et al., University of Stockholm (October, 1959), p. 16. See also R. E. Newnham and Y. M. de Haan, American Crystallographic Association Meeting, Washington, D. C., January, 1960, Paper No. D-5.

TABLE VI. Analogous average distances and ranges in β-Ga$_2$O$_3$ and in yttrium-iron garnet.

Metal-oxygen distances	β-Ga$_2$O$_3$		YIG[a]	
	Averages	Range	Averages	Range
Octahedral	2.00 A	1.95–2.08 A	2.00 A	All equal
Tetrahedral	1.83	1.80–1.85	1.88	All equal
O–O distances				
In octahedron	2.84	2.67–2.90	2.84	2.68–2.99 A
In tetrahedron	3.02	2.93–3.13	3.06	2.87–3.16

[a] S. Geller and M. A. Gilleo, J. Phys. Chem. Solids **3**, 30 (1957); **9**, 235 (1959).

2. Possibility of Disorder

That the structure is ordered appears to be established by the paramagnetic-resonance work by Peter and Schawlow[2] on Cr^{3+}-ion-doped β-Ga$_2$O$_3$, in which it is found that the Cr^{3+} ions prefer only one set of octahedral sites. It is likely that these ions replace the Ga_{II}^{3+} ions in octahedrally coordinated sites: There is not enough space for foreign ions in the remaining octahedrally coordinated holes. Thus it is improbable that there is the type of disorder which would allow drastic change in the environment of any of the Ga_I^{3+} and Ga_{II}^{3+} ions.

3. Importance of β-Ga$_2$O$_3$ Structure Relative to Substitution of Ga^{3+} and Al^{3+} for Fe^{3+} Ions in Yttrium-Iron Garnet

The Ga^{3+} and Fe^{3+} ions have very similar crystal chemistry. Both ions have spherical electronic configuration and are of very nearly the same size, the Ga^{3+} ion being somewhat smaller than Fe^{3+} ion in most structures. The relative radii derived from the perovskitelike compounds[8] put the Ga^{3+} ion $CN(6)$ radius at 0.015 A less than that of the Fe^{3+} ion. This does not mean that average metal-oxygen distances will be exactly the same in different structures. For example, the relative ionic radii derived from the perovskitelike compounds are applicable to the garnets,[5,23,24] but the $CN(6)$ metal-oxygen distances in the garnets are uniformly somewhat larger than the sums of these radii.

Although the structure of yttrium-gallium garnet, $\{Y_3\}[Ga_2](Ga_3)O_{12}$ has not yet been refined, that of yttrium-iron garnet has[25]; it is of interest to compare some analogous distances in this garnet structure with those of β-Ga$_2$O$_3$. The averages and ranges of these analogous distances are compared in Table VI. It is seen that the average Ga_{II}—O distance in β-Ga$_2$O$_3$ is the same as the octahedral Fe—O distance in yttrium-iron garnet. On the other hand, the average Ga_I–O

distance in β-Ga$_2$O$_3$ is substantially smaller than the tetrahedral Fe–O distance in the garnet. The average O–O distances of the octahedra in the two structures are equal but the average O–O distance in the GaO$_4$ tetrahedron in β-Ga$_2$O$_3$ is shorter than the average O–O distance in the FeO$_4$ tetrahedron of the garnet. Now from the least-squares calculations, the aforementioned differences are not significant. However, on a crystal chemical basis, there is reason to believe that the differences are meaningful.

We have shown previously[5] that when the Ga^{3+} ion is substituted for the Fe^{3+} ion in the garnets, it shows a great preference for the tetrahedral $[CN(4)]$ site. Also there is indication that when Fe^{3+} is substituted for the Ga^{3+} ion in yttrium-gallium garnet, it greatly prefers the octahedral $[CN(6)]$ site.[26] We have also mentioned elsewhere that the ratios of effective size of ions in different coordinations may differ and probably depend largely on the nuclear charge and external electronic configuration of the atom.[23,24] The ratios of tetrahedral to octahedral Fe—O distances in yttrium-iron garnet is 0.94; in $Y_3Al_2Al_3O_{12}$[27] the analogous Al–O ratio is 0.91, in β-Ga$_2$O$_3$ the ratio of tetrahedral to octahedral average Ga–O distances is 0.91, in fact very similar to that of the Al–O distances in the aluminum garnet.

Now despite the fact that the Al^{3+} ion is much smaller than the Ga^{3+} ion, the quantitative site preference in the substituted iron garnets of the latter is very close to that of the former[5,9]: this is in agreement with the above considerations.

4. Magnetic Aspects

If an Fe_2O_3 phase isostructural with β-Ga$_2$O$_3$ were found, it should be antiferromagnetic, because the Ga_I–O–Ga_{II} angles of about 123° (Table V) are (and presumably the Fe_I–O–Fe_{II} angles would be) favorable to superexchange interaction[9,25,28,29] and the network of octahedra and tetrahedra involving these favorable angles continues throughout the structure.[29] Counting the possible significant magnetic interactions we find

[23] S. Geller, R. M. Bozorth, M. A. Gilleo, and C. E. Miller, J. Phys. Chem. Solids **12**, 111 (1960).
[24] S. Geller and D. W. Mitchell, Acta Cryst. **12**, 936 (1959).
[25] S. Geller and M. A. Gilleo, J. Phys. Chem. Solids **3**, 30 (1957); **9**, 235 (1959).

[26] S. Geschwind, Phys. Rev. Letters **3**, 207 (1959).
[27] E. Prince, Acta Cryst. **10**, 787 (1957).
[28] M. A. Gilleo, Phys. Rev. **109**, 777 (1958).
[29] M. A. Gilleo, J. Phys. Chem. Solids (to be published).

TABLE VII. β-Ga$_2$O$_3$ powder data (CuKα radiation).

hkl	d_c	d_o	I_c	ΣI_c	I_o
200	5.942	-	0.0	0.0	-
001	5.635	5.62	1.6	1.6	VW
20Ī	4.679	4.67	3.8	3.8	W
201	3.677	3.66	(2.0)	2.0	VW
400	2.971	2.95	21.7	22.8	VS
110	2.945		1.1		
40Ī	2.930	2.92	26.1	26.1	VS
002	2.817	2.81	27.5	45.5	VVS
20Ī			18.0		
11Ī	2.675	2.66	12.7	12.7	W-M
111	2.549	2.536	50.2	50.2	VVS
310	2.412	-	0.2	0.2	-
401	2.403	2.390	17.7	17.7	M-S
31Ī	2.343		29.1		
202	2.340	2.332	1.1	31.8	S
402	2.340		1.6		
311	2.109	2.100	4.5	8.2	W-M
112	2.098		3.7		
60Ī	2.024	2.014	2.4	2.4	W
600	1.980		1.5		
112	1.979	1.971	3.4	13.1	M
312	1.978		8.2		
203	1.927	-	.3	0.3	-
51Ī	1.885		1.1		
003	1.878	-	0.0	1.1	-
510	1.872	1.865	4.8	4.8	M
402	1.838	1.831	2.5	3.4	W
602	1.838		0.9		
403	1.791	1.788	1.6	1.6	VW
601	1.744	1.736	1.0	1.0	VVW
312	1.714		0.0		
512	1.714	-	0.1	0.1	-
511	1.685	1.677	2.8	4.7	W-M
203	1.680		1.9		
113	1.628	1.622	1.4	1.4	VW
313	1.598	1.595	13.2	13.2	M-S
603	1.560	1.559	3.7	3.7	W
113	1.543	1.539	11.8	11.8	M
80Ī	1.528	1.525	5.9	16.4	M-S, Br.
020	1.520		10.5		
71Ī	1.512	-	0.2	0.2	-
800	1.485	1.479	0.2	3.5	W-M
710	1.482		3.3		
220	1.473		0.0		
513	1.470		0.1		
021	1.468	-	0.0	0.2	-
602	1.465		0.1		
802	1.465		0.0		
204	1.450	1.449	7.9	7.9	M
22Ī	1.446	-	0.2	0.2	-
403	1.441		1.0		
512	1.440	1.436	14.9	31.9	VS
712	1.440		16.0		
004	1.409		0.2		
404	1.409	-	0.1	0.4	-
221	1.405		0.1		
313	1.388	-	0.4	0.4	-
711	1.366	-	0.0	0.0	-
801	1.359		3.5		
420	1.353	1.355	1.7	9.2	M,Br.
42Ī	1.349		4.0		
022	1.338		2.4		
222	1.338	1.336	3.1	5.6	W-M
803	1.328		0.7	0.7	-
204	1.303		2.1		
604	1.303		0.8		
713	1.302	1.301	0.6	3.8	W-M
114	1.301		0.0		
314	1.301		0.3		
421	1.285	1.281	4.1	4.1	W
222	1.275		0.6	1.3	-
224	1.275		0.7		
114	1.243		0.1		
514	1.243	-	0.2	0.4	-
91Ī	1.241		0.1		
603	1.226		1.9		
10,0,Ī	1.223	1.223	0.2	2.1	W
513	1.217		0.4		
62Ī	1.215	-	0.8	1.2	-
712	1.212		0.1		
912	1.212	1.209	0.1	1.0	VVW, Br.
910	1.211		0.9		
620	1.206		0.2		
802	1.202	-	0.0	0.2	-
10,0,2	1.201		0.0		
223	1.193		0.2		
10,0,0	1.188	-	0.0	0.2	-
023	1.182	-	0.0	0.0	-
422	1.171		1.0		
622	1.171	1.168	0.4	1.6	VW, Br.
404	1.170		0.1		
804	1.170		0.1		
423	1.159		0.6		
205	1.159	-	0.0	0.6	-
405	1.148		0.1		
314	1.147	1.146	0.9	4.2	W-M
71Ī	1.146		2.8		
621	1.146		0.4		
913	1.136	-	0.0	0.0	-
911	1.134		0.6		
10,0,3	1.132	1.132	1.3	1.9	W
223	1.127		0.9		
005	1.127	-	0.0	0.9	-
10,0,1	1.111	-	0.1	0.1	-
605	1.098	1.098	1.7	1.7	W
623	1.089	1.086	2.2	2.2	VVW
315	1.083	-	1.0	1.0	-
821	1.077		3.6		
115	1.074	1.075	2.1	5.7	W-M, Br.
820	1.062		0.4		
205	1.062	1.061	1.0	1.0	VW
713	1.062		0.0		
515	1.057		1.0		
622	1.055	-	0.1	1.1	-
822	1.055		0.0		
803	1.050		0.5		
224	1.049	1.048	5.1	5.6	M
423	1.046	-	0.7	0.7	-
11,1,Ī	1.043	1.043	1.3	1.3	VVW
604	1.038		0.0		
10,0,4	1.037	-	0.2	0.2	-
514	1.037		2.5		
914	1.036		1.3		
912	1.034		2.7		
11,1,2	1.034	1.033	2.1	10.0	M-S, Br.
024	1.033		0.1		
424	1.033		0.1		
115	1.033		1.2		
805	1.022	-	0.1	0.1	-
11,1,0	1.018		0.5		
12,0,Ī	1.017	1.015	0.6	1.1	VW
821	1.013		2.9		
10,0,2	1.012		0.5		
12,0,2	1.012	1.011	0.5	3.6	W
130	1.010		0.0		
715	1.003		0.1		
823	1.000	1.000	0.6	1.3	VW
131	0.997		0.6		
11,1,3	0.992		1.3		
131	0.990		2.5		
12,0,0	0.990	0.989	1.9	8.3	M-S, Br.
224	0.989		1.9		
624	0.989		0.7		
330	0.982	-	0.1	0.1	-
405	0.980		0.0		
33Ī	0.977	0.976	0.5	1.8	VW
12,0,3	0.977		1.3		
315	0.969	-	0.6	0.6	-
11,1,1	0.965		0.5		
205	0.964	0.964	1.3	2.1	W
405	0.963		0.3		
331	0.958	-	0.4	0.5	-
132	0.957		0.1		
623	0.954	0.952	2.1	2.3	W
10,2,Ī	0.953		0.2		
132	0.944	0.945	0.3	1.1	VVW
332	0.944		0.8		
822	0.943	-	0.0	0.0	-
10,2,2	0.943		0.0		
006	0.939		0.1		
606	0.939	-	0.2		
12,0,1	0.938	0.937	0.3	1.8	W
10,2,0	0.936		0.0		
10,0,5	0.936		1.2		
53Ī	0.934	-	0.1	0.1	-
915	0.932		0.0		
530	0.932		0.6		
913	0.930	0.929	1.0	2.9	W,Br.
714	0.930		0.4		
11,1,4	0.929		0.9		
424	0.927	-	0.0	0.1	-
824	0.927		0.1		
225	0.921		0.0		
316	0.921	-	0.0	0.0	-
804	0.919		0.0		
12,0,4	0.919		0.0		
425	0.916	-	0.1	0.1	-
10,0,3	0.911		0.6		
332	0.911		0.0		
532	0.911		0.0		
116	0.910	0.910	0.0	3.8	W,Br.
516	0.910		1.3		
10,2,3	0.908		1.9		
531	0.906	-	0.5	0.5	-
025	0.905		0.0		
133	0.897		0.3		
10,2,1	0.897		0.2		
13,1,Ī	0.896		0.3		
11,1,2	0.896	0.895	0.1	1.8	VVW, Br.
206	0.896		0.6		
13,1,2	0.895		0.2		
806	0.895		0.0		
515	0.895		0.1		
605	0.893		1.8		
333	0.892	0.892	2.8	7.3	M,Br.
625	0.890		2.7		
133	0.882		2.9		
116	0.880	0.880	0.1	3.3	W
716	0.880		0.3		
73Ī	0.876	-	0.1	0.2	-
13,1,0	0.875		0.1		
13,1,3	0.873	-	0.3	0.3	-
12,0,2	0.872		1.0		
14,0,2	0.872		0.8		
225	0.871	0.870	1.9	4.7	M
14,0,Ī	0.870		0.0		
730	0.870		1.0		
533	0.868	-	0.0	0.0	-
823	0.864	-	1.0	1.0	-
532	0.861	0.861	4.7	9.8	M-S, Br.
732	0.861		5.1		
624	0.857		0.0		
10,2,4	0.857	-	0.4	0.8	-
11,1,5	0.856		0.4		
14,0,3	0.853	-	0.5	0.5	-
12,0,5	0.850		0.0		
333	0.850	-	0.2	0.4	-
14,0,0	0.849		0.0		
825	0.848		0.2		
12,2,Ī	0.845	0.845	1.4	1.4	VW
731	0.845		0.0		
10,2,2	0.843	0.843	0.5	1.7	VW
12,2,2	0.842		1.2		
406	0.840	-	0.1	0.1	-
10,0,6	0.840		0.0		
13,1,1	0.837		2.9		
316	0.835	0.835	4.0	12.0	M-S, Br.
916	0.835		5.1		
914	0.833	0.834	2.1	2.6	W,Br.
13,1,4	0.833		0.5		
12,2,0	0.830		2.3		
733	0.829	0.829	0.4	3.1	W-M
134	0.829		0.3		
334	0.829		0.4		
407	0.828	-	0.1	0.1	-
207	0.824	-	0.0	0.1	-
425	0.823		0.1		
12,2,3	0.822	-	0.4	0.5	-
11,1,3	0.821		0.1		
715	0.819	-	0.1	0.1	-
10,0,4	0.818	0.818	1.9	1.9	W
14,0,4	0.818	0.817	2.7	3.4	W
607	0.816		0.7		
226	0.814	0.814	3.9	4.9	W-M
425	0.814		1.0		
134	0.813		0.2		
534	0.813	-	0.3	0.6	-
93Ī	0.812		0.1		
14,0,1	0.811	-	0.0	0.1	-
805	0.810		0.1		
533	0.806	-	0.4	0.6	-
007	0.805		0.2		
732	0.804		0.1		
932	0.804	-	0.0	0.7	-
930	0.804		0.6		
12,0,3	0.801		0.2		
026	0.800	-	0.2	0.5	-
317	0.800		0.1		
626	0.799		0.9		
12,2,1	0.798	0.798	1.4	8.8	M
10,2,5	0.797		6.3		
517	0.795	0.796	4.9	4.9	W
807	0.790	0.789	1.5	9.8	M
117	0.788		8.1		
13,1,2	0.787		0.3		
15,1,2	0.787	-	0.0	0.3	-
824	0.787		0.0		
12,2,4	0.786	-	0.2	0.2	-
334	0.784		1.6		
734	0.784	0.784	5.1	13.3	M-S
15,1,Ī	0.784		6.6		
516	0.783		0.9		
11,1,6	0.783	0.782	0.5	8.4	W,Br.
13,1,5	0.783		3.3		
10,2,3	0.782		3.7		
933	0.781		0.1		
931	0.780		1.4		
606	0.780	-	0.0	1.6	-
12,0,6	0.780		0.1		
717	0.778	-	0.1	0.1	-
15,1,3	0.775	0.775	15.7	15.7	M-S

* Beginning with this line the α_1, α_2 doublet on the powder photograph was resolved.

† α_2 Line from previous reflection overlaps α_1 of this reflection.

that there are six interactions of a tetrahedrally co-ordinated ion with octahedrally coordinated ions and six interactions of an octahedrally coordinated ion with tetrahedrally coordinated ions. Thus there would be six important magnetic interactions per magnetic ion. From the recent paper by Gilleo,[28] one would estimate a Néel temperature of about 700°K for an Fe$_2$O$_3$ phase isostructural with β-Ga$_2$O$_3$.

Now, the facts that: (1) the β-Ga$_2$O$_3$ structure appears to be favorable to antiferromagnetic interaction, (2) that Fe^{3+} ion has a crystal chemistry similar to that of Ga^{3+} ion, and (3) that the Fe^{3+} ion would prefer octahedral sites if substituted for Ga^{3+} in yttrium-gallium garnet, all would immediately indicate the possibility of producing a ferrimagnetic material from solid solutions of Fe$_2$O$_3$ in β-Ga$_2$O$_3$. However, experiments made by Remeika *prior* to the determination of this structure, indicated that not much Fe^{3+} ion could be made to dissolve in β-Ga$_2$O$_3$ by solid-solid reaction,[30] not enough, that is, to produce strong enough interac-

[30] J. P. Remeika (private communication).

TABLE VIII. Comparison of some relative diffractometer
and calculated intensities.

hkl	I_0	I_c
400 } 110 }	1	1
$40\bar{1}$	0.23	1.15
002 } $20\bar{2}$ }	0.40	2.00
$11\bar{1}$	0.01	0.56
111	0.05	2.19

tion. On the other hand, Remeika has discovered a new structure of formula $Ga_{2-x}Fe_xO_3$ which is ferrimagnetic (and also piezoelectric).[3] Crystals have been made with composition $x=0.7$ to 1.4, and these have been reported by Wood[31] to belong to space group $C_{2v}{}^9-Pc2n$ with eight formula units per cell. Thus there must be in this crystal four sets of metal ions in the general positions, the only positions, in the space group. Because the crystal with $x=1.0$ is still quite ferrimagnetic (n_B at 4.2°K and $H=\infty$ is 0.95)[3] the indication is that the metal ions in the structure show a site preference which gives the net moment. Because both Fe^{3+} and Ga^{3+} ions have spherical electronic configurations, and the difference in their $CN(6)$ radii is presumably much smaller than the difference in their tetrahedral radii, there is the strong implication that there are in the $Ga_{2-x}Fe_xO_3$ two kinds of coordinations for the metal ions.

ACKNOWLEDGMENTS

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[31] E. A. Wood (to be published).

APPENDIX

β-Ga_2O_3 Powder Data

The data obtained from the x-ray diffraction powder pattern of pulverized β-Ga_2O_3 crystals taken with $CuK\alpha$ radiation are in good agreement with those of Kohn et al.[4] However, there are some minor discrepancies. Furthermore, a knowledge of the structure allows us to index the pattern more adequately, although the indexing of the highest-angle lines may still be in some doubt.

In Table VII, the calculated spacings and intensities[32] are compared with those observed. The calculations were carried out with an IBM 704 program devised by Dr. R. G. Treuting. Several calculations of spacings with slightly different values of lattice constants indicated that the values given by Kohn et al.[4] are good to within the limits of error specified. Calculations of spacings only were carried out with a separate IBM 704 program also devised by Dr. Treuting.

It will be noticed immediately that the observed intensities given are only qualitative. It would appear that quantitative intensity measurements taken with a diffractometer would be called for. Attempts were made to do this, but preferred orientation difficulties indicated that obtaining a proper pattern would indeed be a time-consuming project.

A finely divided powder all of which passed through a 400-mesh sieve, was used as the specimen for the revolving specimen holder of the Norelco diffractometer. Examination of Table VIII, in which the intensity of the ($\{400\}$, $\{110\}$) reflection is taken as unity and several others are compared with it, is indicative of the extreme effect.

Examination of the powder specimen with a microscope ($144\times$) indicated that the crystallites were needle- or platelike with the needle axis or plate tending to lie flat. The rotating specimen photographed with the Norelco 114.6 cm camera indicated a much more random distribution of crystallites and gave qualitative intensities in much better agreement with the calculated ones.

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[32] The expression for the calculated relative intensities is $I_c=(p/4)LPF^2\times10^{-4}$ where p is the multiplicity, L the Lorentz factor, P the polarization factor, and F the structure amplitude.