a shortening of the shorter Li–O separations given above. Refinement of model *A* results in a lithium parameter of z equal to 0·1286 (with Li–O values of 1·71 and 2·78 Å); fractional positional parameters for oxygen differed by 1×10^{-5} and B_{ij} (oxygen) differed by a maximum of 0·1σ from values for model *B* listed in Table 2. However, one may rule out model *A* by consideration of the sum of ionic radii (using 0·60 Å for Li^+ and 1·32 to 1·40 Å for O^{2-}; Pauling, 1960).

The final positional and thermal parameters (Table 2) result in a discrepancy index of 0·049. Anisotropic thermal parameters, B_{ijn}, are of the form $\exp\left(-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ijn}h_ih_ja^*_ia^*_j\right)$. Table 3 lists the observed and calculated structure factors scaled by 10 times as indicated. Table 4 lists the interatomic separations and bond angles. Other reported I–O bond lengths and O–I–O angles have been summarized by Ibers (1956), and range from acceptable values of 1·77 to 1·86 (average 1·82) found in $NaIO_3$ (van Eck and MacGillavry, 1943), $Ce(IO_3)_4$ (Cromer & Larson, 1956), $Ce(IO_3)_4\,.\,H_2O$ (Ibers, 1956), and HIO_3 (Rogers & Helmholz, 1941) to improbable values of 2·08 Å (Naray-Szabo & Neugebauer, 1947) or larger (suggested by octahedral iodine in the iodates of cesium, rubidium and ammonium ion).

Table 4. *Interatomic separations in* $LiIO_3$

	Separations	Standard deviation
Li–O	2·038, 2·220 Å	0·06 Å
I–O (bonded)	1·817	0·017
I–O (next neighbor)	2·873	0·017
O–O (intra IO_3^- groups)	2·756	0·024
O–O (inter IO_3^- groups)	2·925, 3·085	0·024
O–I–O	98·65°	0·6°

It is unfortunate in a crystal whose space group is unambiguously established that the iodine atoms are related to each other by a point of inversion, and hence one is not able to utilize their dispersion to resolve the absolute configuration of the packing.

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Cation Distribution and Oxygen Parameter in Magnesium Gallate, $MgGa_2O_4$

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Magnesium gallate, $MgGa_2O_4$, a partially inverted spinel, belongs to space group *Fd*3*m* with $a_0 = 8{\cdot}286 \pm 0{\cdot}003$ Å. The distribution of the di- and trivalent cations on two possible sites, 8(*a*) and 16(*d*), has been determined by the least-squares method. The data used in the refinement were obtained from single crystals by film and counter techniques; the counter data were collected manually and by CCXD, a computer-controlled X-ray diffractometer.

The magnesium ions are distributed between the two sites as follows: 16 ± 2% in the tetrahedral *A* site and 81 ± 1% in the remaining octahedral *B* site. The oxygen parameter as refined in the present study is 0·3824 ± 0·0003, indicating the usual shift for the inverted spinel from the ideal value of 3/8.

Introduction

Magnesium gallate, $MgGa_2O_4$, is a partially inverted spinel with space group *Fd*3*m*. The metal ions fall on sets of special positions 8(*a*) and 16(*d*), frequently referred to as the *A* and *B* sites respectively. The oxygen ions occupy a set of special positions 32(*e*) with one positional parameter to be determined.

Interest in this compound developed through electron spin resonance studies of Cu^{2+} conducted at these Laboratories (Overmeyer, 1963) using magnesium gallate as a host lattice. A substantial broadening is observed in the resonance lines, apparently produced by variations in the crystal field due to the inverse nature of this spinel. Therefore, it is important to know accurately the distribution of the magnesium and gallium ions between the *A* and *B* sites. A survey of the literature shows several previous X-ray investigations of the cation distribution in magnesium gallate; these are summarized in Table 1.

Table 1. *Previous investigations of* $MgGa_2O_4$

	$X_{Mg}\|B\|$*	x
Barth & Posnjak (1932)	1	$0{\cdot}392 \pm 0{\cdot}006$
Machatschki (1932)	0·75	(0·375)†
Huber (1957)	0·67	$0{\cdot}379 \pm 0{\cdot}004$
Schmalzried (1961)	0·84–0·90	(0·375)†

* $X_{Mg}|B|$ indicates percentage of Mg^{2+} on *B* sites. A completely inverted structure has a value of unity.

† These two authors assumed the constant value of $\frac{3}{8}$.

Polycrystalline samples were employed in all of these earlier studies. One investigation (Schmalzried, 1961) reported a decrease in the degree of inversion in samples annealed at increasing temperatures from 900°C to 1400°C. The contradicting results shown in Table 1 indicated a need for further study of this structure. It was decided, therefore, to undertake a single-crystal study which should yield more accurate information about the cation distribution and the oxygen parameter. Magnesium gallate, a relatively simple structure with high symmetry, also provided an excellent material for comparing the merits of data collected by film and counter methods.

Experimental

The single crystals of magnesium gallate used in this study were grown from molten lead-oxide-fluoride solution according to a procedure developed by Giess (1962). Two crystals were selected for the X-ray diffraction measurements and ground into spheres; their diameters were 0·34 and 0·37 mm.

The smaller of the two crystals was oriented to a [100] direction and mounted on a Weissenberg camera. A zero-level photograph with a silicon powder pattern superimposed was taken, using Cu *Kα* radiation, to measure the lattice constant accurately. Intensity data were collected from this crystal on multiple film packs, using the equi-inclination technique with Cu *Kα* radiation to record all six levels about [100]. The crystal was then remounted to a [110] direction, and the zero and first layer lines were recorded to provide a normalized set of data. The same crystal was then transferred to CCXD, a computer-controlled X-ray diffractometer (Cole, Okaya & Chambers, 1963), to repeat a portion of the intensity measurements. Integrated intensities were obtained by a θ–2θ step-scanning method,* using Cu *Kα* radiation and a proportional counter with pulse height discrimination. The second crystal (0·37 mm diameter) was oriented to a [100] direction and mounted on a General Electric single-crystal orienter and a complete set of integrated intensities was recorded by the θ–2θ scanning method, using Cu *Kα* radiation and a scintillation counter with a pulse height discriminator.

Intensities were estimated visually from the film packs, and the Lorentz-polarization and absorption corrections were applied to all film and counter data with a program written for the IBM 7090. In addition, the counter data were later corrected for the secondary extinction.

Crystallographic data

Magnesium gallate is described by space group *Fd*3*m* (O_h^7). Eight formula weights in the unit cell with $a = 8{\cdot}286 \pm 0{\cdot}003$ Å give a calculated density of 5·317 g.cm^{-3}; the linear absorption coefficient for Cu *Kα* radiation ($\lambda = 1{\cdot}5418$ Å), based on this value is 260·1 cm^{-1}. The absorption coefficients for the two spherical crystals used in this study were then $\mu R = 4{\cdot}43$ (0·34 mm sample) and $\mu R = 4{\cdot}79$ (0·37 mm sample).

Refinement of the structure

Since the general details of the structure were known, it was possible to proceed directly into a least-squares refinement. However, the then available least-squares programs had to be modified for a problem of this type in order to handle the cation distribution as a variable. Fortunately, since only two sites are involved in the structure, the mathematical treatment of the problem was not too difficult. For each site, a variable, *k*, is introduced which is the percentage of the site occupied by one ion; for example, Mg^{2+}. The contribution of this site to the structure factor, *F*, can be written as

$$[kf_{Mg} + (1-k)f_{Ga}]\,(\cos\phi_j)\,,$$

where $\cos\phi_j$ represents the trigonometric portion of the structure factor. Then the derivative of *F* which is necessary in determining the parameter shift, Δk, is given by

$$\frac{\partial F}{\partial k} = [f_{Mg} - f_{Ga}]\,(\cos\phi_j)\,.$$

This additional variable was added to the general least-squares program of Trueblood, Gantzel & Sparks (1961) and this modified version was used to refine separately on all three sets of data on an IBM 7094 machine. The atomic scattering factors used throughout were taken from *International Tables for X-ray Crystallography* (1962), and a correction of 1·5 electrons for the real part of the dispersion term was applied to the gallium form factors. The weighting scheme used in the refinement is: $w = 0{\cdot}625$ for $F_{obs} < 32$, $20/F_{obs}$ for $32 \le F_{obs} < 180$ and $10/F_{obs}$ for $180 \le F_{obs}$. Unobserved reflexions were given zero weight or else omitted entirely from the calculations. Since the atoms occupy positions with relatively high symmetry, only

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* Each reflection was integrated in twenty-four steps of intervals of 0·07° over the range of $2\theta = 0°$ to 70°, 0·09° from $2\theta = 70°$ to 130°, and 0·11° from $2\theta = 130°$ to 150° by setting the median of the scanning range at the middle point of the α_1 and α_2 peaks.

isotropic temperature factors were employed to account for the thermal vibration.

A cation distribution with 25% of the magnesium ions on *A* sites and 75% on *B* sites was assumed to start the least-squares refinement. An initial value of $x = 0{\cdot}3750$ was used for the oxygen parameter.

Table 2(*a*) shows a comparison between F_{obs} and F_{calc} from the last cycle of refinement of the multiple-film data. The six strongest reflexions (indicated by asterisks) were considerably affected by extinctions and were omitted in the refinement, being brought in only at the last cycle to give an indication of the size of the effect. No attempt was made to correct the film data for the extinction. A usual reliability index of 7·6% excluding unobserved reflections and those heavily affected by extinction, was obtained. The structure parameters and standard deviations obtained are listed in Table 3(*a*). The calculated standard deviations indicate good results for the oxygen positional parameter and reasonably good results for the site population factors (k_A is the percentage of Mg^{2+} on *A* sites and k_B is the percentage of Mg^{2+} on *B* sites). The errors in temperature factors, however, are naturally quite large.

Table 2. *Comparison between observed and calculated structure factors*

(*a*) *Film data*

h	k	l	F_o	F_c	h	k	l	F_o	F_c
1	1	1	34.93	36.34	6	4	4	0.	2.52
2	2	0	172.74	178.05	8	2	2	96.74	87.39
*3	1	1	203.30	249.67	6	6	0	105.67	92.44
2	2	2	100.11	89.53	7	5	1	133.13	127.89
*4	0	0	231.40	249.94	5	5	5	148.74	152.36
3	3	1	0.	3.02	6	6	2	94.37	81.08
4	2	2	141.84	142.12	8	4	0	110.25	109.21
*5	1	1	203.17	229.69	9	1	1	24.77	25.59
3	3	3	174.91	183.29	7	5	3	0.	3.19
*4	4	0	331.67	444.71	8	4	2	0.	4.55
5	3	1	24.07	20.36	6	6	4	82.31	70.66
4	4	2	0.	3.87	9	3	1	118.22	123.28
6	2	0	113.36	116.54	*8	4	4	199.32	238.49
5	3	3	151.88	173.78	9	3	3	15.68	13.75
6	2	2	103.51	102.37	7	7	1	7.50	6.91
4	4	4	126.30	148.14	7	5	5	16.51	12.11
7	1	1	0.	1.72	10	2	0	67.15	68.91
5	5	1	35.18	32.90	8	6	2	70.96	64.98
6	4	2	117.73	103.17	9	5	1	101.91	118.69
7	3	1	135.96	133.96	7	7	3	81.02	80.21
5	5	3	155.51	161.66	10	2	2	58.37	63.45
*8	0	0	249.27	312.03	6	6	6	60.13	63.30
7	3	3	12.38	10.43					

(*b*) *CCXD data*

h	k	l	F_o	F_c	h	k	l	F_o	F_c
1	1	1	41.69	39.83	1	5	5	31.79	32.44
0	2	2	176.18	175.21	2	4	6	109.94	106.73
1	1	3	251.31	250.52	1	3	7	138.93	140.85
2	2	2	98.96	94.03	3	5	5	161.83	167.04
0	0	4	249.59	255.06	3	3	7	9.47	9.12
2	2	4	146.54	142.54	2	2	8	96.02	92.14
1	1	5	225.19	231.79	0	6	6	95.59	96.66
3	3	3	192.04	187.72	1	5	7	134.13	134.91
1	3	5	25.12	21.51	5	5	5	156.73	157.89
0	2	6	125.23	119.14	2	6	6	88.77	88.49
3	3	5	175.25	178.66	0	4	8	112.67	110.10
2	2	6	108.00	108.87	1	1	9	23.25	24.24
4	4	4	156.16	150.51					

(*c*) *Manual diffractometry*

h	k	l	F_o	F_c	h	k	l	F_o	F_c
1	1	1	41.21	40.93	8	2	2	97.47	96.13
2	2	0	179.35	175.13	6	6	0	97.83	100.74
3	1	1	248.82	252.19	7	5	1	138.23	140.73
2	2	2	97.44	95.19	5	5	5	158.96	164.64
4	0	0	247.45	259.50	6	6	2	90.51	90.87
4	2	2	149.08	144.09	8	4	0	114.72	115.69
5	1	1	227.29	235.10	9	1	1	23.81	24.98
3	3	3	189.99	190.94	6	6	4	86.13	81.06
5	3	1	23.72	22.19	9	3	1	135.84	137.01
6	2	0	125.44	121.78	8	4	4	256.87	265.63
5	3	3	176.75	183.05	9	3	3	13.29	12.81
6	2	2	107.99	110.81	7	5	5	13.61	11.39
4	4	4	153.20	155.73	10	2	0	79.96	79.68
5	5	1	33.56	33.25	8	6	2	78.52	76.02
6	4	2	109.53	110.14	9	5	1	132.44	133.34
7	3	1	142.75	145.70	7	7	3	97.20	94.95
5	5	3	164.46	172.62	10	2	2	73.69	73.79
7	3	3	11.56	9.61	6	6	6	74.30	73.66

Table 2(*b*) and 3(*b*) list the results from the refinement of data obtained on CCXD. Although the results are based on a partial set of data, a reliability index of 2·3% was calculated, giving an indication of the increased accuracy obtainable from counter data. The results from a complete set of data collected manually from the second crystal are given in Table 2(*c*). The 771 reflection was omitted as it contained a strong double reflection component when rotated around [100]. The two strongest reflections, 440 and 800, were also omitted. Although a correction for secondary extinction was applied to a certain extent,* these reflections still showed too much difference between their observed and calculated values. Here a reliability index of 2·6% was obtained. The structure parameters and their standard deviations calculated in this refinement are shown in Table 3(*c*). Although these results do not differ greatly from those obtained from the film data, the error calculations indicate more accurate determinations of the various parameters. In particular, the standard deviations of the site population factors are much more acceptable than those calculated from the film data. Obviously there is no significant difference between the results of the manual measurement and those by CCXD.

Table 3. *Structural parameters*

	(*a*) Film data	(*b*) CCXD	(*c*) Manual diffractometry
x	0·3829 ± 0·0008	0·3826 ± 0·0004	0·3824 ± 0·0003
$B_{O^{2-}}$ (Å^2)	0·34 ± 0·22	0·41 ± 0·13	0·20 ± 0·08
$B_{Mg^{2+}}$ (Å^2)	0·57 ± 0·14	0·28 ± 0·08	0·09 ± 0·05
$B_{Ga^{3+}}$ (Å^2)	0·38 ± 0·14	0·24 ± 0·07	0·12 ± 0·05
k_A	0·12 ± 0·05	0·15 ± 0·03	0·16 ± 0·02
k_B	0·84 ± 0·03	0·82 ± 0·01	0·81 ± 0·01
	$R = 7{\cdot}6$ %	$R = 2{\cdot}3$ %	$R = 2{\cdot}6$ %

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* The correction was applied with the formula

$$(F_{\text{obs}})_{\text{corrected}} = F_{\text{obs}} \cdot \exp\{g \cdot \text{LPF} \cdot F^2_{\text{calc}}\},$$

(all symbols with usual meanings). This is based on the incorrect Darwin formula rather than on the newer formula by Zachariasen (1963); since the effect was relatively small, use of the latter would not change any of the corrected structure factors used in the refinement by more than 1·5 %.

Discussion

Interionic distances and angles were computed from the structural parameters obtained from the refinement of the data gathered manually on the General Electric goniostat. The cation sites in $MgGa_2O_4$ are surrounded by oxygen polyhedra in the following configuration:

A-site tetrahedron

$M^+(a)$–O^{2-}, 4 at 1·900 Å
O^{2-}–O^{2-}, 6 at 3·103 Å

B-site octahedron

$M^+(d)$–O^{2-}, 6 at 2·012 Å
O^{2-}–O^{2-}, 6 at 2·756 Å and 6 at 2·932 Å

Standard deviations in the metal–oxygen and oxygen–oxygen distances are $\sigma = \pm 0{\cdot}004$ Å and $\sigma = \pm 0{\cdot}006$ Å respectively. Fig. 1 illustrates the arrangement detailed above, and also shows some important angles. It can be seen that the oxygen ions form regular tetrahedra about the *A* sites. However, the octahedra about the *B* sites are slightly distorted by the deviation of the oxygen parameter from the ideal value of $x = 0{\cdot}3750$. The observed deviation of x from the ideal value is of the same direction as reported previously for other inverted spinels.

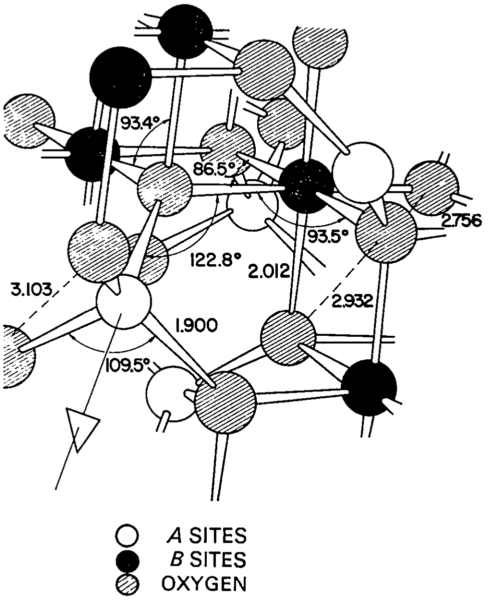

Fig. 1. Interionic distances and angles in magnesium gallate, $MgGa_2O_4$.

It must be mentioned here that there is strong interaction between the temperature factor and site factor of an atom. Fortunately, there is an added condition for the two site factors in magnesium gallate; the sum of k_A and k_B must be equal to unity. This condition was not included as a constraint in the refinement program; the two factors have been allowed to change independently. However, for any cycle in the course of refinements, the sum of k_A and k_B did not differ significantly from unity; usually the difference was less than its standard deviation.

A comparison of the results of the present study with those of previous investigations (Table 1) indicates that the earlier workers have been severely handicapped by the use of powder specimens and film techniques which necessitated restricting assumptions concerning the oxygen position and the cation distribution. The present approach, using accurate counter data obtained from a single crystal allows a simultaneous determination of all structural parameters.

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