Both S_0 and S_1 are real numbers varying for different members of the OD-groupoid family (2). The square of $|F(hkl)|$ is

$$|F(hkl)|^2=s^2|F_0|^2+d^2|F_1|^2+sd(F_0\tilde{F}_1+\tilde{F}_0F_1)\,.$$

From this and from (6) follows that

$$|F(hkl)|^2+|F(\bar{h}kl)|^2=(s^2+d^2)\,[|F_0(hkl)|^2+|F_0(\bar{h}kl)|^2]\,,$$

and taking the symmetry of individual layers into account,

$$|F_0(hkl)|^2=|F_1(hkl)|^2$$
$$=\frac{1}{2(s^2+d^2)}\,[|F(hkl)|^2+|F(\bar{h}kl)|^2]\,.$$

Here $1/2(s^2+d^2)$ is a common weighting factor for all diffuse maxima of the first system. The values $|A(hkl)|^2=|F(hkl)|^2+|F(\bar{h}kl)|^2$ are thus proportional to the values $|F_0(hkl)|^2$ and may thus be used as if they were the $|F|^2$ values of a structure (lattice constants **a**, **b**, **c**) containing only the even-numbered layers of the MDO_1 structure.

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Cation Distribution in $Y_3Al_{5-c}Ga_cO_{12}$ Garnet

BY M. MAREZIO, J. P. REMEIKA AND P. D. DERNIER

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey, U.S.A.

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A direct determination of the cation distribution in the garnet system $Y_3Al_{5-c}Ga_cO_{12}$ (with $c\simeq 1,2,3,4$) from single-crystal X-ray diffraction data has been made. The lattice constants range from 12·002 Å for $Y_3Al_5O_{12}$ to 12·275 Å for $Y_3Ga_5O_{12}$. The results show that even at higher values of c the gallium ions prefer the tetrahedral sites in the garnet structure more than the aluminum ions. Although the gallium ions are reported to have a larger ionic radius than the aluminum ions (the Shannon-Prewitt radii are $Ga^{3+}=0{\cdot}47$, $Al^{3+}=0{\cdot}39$ Å), the fractions of the total Ga^{3+} in the tetrahedral sites are 84%, 77%, 68% and 63% for $c\simeq 1$, 2, 3 and 4 respectively. The value 60% represents a random distribution.

Introduction

Magnetic studies of the systems $Y_3Fe_{5-c}Al_cO_{12}$ and $Y_3Fe_{5-c}Ga_cO_{12}$* have shown that in the garnet structure for $c\le 3$ the Ga^{3+}, Al^{3+} and Fe^{3+} ions have different preferences for the tetrahedral sites. This preference increases on going from Fe^{3+} to Al^{3+} to Ga^{3+}. The studies of the effect of pressure and temperature on the synthetic garnets, $Y_3Fe_5O_{12}$, $Y_3Al_5O_{12}$ and $Y_3Ga_5O_{12}$ (Marezio, Remeika & Jayaraman, 1966; Marezio, Remeika & Dernier, 1966) have corroborated this sequence of site preference, which cannot be explained in terms of a size effect. The Shannon & Prewitt (1968) ionic radii are $Fe^{3+}=0{\cdot}50$, $Al^{3+}=0{\cdot}39$ and $Ga^{3+}=0{\cdot}47$ Å.

In oxide compounds the greater preference of Ga^{3+} ions, over both Fe^{3+} and Al^{3+}, for the tetrahedral sites seems to be the reason for the differences between the gallium oxide compounds and the iron or aluminum

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* For an extensive bibliography see Geller, Cape, Espinosa & Leslie (1966).

oxide compounds (Marezio, Remeika & Dernier, 1966). All the differences in behavior between Al^{3+} and Fe^{3+} in oxide compounds can be explained in terms of the difference in cation size.

In order to determine to what extent in the garnets, the preference of the Ga^{3+} ions for tetrahedral sites, is greater than that of the Al^{3+} ions, a direct determination of the cation distribution in the system $Y_3Al_{5-c}Ga_cO_{12}$, with $c\simeq1$, 2, 3 and 4, from single crystal X-ray intensity data was undertaken.

Experimental

Single crystals of $Y_3Al_{5-c}Ga_cO_{12}$ were grown from a $PbO(B_2O_3)_c$ flux. The materials used were powdered oxides. The melts were contained in platinum crucibles. After solution of the constituent oxides in the flux at 1300 °C, crystals were obtained by slow cooling and self nucleation. Single crystals corresponding to many increments of c were grown, including the end members $Y_3Al_5O_{12}$ and $Y_3Ga_5O_{12}$. To test for homogeneity, large and small crystals from the same melt were powdered and mixed together. A powder photograph was then taken with Cr *Kα* radiation. The crystals of a batch corresponding to a particular composition were considered suitable only when the back reflection lines in the powder photograph had a broadening comparable to the corresponding lines of the end members. The profile of the reflections was determined from the powder photographs with a double-beam microdensitometer. Compositions were determined by atomic absorption analysis. They are believed to be accurate to within ±3% of the amount present. The various compositions and their respective lattice constants are given in Table 1. The X-ray powder photographs were taken at room temperature with a Norelco

Table 1. *Crystal data*

Composition	Lattice* constant	Radius of the sphere	Zone axis along goniostat *Φ* axis
$Y_3Al_5O_{12}$	12·002 Å		
$Y_3Al_{3\cdot97}Ga_{1\cdot03}O_{12}$	12·060	0·089 mm	[001]
$Y_3Al_{3\cdot08}Ga_{1\cdot92}O_{12}$	12·111	0·099	[001]
$Y_3Al_{2\cdot10}Ga_{2\cdot90}O_{12}$	12·163	0·106	[111]
$Y_3Al_{0\cdot92}Ga_{4\cdot08}O_{12}$	12·226	0·120	[001]
$Y_3Ga_5O_{12}$	12·275		

* The observed standard deviations of the lattice constants were in all cases less than 1:25000. As a conservative estimate of limits of error we consider all parameters to be accurate within a precision range of about 1:10000.

Table 2. *Final parameters*

c	1·03	1·92	2·90	4·08
Scale factor	0·0932±0·0009	0·1167±0·0009	0·1278±0·0011	0·1502±0·0009
Yttrium *x*	(0)	(0)	(0)	(0)
y	(0·25)	(0·25)	(0·25)	(0·25)
z	(0·125)	(0·125)	(0·125)	(0·125)
B	0·22±0·04	0·27±0·07	0·29±0·09	(0·26)
Cation (*a*) Ga	0·080±0·017	0·223±0·014	0·470±0·018	0·744±0·014
Al	(0·920)	(0·777)	(0·530)	(0·256)
x	(0)	(0)	(0)	(0)
y	(0)	(0)	(0)	(0)
z	(0)	(0)	(0)	(0)
B	0·26±0·08	0·30±0·06	0·36±0·05	0·54±0·04
Cation (*d*) Ga	(0·290)	(0·491)	(0·653)	(0·863)
Al	(0·710)	(0·509)	0·347)	(0·137)
x	(0)	(0)	(0)	(0)
y	(0·25)	(0·25)	(0·25)	(0·25)
z	(0·375)	(0·375)	(0·375)	(0·375)
B	0·39±0·10	0·35±0·14	0·42±0·15	0·54±0·04
Oxygen *x*	0·9701±0·0006	0·9707±0·0006	0·9706±0·0006	0·9720±0·0005
y	0·0513±0·0006	0·0529±0·0005	0·0543±0·0006	0·0535±0·0004
z	0·1486±0·0006	0·1480±0·0006	0·1498±0·0007	0·1502±0·0005
B	0·42±0·10	0·31±0·09	0·51±0·08	0·55±0·07
R omitting	0·033	0·026	0·026	0·015
wR rejects	0·035	0·026	0·026	0·016
Number of reflections used in the refinement	114	106	108	98

camera 114·6 mm diameter and Cr $K\alpha$ radiation. The final lattice constants were obtained by accurate measurements of the 2θ values of the reflections in the back reflection region. The least-squares method described by Mueller, Heaton & Miller (1960) was used.

The garnet structure is cubic, space group $Ia3d$, with eight formulas per unit cell. Following the bracket notation of Gilleo & Geller (1959) this formula is written as $\{Y\}_3[Al_{1-p}Ga_p]_2(Al_{\frac{3-c+2p}{3}}\,Ga_{\frac{c-2p}{3}})_3O_{12}$. The 24 yttrium atoms are in the special position (b) $[0,\frac{1}{4},\frac{1}{8}]$, dodecahedrally surrounded by oxygen atoms; of the 40 aluminum and gallium atoms, 16 are the special position (a) [0,0,0] and 24 in (d) $[0,\frac{1}{4},\frac{3}{8}]$, octahedrally and tetrahedrally surrounded by oxygen atoms respectively. The 96 oxygen atoms are the general positions.

All intensity measurements were made with a General Electric paper-tape controlled X-ray three-circle diffractometer. Mo $K\alpha$ radiation filtered with Zr foil, and a scintillation counter were used. The specimens were spheres. Their radii and orientations with respect to the Φ axis of the goniostat are reported in Table 1. The integrated intensities were obtained with the stationary-crystal stationary-counter technique with a single filter. The take-off angle was 8°. The background was measured on each side of the peak at 2° off the peak itself and the average was subtracted from the peak-height. All independent reflections up to an angle of $2\theta = 90°$ were measured. The intensity of each independent reflection represented the average of six measurements taken on six different planes of the same crystallographic form. Those reflections for which the

Table 3. *Observed and calculated structure factors*

c	1.03		1.92		2.90		4.08	
$hk\ell$	F_o	$\lvert F_c\rvert$	F_o	$\lvert F_c\rvert$	F_o	$\lvert F_c\rvert$	F_o	$\lvert F_c\rvert$
211	21.2	11.2*	23.4	11.0*	26.0	9.3*	39.8	7.2*
220	19.8	12.5*	22.8	14.1*	19.2	10.9*	19.6	6.1*
321	14.1	8.9*	15.9	8.0*	17.5	6.1*	27.8	3.6*
400	63.7	51.4*	84.3	67.5*	100.9	78.7*	138.3	124.1*
420	68.2	58.9*	85.5	76.1*	98.3	83.7*	126.9	119.8*
332	10.1	5.5*	17.0	10.2*	23.8	14.1*	34.6	20.1*
422	38.1	32.0*	53.2	46.8*	65.9	60.6*	95.3	89.1*
431	14.2	10.3*	16.5	12.8*	16.9	14.1*	21.0	16.5*
521	23.6	19.2*	24.5	21.3*	23.8	20.7*	26.4	20.9*
440	29.0	24.1*	36.1	29.1*	34.4	26.0*	39.1	24.9*
532	18.8	16.6*	19.0	17.6*	16.8	17.0	18.8	16.3*
611	27.0	23.4*	29.3	26.6	27.6	26.3	32.8	27.1*
620	8.6	5.4*						
444	72.6	72.0	91.5	90.8	95.3	96.1	123.3	123.3
640	60.9	60.3	81.3	79.9	92.4	90.0	119.8	119.7
552	17.2	15.7	18.0	17.1	15.3	15.6	17.1	16.1
721	8.1	8.2						
642	44.1	42.7	60.2	58.9	72.1	72.5	100.6	100.4
651	10.7	10.3	10.3	10.2				
800	78.6	81.4	106.1	108.7	126.5	124.4	166.8	180.5
660	12.4	12.9	16.9	16.0	15.1	14.1		
820					11.2	9.3		
822	8.0	7.2	10.3	7.8				
840	38.0	37.1	52.9	51.5	62.9	62.8	86.7	85.7
842	43.0	42.8	56.7	57.0	66.9	65.8	86.4	84.9
655	11.0	11.3	11.7	12.5				
664	33.9	34.1	48.2	47.6	58.4	58.7	80.8	81.0
932	8.8	9.4						
853	9.1	9.6	12.2	11.9	12.6	12.5	16.0	15.2
941	8.8	8.1			11.1	10.5		
772	9.5	10.1						
862	12.7	12.5	14.6	14.9	12.1	12.8		
10.2.0	20.8	20.9	25.3	25.4	23.3	23.4	25.1	22.9
765	12.1	12.2	12.0	13.6	12.1	12.9		
864	36.8	38.6	51.1	51.7	57.4	59.3	75.4	75.4
10.4.0	43.1	43.9	57.0	58.5	64.8	66.3	82.9	84.9
961	9.4	9.6						
10.4.2	31.4	31.8	43.7	44.4	54.3	54.8	73.6	73.9
10.5.1	10.5	11.0						
11.2.1	9.0	9.4						
880	64.1	66.1	86.4	89.0	103.3	105.8	136.5	142.7
10.5.3	8.7	8.8						
866	11.6	12.2	14.6	14.9	13.2	13.1		
10.6.0	13.6	14.5	16.7	17.2	14.6	15.1		
884	27.3	27:0	37.2	37.8	47.7	47.6	66.6	65.5
12.0.0	18.0	20.4	28.9	30.1	38.4	41.2	56.4	57.6
12.2.0	36.0	36.3	48.6	48.8	56.3	56.3	70.4	70.5
10.7.1	9.0	8.8						
10.6.4	25.6	26.7	38.0	37.8	46.2	47.2	64.7	64.1
12.2.2	31.2	30.6	42.8	41.9	51.9	52.1	68.7	70.0
976	8.9	10.2						
11.6.3	11.8	13.2	13.7	15.0	13.1	14.2		
12.4.4	39.8	39.5	51.3	52.1	57.4	57.1	68.3	67.7
10.8.4	36.2	37.3	48.3	50.0	54.4	56.5	70.4	70.9
12.6.0	32.1	32.3	43.4	43.2	49.4	49.0	61.9	62.3
12.6.2	22.7	22.5	32.2	32.0	41.4	40.3	55.7	55.2
888	55.6	56.9	74.5	76.8	87.5	90.9	116.9	119.5
12.8.0	21.8	22.9	31.7	32.2	39.2	40.2	52.9	53.8
12.8.2	32.0	31.1	42.4	41.6	48.4	48.0	61.3	60.3
14.4.0	30.9	30.7	40.9	40.6	46.8	46.0	58.1	58.5
10.10.4	25.5	25.7	36.5	35.7	42.6	43.4	58.1	58.4
12.6.6	22.5	22.4	31.3	31.6	39.2	39.4	51.6	52.3
14.4.2	26.5	26.9	35.9	36.6	44.3	43.5	58.1	58.1
12.8.4	10.6	10.0						
14.6.0	10.0	9.3						
15.3.2	10.4	9.8						
12.8.6	28.7	29.8	39.3	39.7	45.7	45.6	57.6	56.9
12.10.0	27.6	27.6	37.6	37.0	42.7	42.5	53.4	52.7
12.10.2	23.8	22.8	31.9	31.6	39.2	38.0	51.5	50.9
14. 6.4	19.5	19.8	28.1	27.7	35.3	34.7	46.4	47.1
16. 0.0	43.9	43.2	60.4	60.0	72.7	71.8	91.9	94.1
16. 2.2	11.6	9.3						
12. 8.8	20.0	20.7	28.8	28.9	34.4	35.3	46.7	46.7
16. 4.0	20.4	19.5	28.1	27.5	35.4	33.9	47.1	45.4
14. 8.4	26.1	27.1	35.5	35.9	41.2	41.1	51.2	51.1
16. 4.2	29.5	29.3	39.1	39.3	45.1	44.5	56.7	55.2
12.10.6	21.6	21.1	29.1	29.0	34.6	35.2	48.0	46.9
12.12.4	35.9	34.6	45.1	44.3	48.1	47.6	55.5	56.3
12.10.8	23.5	23.7	31.4	31.5	35.5	36.2	46.5	45.4
16. 6.4	25.7	25.4	35.5	33.9	40.0	38.6	48.6	48.1
14.10.4	16.2	16.1	22.7	22.3	28.3	28.5	38.6	38.9
16. 8.0	44.2	44.9	61.7	60.9	70.0	71.6	92.7	92.3
16. 8.4	16.9	16.8	24.3	23.5	29.5	29.5	41.8	39.6
14.12.0	26.3	25.1	34.8	33.3	38.5	37.8	47.2	47.0
18. 4.0	18.8	18.8	25.4	24.5	28.8	29.4	37.0	37.1
12.10.10	14.4	14.1	22.0	20.2	27.0	26.1	37.4	36.2
14.12.2	15.0	14.3	21.1	20.6	25.7	26.6	36.5	36.1
18. 4.2	16.2	16.0	21.8	22.1	28.9	28.0	37.8	37.9
16.10.4	18.1	18.8	26.3	24.7	29.1	28.7	35.8	36.2
14.12.6	15.8	16.9	23.6	23.3	28.1	28.6	38.7	37.9
18. 6.4	15.3	15.5	20.2	21.6	27.2	26.9	35.5	36.0
16. 8.8	36.5	38.6			61.4	61.1	78.1	78.9
16.12.0	17.8	17.5			29.4	28.4	38.2	37.8
20. 0.0	18.4	19.1			28.7	30.6	38.3	40.0
14.12.8	21.2	21.8	29.3	29.2	30.8	32.5	40.7	40.1
16.12.2	21.1	21.2	28.0	28.2	31.9	31.5	40.1	39.2
18. 8.4	20.6	21.9	27.5	29.2	33.0	32.8	40.7	40.5
20. 2.0	25.5	24.2	32.9	32.1	37.2	35.5	44.3	44.2
14.14.4	14.5	13.3	20.1	19.7	25.1	25.5	33.6	33.7
20. 2.2	18.9	17.1	26.4	23.9	30.2	28.7	38.6	37.9
12.12.12	25.2	24.7	33.0	32.1	31.7	34.2	42.6	40.1
20. 4.4	25.5	26.2	33.6	34.0	38.2	36.3	41.5	42.5
16.12.6	18.9	19.2	26.3	25.5	29.6	29.1	36.4	36.3
20. 6.0	16.7	16.6	22.5	21.7	26.2	25.2	31.9	31.4
14.12.10	14.6	14.3	19.6	20.2	23.6	25.1	32.8	33.1
18.10.4			17.4	18.2	21.0	22.6	31.0	30.4
20. 6.2	15.0	14.1	20.3	19.5	26.1	23.9	33.0	32.1
16.12.8	12.3	13.5	18.8	18.8	21.9	23.2	31.5	31.5
20. 8.0	12.5	13.6	18.5	19.1	22.4	23.1	31.1	31.8
16.14.4	19.5	18.8	25.1	25.3	28.8	28.8	35.6	35.6
18.12.0	20.7	21.1	28.3	28.0	30.6	31.6	38.2	38.8
20. 8.2	20.6	20.5	28.1	27.5	31.8	30.4	38.3	37.7
18.12.2	13.0	14.1	20.1	19.8	23.3	23.8	31.4	31.5
20. 6.6	14.2	14.5	19.7	20.3	25.8	24.7	33.8	33.0
16.12.10	18.5	19.9	26.4	26.4	29.2	29.7	37.1	36.3
20. 8.6	18.7	18.9	24.7	25.3	29.3	28.3	35.0	35.1
20.10.0	18.0	17.7	23.7	23.5	26.2	26.6	32.9	32.9
22. 4.0	14.9	15.2	20.7	20.6	23.7	24.3	28.6	29.6
18.12.6	13.8	13.0	16.6	18.0	20.7	22.2	31.1	30.1
20.10.2			16.2	14.7	19.5	19.1	28.2	26.2
22. 4.2			15.3	17.4	22.7	21.5	29.0	28.8
16.16.0	30.3	29.6	41.3	39.1	45.9	45.8	58.8	59.7
16.16.4	15.6	13.0	18.1	18.2	21.2	21.9	31.4	29.0
20. 8.8	12.1	12.7	17.2	17.9	20.2	21.5	26.9	28.5
18.12.8	15.1	16.8	21.8	22.3	24.0	25.0	30.7	31.0
14.14.12	13.5	13.9	17.2	18.7	17.4	21.8	29.1	29.1
18.14.4	12.4	13.3	17.1	18.9	21.3	22.7	28.9	29.7
20.10.6			15.2	15.4	19.5	19.5	27.7	26.2
22. 6.4	11.7	11.7	16.9	16.2	20.3	20.2	26.5	27.0
20.12.4	19.1	21.4	27.2	27.5	27.2	29.0	35.0	34.1
20.10.8	13.2	14.1	18.6	18.5	21.2	21.6	26.2	26.9
22. 8.4	14.6	16.1	21.1	21.5	24.5	24.7	32.0	30.5
18.12.10			14.8	15.1	17.4	19.4	26.0	25.9
16.16.8			32.1	33.0	36.6	39.2	51.1	51.0
24. 0.0			32.9	31.2	38.5	37.8	47.6	49.0

[*] These reflections were not included in the final refinements because of large background errors.

peak-height was less than twice the background were regarded as unobserved. Spot checks on medium and weak reflections showed that the wavelength independent multiple diffraction effects were negligible. Corrections to the integrated intensities by means of Lorentz, polarization and absorption factors were made using the program developed by Wuensch & Prewitt (1965).

Refinement

The refinements of these structures were carried out with the least-squares program written by C. T. Prewitt. In this program the atomic scattering factor for each atomic position is $GQf_n + GRf_m$, where GQ and GR can be varied. According to the formula given above the scattering factors of the atoms in the positions 16(a) and 24(d) were taken as $GQ_1f_{\text{Ga}} + GR_1f_{\text{Al}}$ and $GQ_2f_{\text{Ga}} + GR_2f_{\text{Al}}$ respectively, with $GR_1 = 1 - GQ_1$, $GQ_2 = (c - 2GQ_1)/3$, $GR_2 = (3 - c + 2GQ_1)/3$. Only GQ_1 was allowed to vary and GR_1, GQ_2 and GR_2 were reset at the end of each cycle. The atomic scattering tables (for neutral atoms) and the real and imaginary correction coefficients were taken from the values reported by Cromer & Waber (1965) and by Cromer (1965) respectively. The starting values for the positional parameters and the isotropic temperature factors were a weighted average of the values given by Euler & Bruce (1965) for $Y_3Al_5O_{12}$ and $Y_3Ga_5O_{12}$. A random cation distribution was assumed and appropriate starting values taken for GQ_1, GR_1, GQ_2 and GR_2. Each observed reflection was weighted by $w = \frac{1}{\sigma^2}$ where $\sigma^2 = \frac{1}{n(n-1)} \sum_i (F_{oi} - \bar{F}_o)^2$; zero weight was given to those reflections which were considered to be unobserved. The secondary extinction correction was applied by using the Zachariasen (1963) formula, $F_{\text{corr}} \simeq F_o(1 + \beta C I_o)$. The value of the C coefficient was refined together with the positional, thermal and distribution parameters. Convergence was achieved within three cycles in each refinement. In the last stage of the refinements, anisotropic temperature factors were introduced. The β_{ij} values and the respective standard deviations showed that it would be a good approximation to consider the thermal motions of the ions to be isotropic. The final positional, thermal, and cation distribution parameters are reported in Table 2. The degree of agreement between observed and calculated structure factors is shown in Table 3. As expected (Geller, 1961; Weidenborner, 1961) a strong parameter interaction was found between the thermal parameters of the Y^{3+} ion and the metal ion in 24(d). This interaction increases with increasing c as one can see from the correlation matrix coefficients. At $c = 4{\cdot}08$ the thermal parameters of the above cations were not reliable as their standard deviations were abnormally large. Therefore, in the final refinement of the structure with $c = 4{\cdot}08$ the thermal parameter of yttrium was kept constant at 0·26 which is the average of the B_Y values

Table 4. *Interatomic distances* (Å) *and angles* (°)

c	1·03	1·92	2·90	4·08
Dodecahedron				
Y–O (4)	2·317	2·330	2·335	2·328
Y–O (4)	2·440	2·423	2·426	2·446
O–O (4)	2·640	2·633	2·672	2·671
O–O (4)	2·860	2·847	2·816	2·819
O–O (2)	2·741	2·783	2·772	2·769
O–O (2)	2·935	2·926	2·922	2·977
Octahedron				
Cation (a)–O (6)	1·930	1·937	1·971	1·979
O–O (6)	2·640	2·633	2·672	2·671
O–O (6)	2·815	2·841	2·898	2·920
Tetrahedron				
Cation (d)–O (4)	1·787	1·810	1·809	1·823
O–O (4)	3·002	3·040	3·041	3·075
O–O (2)	2·741	2·783	2·772	2·769
Cation (a)–Cation (d)	3·371	3·385	3·400	3·417
Cation (a)–Y	3·371	3·385	3·400	3·417
Cation (d)–Y	3·015	3·028	3·041	3·056
Cation (d)–Y	3·693	3·708	3·724	3·743
Cation (a)–O–Cation (d)	130·1	129·2	128·1	128·0
Cation (a)–O–Y	100·3	101·1	100·8	100·6
Cation (a)–O–Y	104·7	104·6	104·0	104·7
Cation (d)–O–Y	93·7	93·1	93·5	94·1
Cation (d)–O–Y	121·0	122·1	122·5	121·8
Y–O–Y	101·8	102·4	102·9	103·2

The standard deviations of the cation-oxygen and oxygen-oxygen distances are ±0·006 Å and ±0·01 Å respectively. The standard deviation of the interatomic angles is ±0·3°.

found in the other three refinements. No significant differences were found between the positional and distribution parameters obtained after the refinement in which B_Y was varied, and those obtained after the refinement in which B_Y was kept constant. This seems to indicate that the strong interaction between the two cations' thermal parameters does not affect the determination of the positional and cation distribution parameters. In fact, the correlation coefficients between thermal parameters and the positional and distribution parameters are quite small.

Results

The interatomic distances and angles in $Y_3Al_{5-c}Ga_cO_{12}$ are given in Table 4.

Table 5. *Cation distribution parameters*

$Y_3Al_{5-c}Ga_cO_{12}$*			$Y_3Fe_{5-c}Ga_cO_{12}$†	
c	p	f_t	f_t	c
1·03	0·08	0·84 ± 0·03	0·87 ± 0·06	1·3
1·92	0·22	0·77 ± 0·02	0·79 ± 0·03	2·0
2·90	0·47	0·68 ± 0·01	0·76 ± 0·03	3·0
4·08	0·74	0·63 ± 0·01	0·69 ± 0·02	4·0

* Present work.
† Fischer *et al.* (1966).

Table 5 gives the f_t values together with the p values and the compositions. f_t represents the fraction of Ga^{3+} ions in tetrahedral sites where $f_t = 1 - \frac{2p}{c}$.

Note that even at $c = 4{\cdot}08$, 63% of the Ga^{3+} ions occupy the tetrahedral sites, whereas 37% occupy the octahedral sites. At almost the same concentration of Al^{3+} ions, $5 - c = 3{\cdot}97$, only 16% of the Al^{3+} ions occupy the tetrahedral sites while 84% occupy the octahedral sites. The values of 60% and 40% in the tetrahedral and octahedral sites respectively correspond to a random distribution. These results strongly corroborate the suggestions which were made to explain the different behavior of the synthetic garnets, $Y_3Fe_5O_{12}$, $Y_3Al_5O_{12}$ and $Y_3Ga_5O_{12}$ at high pressure and high temperature (Marezio, Remeika & Jayaraman, 1966).

Fischer, Hälz, Stoll & Segmüller (1966) have made a direct determination of the Ga^{3+} ion distribution in the system $Y_3Fe_{5-c}Ga_cO_{12}$ from powder X-ray and neutron diffraction data. Their f_t values and the corresponding concentrations of the Ga^{3+} ions are reported in Table 5. It can be seen that the preference of the Ga^{3+} ions to occupy the tetrahedral sites is slightly higher for the system $Y_3Fe_{5-c}Ga_cO_{12}$ and this is not unreasonable since the Fe^{3+} ions are larger than the Al^{3+} ions.

At present no reason can be found to explain why the Ga^{3+} ions preferentially occupy the smaller of the two sites available and the Al^{3+} ions or the Fe^{3+} ions the larger. This occurs even though the Ga^{3+} ion is nearly the same size as the Fe^{3+} ion, and is much larger than the Al^{3+} ion.

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