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X-ray and Neutron Diffraction Study of the Substitutional Disorder in the Yttrium–Iron–Gallium Garnets

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The distribution of Ga^{3+} and Fe^{3+} ions on the tetrahedral and octahedral sites, (*d*) and (*a*), of the yttrium–iron–gallium garnets has been determined from X-ray and neutron diffraction intensity measurements on powder samples by a least-squares refinement. The results of both methods are in good agreement. The preference of the smaller Ga^{3+} ions for the smaller tetrahedral sites (*a*), already concluded from magnetic measurements, has been confirmed. No deviation from Néel's model of antiferrimagnetism could be observed.

Introduction

The yttrium–gallium–iron–garnet system is ideal for studying the statistical ferrimagnet (Gilleo & Geller, 1958; Villers, Pauthenet & Loriers, 1959; Lüthi & Henningsen, 1964; Prince, 1965; Streever & Uriano, 1965). For comparison of the magnetic properties with theory, it is important to know how the Ga^{3+} and Fe^{3+} ions are distributed on the two different sites with octahedral (*a*) and tetrahedral (*d*) coordination of the O^{2-} ions. Starting from the well-established structure of the yttrium–iron garnet, $Y_3Fe_2(FeO_4)_3$, with space group *Ia*3*d* and atomic positions as given in Table 1 (Bertaut, Forrat, Herpin & Meriel, 1956; Geller & Gilleo, 1957; Prince, 1957), the distribution of the Ga^{3+} ions can be obtained by a least-squares refinement based on X-ray or neutron-diffraction intensities. Since suitable single crystals are often difficult to obtain, powder samples were used for the intensity measurements of this study in order to prove whether, also without single crystals, reliable values of the distribution parameters could be computed. Besides easy preparation, the advantage in using powders is also the absence of extinction, and, for flat samples, the simple absorption factor. From X-ray powder measurements, naturally the oxygen coordinates cannot be obtained, owing to the small atomic scattering factor of O^{2-}. The neutron diffraction, however, yields these parameters because of the favorable size of the neutron scattering amplitude of the oxygen atom.

X-ray diffraction method

Experimental details

Powder samples of $Y_3Fe_{5-c}Ga_cO_{12}$ with $c=2{\cdot}0$, 2·5, 3·0, 4·0, were prepared by sintering the mixed oxides twice at about 1370°C for about six hours and pressing them into flat pills of about 1 cm diameter. The homogeneity of the samples is evidenced by the fact that all lines found in Debye–Scherrer photographs and X-ray diffractometer graphs could be indexed as garnet lines and could be used for the least-squares refinement. On an automatic diffractometer (Keller & Segmüller, 1963) θ–2θ-step scans were performed on each line with filtered Co $K\alpha$ radiation and pulse height discrimination, and total intensities were calculated by numerical computation.

Least-squares refinement procedure

The least-squares refinement of the crystal parameters was performed by a FORTRAN program of Busing & Levy (1962) which was modified for the evaluation of X-ray measurements in order to include coincident powder reflexions.* Therefore the refinement is based on the minimization of

$$R = \sum_{K} (I_{\mathrm{tot},\,k} - G \,.\, \sum_{i=1}^{N} p_i \,.\, |F_{i,\,k}|^2)^2/\sigma^2_{Ik}, \qquad (3)$$

Table 1. *Structure of* $Y_3Fe_{5-c}Ga_cO_{12}$, *space group Ia* 3*d*

Atom	Symmetry position	Coordinates	Oxygen coordination polyhedron
Fe, Ga	16(*a*) $\bar{3}$	0, 0, 0; *etc.*	Octahedron
Fe, Ga	24(*d*) $\bar{4}$	$\frac{3}{8}$, 0, $\frac{1}{4}$; *etc.*	Tetrahedron
Y	24(*c*) 222	$\frac{1}{8}$, 0, $\frac{1}{4}$; *etc.*	Eight-cornered dodecahedron
O	96(*h*) 1	*x*, *y*, *z*; *etc.*	–

Crystal	*x*	*y*	*z*	
$Y_3Fe_5O_{12}$	$-0{\cdot}0270 \pm 4$	$0{\cdot}0569 \pm 5$	$0{\cdot}1505 \pm 5$	Euler & Bruce (1965)
$Y_3Ga_5O_{12}$	$-0{\cdot}0272 \pm 2$	$0{\cdot}0558 \pm 3$	$0{\cdot}1501 \pm 3$	

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* The program written in FORTRAN II and IV is available from one of the authors (A.S.) on request.

where I_{tot} is the total intensity, σ_I their standard deviation, G the scale factor and where the inner summation goes over N coincident reflexions i with structure factor $F_{i,k}$ and multiplicity factor p_i. In the original program of Busing & Levy (1962) the trigonometric terms of each atom were multiplied by an atomic multiplier AI and an atomic scattering factor SF which could both be varied independently. The variability of SF was discarded because the scattering factor was, of course, interpolated from stored tables. The scattering factors, corrected for anomalous dispersion, were taken from *International Tables for X-ray Crystallography* (1962). For atoms at special positions, subsets of the symmetry transformations were used in order to avoid superfluous computations. If two different atoms I and J occupy the same location, their multipliers AI(I) and AI(J) are used as probabilites for finding atom I or J at this place. If we label Fe and Ga at the octahedral locations (a) with 1 and 2, and Fe and Ga at the tetrahedral locations (d) with 3 and 4, the distribution parameters AI(I) have to be constrained by the following conditions:

$$\begin{aligned} \mathrm{AI}(1)+\mathrm{AI}(2)&=1 \\ \mathrm{AI}(3)+\mathrm{AI}(4)&=1 \\ 2\mathrm{AI}(2)+3\mathrm{AI}(4)&=c \end{aligned} \tag{4}$$

where c is the number of Ga atoms per formula unit. Two FORTRAN subroutines were used to introduce these constraints:

One at the end of the calculations of the derivatives for each group of coincident reflexions according to the formula

$$\frac{d\varphi}{d\mathrm{AI}(2)} = -\frac{\partial\varphi}{\partial\mathrm{AI}(1)} + \frac{\partial\varphi}{\partial\mathrm{AI}(2)} + \frac{2}{3}\left(\frac{\partial\varphi}{\partial\mathrm{AI}(3)} - \frac{\partial\varphi}{\partial\mathrm{AI}(4)}\right), \tag{5}$$

the other at the end of each refinement cycle to reset the unvaried parameters AI(1), AI(3) and AI(4) according to the constraints and the change of the varied parameter AI(2).

Only an over-all temperature factor was used because separate temperature factors for each location gave worse results and did not seem to have any physical significance.

Thus, only three parameters had to be varied: The atomic multiplier AI(2), the over-all temperature factor and the scale factor. The oxygen positions were not varied because the X-ray measurements on powder samples do not provide sufficient accuracy to do so. Two residuals were calculated:

$$R_1 = \sum_k |I_{\text{tot},k} - G \,.\, \sum_i p_i \,.\, |F_{i,k}|^2| / \sum_k I_{\text{tot},k} \tag{6}$$

over all and only over non-zero observations, and

$$R_2 = \sum_k (I_{\text{tot},k} - G \,.\, \sum_i p_i \,.\, |F_{i,k}|^2)^2 / \sigma^2_{I,k} / \sum_k (I_{\text{tot},k}/\sigma_{I,k})^2 \tag{6a}$$

only over non-zero observations.

For the sample with the best fit (smallest residual), namely with $c=4$, also a refinement varying the distribution of Fe and Ga independently at both locations (a) and (d) was performed. Then only the first and the second of the constraining equations (4) had to be used. The results of this refinement agree fairly well with that of the refinement varying only one distribution parameter as shown in Table 2, and so provide a sort of check of the refinement procedure.

Table 3 shows the good agreement of observed and calculated intensities for the sample with $c=4$ after the last refinement cycle and with only one atomic multiplier varied.

Neutron diffraction method

Experimental details

Powders of $Y_3Fe_{5-c}Ga_cO_{12}$ prepared as described above with $c=1{\cdot}3$, $2{\cdot}0$, $2{\cdot}5$, $3{\cdot}0$, were filled into cylindrical containers of thin vanadium or aluminum sheet, 5 cm long and with a diameter of 1 to 2 cm. The two-axes neutron diffractometer at the reactor Diorit in Würenlingen (Hälg, Meier & Gasser, 1964) was used for the intensity measurements. In order to achieve a high resolution, a neutron wave length of 1·30 Å was chosen by reflexion from the (311) planes of an aluminum single crystal. Since for this wave length the contribution of the high-order components would be larger than for the normally used wavelength of about 1·1 Å, a 0·05 mm thick cadmium foil was placed between sample and detector (Stoll & Hälg, 1965). Automatic step scans with a step width $\Delta 2\theta = 30$ dig $(= 0{\cdot}108^\circ)$* were performed.

Fig. 1 shows the neutron diffraction pattern of the sample with $c=2{\cdot}5$. The high resolution is remarkable. At each step, the diffracted neutrons were counted for a period of 5 to 10 minutes, which was determined by the preset number of neutrons counted by the monitor placed in the primary beam. The primary intensity was of the order of 10^5 (monochromatic) neutrons cm^{-2}. sec^{-1}.

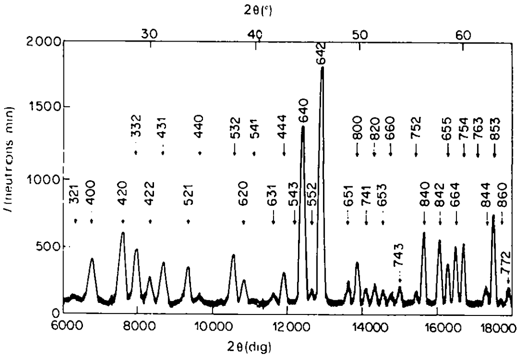

Fig. 1. Neutron diffraction pattern of $Y_3Fe_{2\cdot5}Ga_{2\cdot5}O_{12}$ powder. The discrete measurement points cannot be shown on this graph owing to their density. They practically agree with the smooth peak curves, whereas the broadening in the background indicates the variation of the intensity measured there.

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* 1 dig $= 0{\cdot}0036^\circ\, 2\theta$ is the unit of our digitizer.

Table 2. *Comparison of two X-ray diffraction refinement jobs on the sample with c* = 4; *the first one varying only one atomic multiplier, the other varying two multipliers independently*

No.	Value	AI(2)*	AI(4)*	TO†	Scale factor	$R_{1,0}$‡	R_1§	R_2§
1	before cycle 1	0·800		0·60	10·00	0·211	0·203	0·197
	2	0·560		0·35	10·86	0·049	0·039	0·052
	3	0·610		0·41	10·83	0·048	0·038	0·044
	after cycle 3	0·611		0·41	10·83	0·048	0·038	0·044
		±0·021		±0·06	±0·06			
2	before cycle 1	0·800	0·800	0·60	10·00	0·211	0·203	0·197
	2	0·568	0·964	0·35	10·85	0·050	0·040	0·051
	3	0·627	0·943	0·41	10·81	0·048	0·039	0·044
	after cycle 3	0·631	0·943	0·41	10·81	0·048	0·039	0·044
		±0·033	±0·026	±0·07	±0·07			
		2AI(2)+3AI(4)=4·091						

* AI: atomic multiplier.

† TO: over-all temperature factor (Å^2).

‡ Residual with observations of zero intensity.

§ Residual without observations of zero intensity.

Table 3. *Calculated and observed intensities and standard deviations* (SIG*YO*) *of the X-ray diffraction measurements for c* = 4·0 Ga *atoms per formula unit*

H	*K*	*L*	*Y*CALC	*Y*OBS	SIG*YO**
2	1	1	0·54	0·48	0·10
2	2	0	0·15	0·16	0·10
3	2	1	0·20	0·22	0·15
4	0	0	17·98	18·20	1·30
4	2	0	72·21	72·60	2·00
3	3	2	2·10	1·64	0·60
4	2	2	39·55	38·30	4·00
4	3	1	2·72	3·00	0·90
5	2	1	5·02	5·12	1·20
4	4	0	2·02	1·62	0·90
5	3	2	6·75	7·53	1·90
6	1	1			
6	2	0	0·01	0·0	0·0
6	3	1	0·00	0·0	0·0
4	4	4	26·37	26·80	3·00
6	4	0	77·89	76·30	5·70
5	5	2	2·05	2·35	1·50
6	3	3			
7	2	1			
6	4	2	99·67	99·70	12·00
6	5	1	0·70	0·74	0·80
7	3	2			
8	0	0	41·43	38·70	6·00
6	5	3	0·00	0·0	0·0
6	6	0	0·78	1·25	1·30
8	2	2			
7	5	2	0·00	0·0	0·0
8	4	0	35·32	37·00	5·80
8	4	2	74·41	76·30	11·00
6	5	5	1·31	0·61	0·60
7	6	1			
9	2	1			
6	6	4	30·81	30·20	8·00
7	6	3	0·80	0·0	0·0
9	3	2			
8	4	4	0·03	0·0	0·0
7	7	2	0·57	0·0	0·0
10	1	1			
8	6	2	5·43	3·83	3·50
10	2	0			
H	*K*	*L*	*Y*CALC	*Y*OBS	SIG*YO*
7	6	5	2·63	3·52	3·20
9	5	2			
10	3	1			
8	6	4	94·54	100·00	13·00
10	4	0			
9	6	1	1·13	0·0	0·0
10	3	3			
10	4	2	50·19	51·80	8·00
9	6	3	3·57	3·93	2·80
10	5	1			
11	2	1			
8	8	0	48·51	52·70	10·00
7	7	6	0·72	0·99	1·00
9	7	2			
10	5	3			
11	3	2			
8	6	6	2·87	3·09	2·00
10	6	0			
10	6	2	0·79	0·0	0·0
9	6	5	0·57	0·0	0·0
8	8	4	23·14	23·00	4·00
12	0	0			
12	2	0	26·15	24·30	6·00
10	5	5	1·55	0·0	0·0
10	7	1			
11	5	2			
10	6	4	59·23	60·00	10·00
12	2	2			
10	7	3	0·68	0·0	0·0
11	6	1			
12	4	0	0·28	0·0	0·0
10	8	0	0·14	0·0	0·0
12	4	2			
9	7	6	4·29	4·16	2·20
9	9	2			
11	6	3			
10	8	2	0·65	0·0	0·0
10	7	5	1·03	0·0	0·0
11	7	2			
13	2	1			
12	4	4	26·85	24·50	5·40

* Observations with SIG*YO* = 0 were dropped for the least-squares refinement. Not listed are most of the reflexions due only to the oxygen ions.

All samples were measured above their Curie point (Lüthi & Henningsen, 1965); *i.e.* the sample with $c=1{\cdot}3$ at 200°C, all others at room temperature. The samples with $c=1{\cdot}3$ and $c=2{\cdot}5$ were also measured in the ferrimagnetic state at room and liquid nitrogen temperature, respectively.

Least-squares refinement procedure

As neutron diffraction yields sufficient accuracy also at higher scattering angles, coincident powder reflexions were not considered. Therefore, the original least-squares refinement program of Busing & Levy (1962) could be used. The refinement was based on the square of the structure factor and the observations were weighted with the standard deviations. The eight varied parameters were: the scale factor and the over-all temperature factor, the coordinates x,y,z, of the O^{2-} ion and the scattering amplitudes of the sites with tetrahedral (d), octahedral (a) and eight-cornered (c) coordination of oxygen b_d, b_a and b_c, for which the following relations hold:

$$\begin{aligned} b_d &= b_{\mathrm{Fe}}(1-p)+b_{\mathrm{Ga}}\,.\,p \\ b_a &= b_{\mathrm{Fe}}(1-q)+b_{\mathrm{Ga}}\,.\,q \\ b_c &= b_{\mathrm{Y}} \\ c &= 3p+2q \end{aligned} \qquad (9)$$

where b_{Fe}, b_{Ga}, b_{Y} are the coherent scattering amplitudes of Fe, Ga and Y, respectively; p and q the probabilities of finding a Ga ion on sites (d) or (a), respectively; and c the number of Ga ions per formula unit. From geometric considerations of the ion size, it is evident that the Y^{3+} ion can only occupy site (c), and, therefore, the Ga^{3+} ions have to be distributed on the (a) and (d) sites only. The scattering amplitudes of Fe and O were taken from the literature: $b_{\mathrm{Fe}}=0{\cdot}96\,.\,10^{-12}$ cm; $b_{\mathrm{O}}=0{\cdot}577\,.\,10^{-12}$ cm (Bacon, 1962).

If b_{Fe} is known, b_{Ga} and the distribution parameter p can be calculated from b_a and b_d according to equations (9). For estimation of the error of p and b_{Ga}, the error of the value for b_{Fe} (Bacon, 1962) was assumed to be smaller than $0{\cdot}01\,.\,10^{-12}\,\mathrm{cm}^2$.

Table 4 shows a comparison of theoretical and experimental intensities after the last refinement cycle for the sample with $c=2{\cdot}5$.

Results

The results of the X-ray and neutron diffraction measurements are shown in Table 5. Preliminary results have been shown in a conference report (Fischer, Hälg, Stoll, Lüthi & Segmüller, 1965).

Though the determination of the distribution parameter P is based on two quite different methods, the one using atomic scattering factors calculated from theoretical electron wave functions, the other using experimental values of the neutron scattering amplitudes, the agreement is completely within the range of the probable error. The probability of finding a Ga^{3+} ion at a tetrahedral site is always greater than would be expected from a proportional substitution of Ga on the two sites. Since the radius of the Ga^{3+} ion (0·62 Å) is smaller than that of the Fe^{3+} ion (0·64–0·67 Å) (Koritnig, 1955), which is also indicated by the dependence of the lattice constant a on the Ga concentration, it is

Table 4. *Calculated and observed intensities and standard deviations of the neutron diffraction measurements for* $c=2{\cdot}5$ Ga *atoms per formula unit*

H	K	L	YCALC	YOBS	SIGYO
3	2	1	0·33	0·41	0·04
4	0	0	31·58	31·38	0·51
4	2	0	15·68	15·73	0·20
3	3	2	13·09	12·97	0·20
4	2	2	5·29	5·46	0·17
4	3	1	5·06	4·93	0·10
5	2	1	4·36	4·50	0·11
4	4	0	3·51	4·75	0·39
6	2	0	6·85	7·26	0·24
5	4	1	0·47	0·75	0·11
6	3	1	1·39	1·88	0·13
4	4	4	28·70	29·40	0·94
5	4	3	0·17	0·31	0·13
6	4	0	62·34	62·17	0·56
6	4	2	41·21	41·07	0·33
8	0	0	63·76	63·72	0·16
7	4	1	2·53	2·47	0·16
8	2	0	6·20	6·16	0·55
6	5	3	2·26	1·97	0·15
7	5	2	2·20	2·02	0·18
8	4	0	27·81	27·25	0·54
8	4	2	11·18	11·56	0·25
6	6	4	22·23	22·59	0·51
8	4	4	5·65	6·70	0·40
8	6	0	0·15	1·10	0·40

Table 5. *Crystal parameters of* $Y_3Fe_{5-c}Ga_cO_{12}$ *as determined from X-ray* (x) *and neutron* (n) *diffraction measurements*

c	a(Å)$^{(a)}$	$P_x{}^{(b)}$	$P_n{}^{(b)}$	$TO_x{}^{(c)}$	$TO_n{}^{(c)}$	$R_{1x}{}^{(d)}$	$R_{1n}{}^{(d)}$
1·3	12·360	–	0·87 ± 0·06	–	0·8 ± 0·1	–	0·026
2·0	12·341	0·80 ± 0·03	0·79 ± 0·03	0·56 ± 0·07	0·2 ± 0·1	0·054	0·014
2·5	12·331	0·75 ± 0·03	0·77 ± 0·03	0·66 ± 0·08	0·5 ± 0·1	0·062	0·023
3·0	12·321	0·77 ± 0·03	0·76 ± 0·03	0·54 ± 0·06	0·7 ± 0·2	0·059	0·027
4·0	12·299	0·69 ± 0·02	–	0·41 ± 0·06	–	0·038	
0·0	12·376$^{(e)}$						
5·0	12·280$^{(f)}$	12·273$^{(e)}$					

(*a*) Lattice constant from X-ray diffraction (± 0·005).
(*b*) Fraction of gallium atoms on tetrahedral sites $P=3\,p/c$; for distribution proportional to the number of (a) and (d) sites $P=0{\cdot}60$.
(*c*) Over-all temperature factor ($Å^2$).
(*d*) Residual without zero observations.
(*e*) Gilleo & Geller (1958).
(*f*) Euler & Bruce (1965).

plausible that the Ga^{3+} ion preferentially occupies the smaller of the two available positions. This agrees well with the results of magnetic investigations (Gilleo & Geller, 1958; Villers, Pauthenet & Loriers, 1959; Lüthi & Henningsen, 1964; Prince, 1965; Streever & Uriano, 1965). Fig. 2 shows the fraction of Ga atoms on (*d*) sites $P=3p/c$ and the lattice constant *a versus c*.

The temperature factor for X-ray diffraction shows a maximum for the crystal with half of the iron atoms substituted by gallium, probably due to the highest degree of substitutional disorder for this composition. The temperature factor for neutron diffraction determined from a lesser variation of $\sin\theta/\lambda$ shows only an increase with increasing Ga concentration, besides the factor of the crystal with lowest concentration, which was measured at elevated temperature.

As a sort of consistency check, the other varied parameters as determined by neutron diffraction are to be compared with the values in the literature. The oxygen coordinates agree fairly well with those of Euler & Bruce (1965) in Table 1. Also the neutron scattering length of Ga, $b_{\mathrm{Ga}}=(0{\cdot}72\pm0{\cdot}02)\,.\,10^{-12}$ cm, agrees well with that determined by Konakhovich & Somenkov (1963), $b_{\mathrm{Ga}}=(0{\cdot}73\pm0{\cdot}03)\,.\,10^{-12}$ cm, and by Kuz'minov & Belov (1963), $b_{\mathrm{Ga}}=(0{\cdot}72\pm0{\cdot}05)\,.\,10^{-12}$ cm. However, the neutron scattering length of yttrium, $b_{\mathrm{Y}}=(0{\cdot}75\pm0{\cdot}02)\,.\,10^{-12}$ cm deviates from the recent measurement of Paton & Maslen (1965), $b_{\mathrm{Y}}=(0{\cdot}781\pm0{\cdot}008)\,.\,10^{-12}$ cm, but a refinement using their value of b_{Y} as a fixed parameter and varying individual isotropic temperature factors for each site, resulted in an *R* index twice as large and in a nearly equal distribution of gallium.

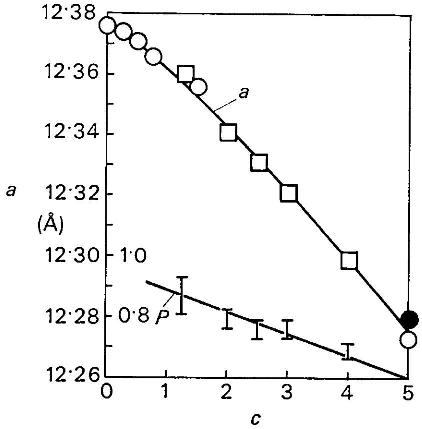

Fig. 2. The fraction of Ga^+ ions on the tetrahedral sites $P=3p/c$ and the lattice constant *a versus* the number of Ga atoms per formula unit *c*. For a distribution of the Ga^+ ions on (*d*) and (*a*) sites proportional to the number of available sites the relation $P=0{\cdot}6$ would hold. Open circles, Gilleo & Geller (1958); solid circle, Euler & Bruce (1965); squares, this work.

With regard to the neutron diffraction on the samples in the ferrimagnetic state ($c=1{\cdot}3$ and $c=2{\cdot}5$), no extra magnetic lines could be detected, whereas the intensity increase of the reflections with contributions from the (*a*) and (*d*) sites was in qualitative agreement with the intensity of magnetic lines expected from Néel's model of ferrimagnetism (Bertaut *et al.*, 1956; Prince, 1957, 1965; Kuz'minov, Yamzin & Belov, 1963). Therefore, there is no reason to abandon Néel's model of antiferrimagnetic coupling of the (*a*) and (*d*) sublattices up to concentrations of $c=2{\cdot}5$.

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