Another two oxygen contacts under 4 Å are found (3·32 and 3·35 Å). The angle C–OH···O is 116°. The carboxyl group and C_2 are planar within 0·05 Å. The planes of two hydrogen bonded groups do not coincide but are displaced by 0·35 Å. The carboxyl group plane is twisted 26° from the plane of the adjoining carbon chain.

The tilt (56·5°) of the end part of the chain to the methyl group contact planes is similar to that of most straight long-chain compounds. The layer structure therefore shows usual methyl group packing distances, the closest approaches being 3·75 and 4·21 Å.

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A Procedure for Parameter Refinement in Simple Structures*

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A procedure for the refinement of atomic position parameters in suitable simple structures is described. The method has been applied to the refinement of published position parameters of the oxygen atom in yttrium iron garnet. The new values are:

$$x = -0{\cdot}0269 \pm 0{\cdot}0001,\quad y = 0{\cdot}0581 \pm 0{\cdot}0003,\quad z = 0{\cdot}1495 \pm 0{\cdot}0001\,.$$

In the investigation of the structures of simple crystals in which certain atoms occupy special positions, the primary objective is often limited to the precise determination of a small number of atomic position coordinates. In recent years problems of this sort have usually been dealt with by least squares techniques. It is well known that, even in simple cases where the number of observations far exceeds the number of variable parameters, many serious errors may affect the accuracy of the least squares results. These include errors resulting from uncertainties in our knowledge of atomic scattering factors, inadequate corrections for dispersion factors, errors due to absorption, and errors in the determination of scale and temperature factors. Geller (1961) has analyzed parameter interactions in least squares structure refinements; such interactions may be very strong in just those simple structures under consideration.

In this paper we describe a simple technique for coordinate refinement which, though limited to a relatively small number of structure types, does make it possible to avoid most of the errors listed above in cases where it can be applied. In this procedure, calculations are based not on structure factors but on the *ratios* of intensities of selected pairs of reflections. In cubic crystals the members of each of these

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pairs should have different *hkl* indices and the same *d* spacing. Effective use of the method requires careful measurement of reflection intensities, the use of spherical crystals and a number of additional considerations which are best specified in a description of an actual structure refinement.

Experimental

Yttrium iron garnet was selected to illustrate the use of the 'ratio' method for a number of reasons. It is a cubic crystal and many pairs of independent reflections occur at the same Bragg angle. The parameters have recently been determined by Geller & Gilleo (1957 and 1959) with satisfactory precision and these could be used as a starting point for this work. Good single crystals, prepared by Microwave Chemicals, Inc., were available, and two of these were readily ground to spherical shape.

Yttrium iron garnet has the formula $Y_3Fe_2(FeO_4)_3$. The unit cell is cubic, $a = 12{\cdot}376 \pm 0{\cdot}001$ Å, the space group is $Ia3d$ and there are eight formula units per unit cell. All the metal atoms are in special positions, fixed by symmetry: the Y atoms are in 24(*c*); the Fe atoms occupy positions 16(*a*) and 24(*d*). The oxygen atoms occupy the general positions 96(*h*). Only three position coordinates are variable, i.e. the *x*, *y* and *z* coordinates of one oxygen atom.

Geller & Gilleo (1957 and 1959) and, more recently, Wiedenborner (1961) in his work on the structure of the isomorphous gadolinium iron garnet, have based their analyses on reflections to which oxygen atoms make major contributions. These are of two types: first, those to which only the oxygen atoms contribute, and second, those which receive, in addition to oxygen contributions, contributions from metal atoms in positions 24(*c*) and 24(*d*). In the latter type, contributions from 24(*c*) atoms are opposite in phase from 24(*d*) contributions; metal atoms in 16(*a*) do not contribute at all to these reflections. It is clear that these reflections must be particularly sensitive to oxygen parameters. The reflections to which only the oxygen atoms contribute are the following:

(*a*) two indices are of the type $8n+4$, and the third equals $4n+2$;
(*b*) all indices are of the type $4n+2$;
(*c*) two indices are odd and the third is divisible by four.

In the present work measurements were confined to reflections to which only the oxygen atoms contributed.

Intensity measurements were made using two spherical crystals with radii 0·220 and 0·735 mm. Filtered copper radiation was used. Measurements were made on a G.E. crystal orienter, using an argon-filled proportional counter as radiation detector.

Measured intensities and ratios of pairs of intensities are listed in Table 1. Eight sets were measured; one of these (7,3,4; 3,9,12; 7,11,8) included three oxygen reflections—all at the same Bragg angle.

Table 1. *Measured intensities*

hkl	Aver. counting rate counts/sec.	R_o
3,7,4	37·18	5·48
1,3,8	6·79	
5,7,4	93·13	1·50
1,5,8	62·22	
3,5,8	134·63	1·60
1,9,4	84·30	
1,9,8	71·72	3·18
3,11,4	22·53	
3,13,4	42·10	2·12
7,9,8	21·22	
5,11,8	96·08	4·25
5,13,4	22·61	
9,11,4	43·01	1·89
5,7,12	23·15	
7,13,4	99·14	1·16
3,9,12	85·36	0·98
7,11,8	100·79	1·18

In view of the fact that comparisons of intensities were confined to reflections occurring at identical Bragg angles, it appeared likely that comparisons of peak heights would yield essentially the same answers as comparisons of integrated intensities. Two sets of reflections were measured by both methods, i.e. by 'θ, 2θ' scans to obtain 'integrated' intensities, and by holding the counter at peak maxima until a fixed number of counts had been accumulated. The two sets of intensity ratios agreed within one standard deviation and subsequent measurements were restricted to counting at peak maxima.

It is clear that geometrical and instrumental factors which lead to peak broadening are the same for all members of any one set; the results obtained above indicated that the mosaic spread in our yttrium iron garnet crystals was effectively isotropic. Where this is not the case, integrated intensities should be compared.

Discussion

The square roots of the intensities of the 'oxygen' reflections may be represented as:

$$\sqrt{I} = (k)(\text{L.P.})(A) \sum_i \left[f_{(o)}(D) \exp(-M)(\text{trig.}) \right] ,$$

where k is the scale factor, (L.P.) is the Lorentz-polarization correction, (A) the absorption factor, $f_{(o)}$ the scattering factor of oxygen atoms, (D) the dispersion correction, $\exp(-M)$ the temperature factor, and 'trig.' is the trigonometric part of the structure factor expression. Terms which are functions of diffraction angle only may be taken out of the summation bracket; that is true of L.P., F_o, and D; it is also true for the absorption correction when spherical crystals are used. The $\exp(-M)$ term may also be placed outside the summation bracket for similar reasons though this procedure may introduce a small error since it involves the assumption that, to a good approximation, the temperature factor of the oxygen atom is spherically symmetrical and therefore a function of reflection angle only. Actually, even if the thermal ellipsoid of the oxygen atom deviated significantly from spherical shape (and this is unlikely in the relatively symmetrical environment of oxygen atoms in this structure), the summation over the large number of symmetry related oxygens leads to an average ellipsoid which clearly can differ only very slightly from an effective sphere.

The ratio of the square roots of reflection intensities of two reflections occurring at the same Bragg angle may therefore be written as:

$$R = (I_{h_1k_1l_1})^{\frac{1}{2}}/(I_{h_2k_2l_2})^{\frac{1}{2}}$$

$$= \frac{(k)(\mathrm{L.P.})(A)(f_o)(D)(\exp -M)_t(\mathrm{trig}_1)}{(k)(\mathrm{L.P.})(A)(f_o)(D)(\exp -M)_t(\mathrm{trig}_2)} .$$

i.e. $R = (\mathrm{trig}_1)/(\mathrm{trig}_2)$.

R is clearly a function of the oxygen position coordinates only.

The calculation of R for any pair of reflections was a simple matter; coordinates reported by Geller & Gilleo (1957) were used as starting points. The refinement was based on a least squares minimization of

$$\Delta R = R_o - R_c = \frac{\partial R}{\partial x}\Delta x + \frac{\partial R}{\partial y}\Delta y + \frac{\partial R}{\partial z}\Delta z .$$

Since only three variables were involved and since only eight sets of reflections were used in the calculation, the refinement was carried out using a desk computer. Results are shown in Table 2; the Geller & Gilleo coordinates are also listed for comparison.

Table 2. *Oxygen coordinates*

	Geller & Gilleo (1957)	This work
x	−0·0274 ± 0·0009	−0·0269 ± 0·0001
y	0·0572 ± 0·0009	0·0581 ± 0·0003
z	0·1492 ± 0·0009	0·1495 ± 0·0001

Bond lengths are listed in Table 3. The structure has already been described in detail by Geller & Gilleo (1957) and this need not be repeated here.

Table 3. *Bond lengths in* Å

	Geller & Gilleo		This work	
Fe(*d*)–O	1·88		1·880	
O–O	2·87(2)	3·16(4)	2·872(2)	3·163(4)
Fe(*a*)–O	2·00		2·012	
O–O	2·68(6)	2·99(6)	2·675(6)	2·987(6)
Y(*c*)–O	2·43(4)	2·37(4)	2·419(4)	2·368(4)
O–O	2·96(2)	2·87(2)	2·951(2)	2·872(2)
	2·68(4)	2·81(4)	2·674(4)	2·780(4)

Values of R_o and R_c, based on the coordinates in Table 2, are listed in Table 4. The 'discrepancy coefficient' for the ten ratios is 7·7%.

Table 4. *Calculated and 'observed' ratios*

Set	*hkl*	F_c	F_c^2	R_c	R_o
1	3,7,4	16·656	277·42	5·13	5·48
	1,3,8	7·354	54·08		
2	5,7,4	23·946	573·41	1·53	1·50
	1,5,8	19·378	375·51		
3	3,5,8	29·157	850·13	1·68	1·60
	1,9,4	22·489	505·76		
4	1,9,8	21·072	444·03	3·75	3·18
	3,11,4	10·875	118·27		
5	3,13,4	11·891	141·40	2·13	2·12
	7,9,8	8·152	66·46		
6	5,11,8	13·698	187·64	4·45	4·25
	1,13,4	6·492	42·15		
7	9,11,4	9·133	83·41	1·87	1·89
	5,7,12	6·675	44·56		
8_1	7,13,4	12·555	157·63	1·56	1·16
	3,9,12	10·049	100·98		
8_2	7,13,4	12·555	157·63	1·24	0·98
	7,11,8	11·289	127·44		
8_3	7,11,8	11·289	127·44	1·26	1·18
	3,9,12	10·049	100·98		

This method requires that reflection intensities from a spherical crystal be measured with great care. We feel that, in suitable cases, it permits maximum benefit to be derived from the accurate intensity measurement techniques now available.

A detailed description of the seriousness of the difficulties encountered in a least squares refinement of the gadolinium iron garnet structure has been given by Weidenborner (1961). It is felt that many of these difficulties would have been avoided had he simply limited his analysis to 'oxygen' reflections. It is interesting to note that the coordinates he computed from 'oxygen' reflections alone, differ from those based on his more complete analysis by less than one standard deviation for each coordinate. It is probable that the use of the 'ratio' method with the oxygen reflections (even without counter measurements) would have improved the precision of his results considerably by eliminating errors due to uncertainties in scale factors, oxygen form factors and temperature factors.

The standard deviations of the coordinates computed in this work are, as might be expected, considerably smaller than those previously reported. The method appears to be suitable for the precise determination of position parameters in simple oxides of the rutile, spinel, or Al_2O_3 types and in simple intermetallic compounds.

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