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Refinement of the Structure of Yttrium Iron Garnet (YIG). A Case of Severe Extinction and Absorption

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The positional and thermal parameters of yttrium iron garnet have been refined by the use of 503 reflexions measured by Mo $K\alpha$ radiation on an automatic three-circle diffractometer. It was noticed that numerous reflexions suffer severely from extinction. Several models for extinction correction have been examined. It is shown that the positional and thermal parameters are only slightly influenced by the choice of a particular extinction correction model. The best fit is obtained by using the Zachariasen theory with inclusion of anomalous transmission and modified by Becker and Coppens with two independent parameters (t and g) for extinction and a Gaussian fit. The importance of an appropriate correction for anomalous transmission (Borrmann effect) is shown for the case of severe extinction and absorption. The R value obtained is $R(F^2)=0{\cdot}032$. The positional parameters of the oxygen atom agree well with previous work. Thermal parameters were obtained for all atoms.

Introduction

The synthetic garnets of rare-earth elements and iron were first prepared by Bertaut & Forrat (1956) and were shown to be isomorphous with the naturally occurring garnets, the structure of which was first determined by Menzer (1927). These compounds have been subjected to numerous magnetic and crystallographic studies (*e.g.* Pauthenet, 1958; Batt & Post, 1962; Euler & Bruce, 1965).

We are at present investigating yttrium iron garnet (YIG) and terbium iron garnet (TbIG) by polarized neutron techniques in order to determine the magnetic moments and the magnetic form factors of the magnetic ions in these compounds. The first results on YIG have been published recently (Bonnet, Delapalme, Tchéou & Fuess, 1974).

As the normalization of polarized neutron measurements depends strongly on an exact knowledge of the crystal structure and as the published structural parameters, especially the thermal ones, were not consistent (see Table 5) we re-examined the structure of yttrium iron garnet.

This examination was performed with X-rays as well as with neutrons in order to allow a cross-check of the results. The neutron study was performed on powders (at 300 K and 4 K) and on a single crystal. The results are almost identical with those of the present X-ray study. In this paper we report the single-crystal X-ray study for yttrium iron garnet which turned out to be a case of both severe absorption and severe extinction. We therefore considered the various models for extinction at present described in the literature.

Crystal structure

The rare-earth iron garnets ($T_3Fe_5O_{12}$, T = rare earth or yttrium) crystallize in space group *Ia*3*d* with eight formula units per cell. The cell dimension is 12·376 Å, $\sigma=0{\cdot}003$ Å (Espinosa, 1962) for YIG at room temperature. The following positions are occupied

T^{3+} in 24(*c*) $\frac{1}{8},0,\frac{1}{4}$ *etc.*
Fe^{3+} in 16(*a*) 0,0,0 *etc.*, octahedral
Fe^{3+} in 24(*d*) $\frac{3}{8},0,\frac{1}{4}$ *etc.*, tetrahedral
O^{2-} in 96(*h*) x,y,z *etc.*

Our experimental approach was guided by some peculiarities of the garnet structure which lead to special contributions of the four ions to special *hkl* values. Accordingly we may distinguish between three different classes of reflexions which we call (*a*), (*b*) and (*c*).

(*a*) *Reflexions with contribution from oxygen atoms alone*

$$\begin{array}{lll} h=2n+1\,, & k=2n+1\,, & l=4n \\ h=4n+2\,, & k=4n+2\,, & l=4n+2 \\ h=8n+4\,, & k=8n+4\,, & l=4n+2 \\ h=8n\,, & k=8n\,, & l=4n+2\,. \end{array}$$

These reflexions are rather weak and need a fairly long measuring time. Their intensities allow the determination of the parameters of the oxygen atom. The interpretation of the polarized neutron data on YIG requires a precise knowledge of the thermal parameters of all atoms. We therefore have to include reflexions from the classes (*b*) and (*c*) into our refinement.

(*b*) *Reflexions with no contribution from the iron atom in* 16(*a*)

$$h=2n+1\ ,\quad k=2n+1\ ,\quad l=2n\ .$$

The intensities of these reflexions are medium. They should in principle allow a determination of the thermal parameters of both the tetrahedrally coordinated iron atom and of the yttrium atom. There is however a strong correlation between these parameters. Geller (1961) gives a correlation value of 0·99.

(*c*) *Contribution from all atoms*

hkl all$=2n$ [with the exception given under (*a*)]. This group of reflexions is needed to determine the thermal parameters of the iron atom in the octahedral site and to lower the correlation between the thermal parameters of yttrium and tetrahedrally coordinated iron. These reflexions are however very strong and suffer considerably from extinction.

Model calculations for extinction corrections

The crucial point in the refinement of the experimental data is an appropriate extinction correction. We therefore summarize the model calculations for extinction corrections which are at present given in the literature and which were applied during our refinement by introducing additional parameters into the least-squares program *ORXFLS*3 (Busing, 1971).

Our refinements were based on the model given by Zachariasen (1967), the extension which allows a treatment of anomalous transmission or Borrmann effect (Zachariasen, 1968) and the extension given by Becker & Coppens (1974). These papers are cited as Z1, Z2 and BC in the following text. The Zachariasen model is based on a solution of the transfer equations of Darwin (1922) which describe the intensity coupling between the incident and diffracted beam. This model then gives an expression for a correction factor y which by equation (1) is applied to the observed integrated intensities P.

$$P=P_k y \quad [\mathrm{Z1}-(1)] \tag{1}$$

P_k is the integrated intensity in the kinematical approximation, where y is the product $y=y_p y_s$ (y_p stands for primary, y_s for secondary extinction).

When only secondary extinction is important equations (2) and (3) hold ($y=y_s$; $y_p=1$)

$$y_s=(1+2x)^{-1/2} \quad [\mathrm{Z1}-(38b)] \tag{2}$$

$$2x=2\,\frac{P_2}{P_1}\,\frac{\bar{T}_\mu\lambda^3}{V^2\sin 2\theta}\cdot g^*F^2. \tag{3}$$

Formula (3) was given by Coppens & Hamilton (1970) and was introduced into the program *ORXFLS*3. The quantities in equation (3) have the following meaning. P_2/P_1: term related to the polarization of X-rays. V: volume of the unit cell. F: structure factor. λ: wavelength. θ: Bragg angle. g^* is the isotropic extinction parameter used as a variable in *ORXFLS*3 [equation (5)]. $\bar{T}_\mu$ is the distance of travel within the crystal. This distance is defined by the absorption coefficient.

$$\bar{T}_\mu=-\frac{1}{A}\frac{\mathrm{d}A}{\mathrm{d}\mu} \tag{4}$$

and an approximation often applied is

$$\bar{T}'_\mu=-\frac{1}{\mu}\ln A\ . \tag{4a}$$

This approximation is only valid for values of $\mu\bar{T}_\mu\lesssim 0{\cdot}25$. In our case with $\mu=252\ \mathrm{cm}^{-1}$ we obtained the values of $\bar{T}_\mu$ by a numerical evaluation of equation (4) based on absorption tables of Weber (1969). It may be noted here that the differences between the approximate value for $\bar{T}'_\mu$ [equation (4*a*)] and the rigid formulation of $\bar{T}_\mu$ [equation (4)] differ by as much as a factor of 2.

The parameter g^* was given by Z1 as a combination of two other parameters: g which describes the angular disorientation of the mosaic blocks and t which gives the size of these blocks.

$$g^*=\tfrac{2}{3}[(\lambda/t)^2+\tfrac{1}{2}g^2]^{-1/2}. \tag{5}$$

It was later experimentally shown by Cooper & Rouse (1970) and by BC based on more rigid assumptions that in fact an angular dependence is missing in (5). Without this angular dependence it is not possible from (5) to refine both parameters t and g simultaneously. Only g^* is fitted in *ORXFLS*3. Furthermore the general extinction treatment of Z1 is not valid in the case of high absorption. In this case the extinction effect is 'overcorrected'. This fact is due to anomalous transmission and is dealt with in Z2. In case of simultaneous diffraction and absorption the absorption coefficient μ has to be modified, equation (6).

$$\mu=\mu_0\pm K\mu_H\bar{\kappa}_K \quad [\mathrm{Z2}-(18)] \tag{6}$$

μ_0 is the true absorption. The coefficient K is $K=1$ for the component normal and $K=\cos 2\theta$ for the component parallel to the diffraction plane. μ_H is a term related to diffraction. $\bar{\kappa}_K$ is given by

$$\bar{\kappa}_K=\frac{z}{\pi\sqrt{1-z^2}}\ln\frac{1+\sqrt{1-z^2}}{1-\sqrt{1-z^2}} \quad [\mathrm{Z2}-(22)] \tag{7}$$

with

$$z=2r^*_B K|F|e^2\lambda/mc^2V\sin 2\theta \quad [\mathrm{Z2}-(22)] \tag{8}$$

where e,m,c have their usual meaning and where r^*_B is introduced as a constant value to take into account the Borrmann effect. This parameter has the same physical meaning as the fitting parameter for extinction $r^*=g^*\lambda$. We give them different symbols in order to distinguish between them in the presentation of our results. $\bar{\kappa}_K$ has a maximum value of $2/\pi$. For each component of the polarization a special absorption correction $A_{\pm K}$ is calculated which defines a distance $T_{\mu\pm K}$

which then determines the secondary extinction correction $y_{s\pm K}$. The extinction correction is then given by (9).

$$y=[A_{+1}y_{+1}+A_{-1}y_{-1}+K^2(A_{+K}y_{+K}+A_{-K}y_{-K})]/2A_0(1+K^2) \quad [\mathrm{Z2}-(26)] \quad (9)$$

with A_0 the absorption correction for μ_0.

The more rigid treatment of BC modified the Zachariasen model somewhat. On practical grounds two modifications ought to be considered. First, as already mentioned, equation (5) is modified by introducing an angular dependence.

$$g^*=\tfrac{2}{3}\left[\left(\frac{\lambda}{t\sin 2\theta}\right)^2+\frac{1}{2g^2}\right]^{-1/2} =\tfrac{2}{3}\left[\left(\frac{d}{t\cos\theta}\right)^2+\frac{1}{2g^2}\right]^{-1/2} \quad (10)$$

where d is the interplanar spacing. It is to be noted that g^* may be dominated either by the particle size t (secondary extinction of type II) or by the mosaic distribution g (secondary extinction of type I). The first term in equation (10) depends strongly on two of the three quantities λ, θ and d and may show an important variation with λ as compared with the invariant second term. Therefore a continuous change between type I and type II behaviour may be observed. For low scattering angles the variation of the first term depends mainly on the d-spacing, for higher values of θ (near to $\theta=90°$) the variation of $\cos\theta$ becomes the more important. The angular dependence of g^* allows a refinement on both parameters t and g even for one-wavelength measurements.

Secondly the development of secondary extinction is modified. For a sphere the following expression is given by BC.

$$y_s=\left[1+2x+\frac{A(\theta,\mu)x^2}{1+B(\theta,\mu)x}\right]^{-1/2} \quad [\mathrm{BC}-(37)]\,. \quad (11)$$

The coefficients $A(\theta,\mu)$ and $B(\theta,\mu)$ are dependent on absorption and Bragg angle and on the distribution law adopted for the mosaic blocks which may be described as Gaussian or Lorentzian. They are tabulated for a crystal of spherical form (BC). The treatment in *ORXFLS*3 only deals with secondary extinction [see equations (2) and (3)]. When introducing the Borrmann effect and the BC-modifications into the program we introduced primary extinction at the same time. The extinction correction is then

$$y_{\pm K}=y_p(x_p)\,.\,y_{s\pm K}(x_s\,.\,y_p)\,. \quad (12)$$

BC give for y_p a development identical with equation (11). The coefficients A and B are tabulated. As primary extinction has to be treated by amplitude coupling rather than by intensity coupling this treatment is only an approximation valid for small primary extinction.

Experimental

The crystal used in this study was supplied by LETI (CENG) and was grown in PbO by a flux method. The composition was checked by X-ray fluorescence methods. The crystal form was a sphere of a diameter of $\varphi=405$ μm ± 3 μm and it was mounted with the [110] axis vertical. The absorption coefficient for YIG is $\mu(\text{Mo } K\alpha)=252$ cm^{-1}.

We collected 2039 reflexions of which 508 were symmetry-independent on an automatic three-circle Siemens diffractometer at ILL. The distribution of the reflexions within the three classes is (*a*) 133, (*b*) 152 and (*c*) 223. The data collection was done in the θ–2θ scan mode and the angular range extended between 5° and 70° (θ). The scan range $\Delta\theta$ was experimentally determined as a function of θ. Zr-filtered Mo $K\alpha$ radiation was used and the power of the tube was set to 40 kV and 30 mA. A scintillation counter was used and the electronic discrimination was adjusted to suppress unwanted white radiation.

The intensity measurements were carried out in the so-called five-point mode which consists of a stationary background registration at the beginning and end of the scan range (intensities I_2 and I_4) and a double scan over the peak (intensities I_1, I_3 and I_5). The integrated intensities are then obtained

$$I_{\text{obs}}=(I_1+I_3+I_5)/2-(I_2+I_4) \quad (13)$$

and the variance from counting statistics is

$$\sigma_c^2(I_{\text{obs}})=\tfrac{1}{4}(I_1+I_3+I_5)+I_2+I_4\,. \quad (14)$$

F^2 and its variance is obtained after absorption correction [numerical values from Weber (1969)].

The symmetry-related F^2 values were averaged by equation (15)

$$\bar{F}^2=(\sum_i F_i^2/\sigma_{c_i}^2)/\sum_i 1/\sigma_{c_i}^2\,. \quad (15)$$

The variance of the averaged intensity was calculated by equation (16) and introduced into the refinement procedure.

$$\sigma_\alpha^2(\bar{F}^2)=1/\sum_{i=1}^{n}(1/\sigma_{c_i}^2(F^2)\,. \quad (16)$$

In order to check the overall agreement of our data set, we calculated the variance σ_β estimated from the discrepancy between equivalent reflexions (Hamilton, 1972).

$$\sigma_\beta^2=\frac{1}{n-1}\sum_{i=1}^{n}(F_i^2-\bar{F}^2)^2w_i/\sum_{i=1}^{n}w_i \quad (17)$$

with the weight $w_i=1/\sigma_{c_i}^2$. Only 18 reflexions of the strong ones [class (*c*)] have shown differences (on a 5% level of significance) between symmetry-equivalent F^2 values. We can exclude anomalous dispersion as a reason for these differences because the structure is centrosymmetric. Another possible source for this difference is the anisotropy of extinction. But this effect cannot be pronounced because the overwhelming majority of the strong reflexions agree well between symmetry-equivalent ones. Another evidence for isotropic behaviour of the extinction is given by γ-ray measurements (Schneider, 1974) of several symmetry-equivalent reflexions at different places on a bigger crystal plate of YIG.

After deconvolution of various rocking curves almost the same mosaic spread was found. We therefore concluded that we could base our refinement on the averaged data set.

Refinement

The atomic form factors for Fe^{3+} and Y^{3+} used in the calculation are those given by Cromer & Mann (1968), that for O^{2-} has been adopted from Tokonami (1965). The factors for anomalous dispersion are those from Cromer & Liberman (1970) (see Table 1).

Table 1. *Anomalous dispersion corrections for* Mo *Kα* (*Cromer & Liberman*, 1970)

	$\Delta f'$	$\Delta f''$
O^{2-}	0·008	0·006
Fe^{3+}	0·301	0·845
Y^{3+}	−2·951	3·542

The function minimized in *ORXFLS*3 is

$$R=\sum_i w_i(F^2_{i_o}-F^2_{i_c})^2 \qquad (18)$$

with $w_i=1/\sigma_i^2$. The variance σ_i was modified by a subprogram according to

$$\sigma_i^2(F^2)=\sigma_\alpha^2(F^2)+(k_wF^2)^2 \qquad (19)$$

where k_w is a constant which allows the adjustment of the variance of strong reflexions to obtain a value of the standard deviation of the observation of unit weight S [equation (20)] being near to unity (Hamilton, 1972).

$$S=\left[\frac{1}{\mathrm{NO}-\mathrm{NV}}\sum_i w_i(F^2_{i_o}-F^2_{i_c})^2\right]^{1/2}. \qquad (20)$$

The value of k_w can be calculated by the expression (21). From the discrepancy between equivalent reflexions

$$k_w=\left[\frac{\sum(F^2-\bar{F}^2)^2/\sigma^2_{c_i}(F^2)}{\sum F^4/\sigma^2_{c_i}(F^2)}\right]^{1/2}. \qquad (21)$$

Calculations from (21) give $k_w=0·026$; we therefore introduced in (19) the value $k_w=0·03$ for all three classes of reflexions. The definitions of other quantities in the program mentioed later are: the calculated structure factor F_c, the conventional R value $R(F^2)$ and the weighted R value $R_w(F^2)$

$$F_c^2=kF^2y \qquad (22)$$

$$R(F^2)=[\sum_i (F^2_{o_i}-F^2_{c_i})^2/\sum_i F^4_{o_i}]^{1/2} \qquad (23)$$

$$R_w(F^2)=[\sum w_i(F^2_{o_i}-F^2_{c_i})^2/\sum_i w_iF^4_{o_i}]^{1/2}. \qquad (24)$$

In equations (20)–(24) NO is the number of observations, NV the number of parameters varied, k the scale factor. In all runs the xyz parameters of the oxygen atom, the anisotropic temperature factors of all atoms and the scale factor were varied together with the relevant extinction parameters of the model under consideration. In the course of the refinement we found some discrepancy for five reflexions having a value for $[F^2(\mathrm{obs})-F^2(\mathrm{calc})]/\sigma(F^2)$ higher than six. These reflexions were all at low θ angles and their observed intensities are smaller than the calculated values. In the final run these reflexions were excluded from the data set by a subprogram. They are marked by an asterisk in the deposited list of structure factors.† The results of the final runs on 503 reflexions with various extinction models are given in Table 2 where the columns 1–4 correspond each to a different extinction model. Column 2.1 contains the refined parameters obtained by a single parameter for extinction [g^* of equation (5)]. Despite a fairly good overall agreement [$R_w(F^2)=0·049$] large differences for the strong reflexions which were 'overcorrected' persisted (see Table 4).

Column 2.2 refers to the results of a refinement corresponding to the previous treatment and additional correction of the anomalous transmission introduced in a simplified version where equation (9) was replaced by (25)

$$y=(A_{+1}+A_{-1})y_0/2A_0\,. \qquad (25)$$

y_0 is given by the development of Z(2) with $\mu=\mu_0$. The fit parameter used was $r^*=g^*\lambda$. The quantity introduced to calculate the effect of anomalous transmission r_B^* [equation (8)] has the same meaning but was kept constant. Finally both values should converge to give the same numerical value. The best agreement value $R_w(F^2)=0·043$ was obtained for a value of $r_B^*=0·5$ which, however, is about six times smaller than the refined extinction parameter $r^*=2·98$ (all numerical values of r^*, r_B^*, t_B and t are given in units of 10^{-4} cm). The divergence between r^* and r_B^* in 2.2 indicates that the Zachariasen development [equation (2)] is not adequate for extinction correction in cases of severe extinction and strong absorption.

Column 2.3 reports the results of the refinement with the BC development of secondary extinction [equation (11)] with primary extinction and Gaussian distribution law. We refined simultaneously t and g [equation (10)]. The numerical values for $A(\theta,\mu)$ and $B(\theta,\mu)$ were taken from BC for the highest value of μR tab-

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† This list has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31002 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Refinement for different extinction models*

The thermal factors are given as exp $[-(h^2\beta_{11}+\ldots)]$.

	1			2			3			4			5
t_B										7·0			7·0
r_B^*	0·			0·5			0·						
g_B										5·0			5·0
t							5·19 (21)			7·04 (17)			7·07 (27)
r^*	2·28 (7)			2·98 (8)									
g							3·14 (32)			5·41 (40)			5·39 (64)
k	0·756 (3)			0·767 (3)			0·748 (4)			0·764 (3)			0·765 (4)
$R(F^2)$	0·055			0·033			0·083			0·032			0·040
$R_w(F^2)$	0·049			0·043			0·057			0·044			0·071
s	1·07			0·95			1·25			0·96			1·55
x	−0·0271 (1)			−0·0271 (1)			−0·0270 (1)			−0·0271 (1)			−0·0269 (2)
y	0·0568 (1)			0·0568 (1)			0·0567 (1)			0·0567 (1)			0·0567 (2)
z	0·1504 (1)			0·1504 (1)			0·1503 (1)			0·1504 (1)			0·1504 (2)
β(Y) ($\times 10^2$)	3·5 (1)	5·5 (1)	5·5	3·7 (1)	5·7 (1)	5·7	3·3 (2)	5·3 (1)	5·3	3·6 (1)	5·6 (1)	5·6	0·30 (1)
	0	0	0·7 (1)	0	0	0·7 (1)	0	0	0·7 (1)	0	0	0·7 (1)	
β(FeT)	4·1 (2)	6·3 (1)	6·3	4·1 (2)	6·3 (1)	6·3	4·0 (2)	6·2 (1)	6·2	4·1 (2)	6·2 (1)	6·2	0·34 (1)
	0	0	0	0	0	0	0	0	0	0	0	0	
β(FeO)	5·5 (1)	5·5	5·5	5·6 (1)	5·6 (1)	5·6(1)	5·4 (1)	5·4	5·4	5·5 (1)	5·5	5·5	0·35 (1)
	−0·4 (1)	−0·4	−0·4	−0·4 (1)	−0·4	−0·4	−0·4 (1)	−0·4	−0·4	−0·4 (1)	−0·4	−0·4	
β(O)	5·9 (5)	8·0 (5)	5·3 (5)	6·4 (4)	8·3 (4)	5·6 (4)	5·5 (5)	8·1 (5)	4·9 (5)	6·1 (4)	8·3 (4)	5·5 (4)	0·42 (2)
	−0·1 (4)	0·8 (4)	0·2 (4)	−0·1 (3)	0·8 (4)	0·3 (4)	−0·2 (4)	0·7 (5)	0·3 (4)	−0·1 (3)	0·9 (4)	0·3 (3)	

The columns in this table correspond to the following extinction models: (1) Secondary extinction (Zachariasen, 1967). (2) Secondary extinction with Borrmann correction (Zachariasen, 1968), $r_B^*=0{\cdot}5$. (3) Primary and secondary extinction with two parameters (Becker & Coppens, 1974) Gaussian distribution. (4) As 3 but with Borrmann correction. (5) As 4 but isotropic temperature factors. All values of r^*, r_B^*, t_B and t are given in terms of 10^{-4} cm.

ulated ($\mu R=4$). The agreement is not very good $[R_w(F^2)=0{\cdot}057]$ in this case and large discrepancies are observed for the strongest reflexions (Table 4).

Columns 2.4 and 2.5 contain the results of the most extensive extinction treatment. In addition to the treatment of 2.3 anomalous transmission was included. In this case the value r_B^* for the Borrmann correction has to be replaced by the two constants t_B and g_B. The best R value was obtained for the Gaussian distribution, the Lorentzian case resulted in divergence. The refined values of $t=7{\cdot}04\times10^{-4}$ cm and $g=5{\cdot}41$ indicate that the crystal is best described as a type II crystal. The refinement with both anisotropic (col. 2.4) and isotropic (col. 2.5) temperature factors resulted in a good agreement between the introduced constant values of t_B and g_B and the refined quantities of t and g. The agreement for the strongest reflexions (Table 4) is much better than in all previous cases.

Table 3. *Extinction values for some reflexions*

$h\ k\ l$	Primary extinction y_p	Secondary extinction y_{s+1}	Secondary extinction y_{s-1}	Total extinction with Borrmann effect y	$\frac{10^{-3}F_o^2}{k^2y}$	$10^{-3}F_c^2$
4 0 0	0·83	0·30	0·20	0·24	600	575
4 2 0	0·84	0·20	0·35	0·31	517	527
4 4 4	0·83	0·22	0·44	0·41	629	564
6 4 0	0·83	0·41	0·24	0·35	646	589
8 0 0	0·70	0·36	0·12	0·37	1186	1230
8 4 2	0·91	0·45	0·61	0·58	261	271
8 8 0	0·79	0·50	0·23	0·48	770	750
8 8 8	0·84	0·60	0·34	0·58	589	539
16 0 0	0·89	0·69	0·48	0·69	342	348
16 8 0	0·89	0·70	0·51	0·69	357	351
16 8 8	0·91	0·76	0·60	0·74	275	266

Results and discussion

We show in Table 3 the values for the parameters of primary (y_p) and secondary (y_s) extinction corresponding to column 4 of Table 2, together with the agreement obtained between observed and calculated F^2 values. We give in Table 4 these same reflexions for a Z1 treatment (col. 2.1), a BC-development without anomalous transmission and the complete refinement corresponding to the parameters of col. 2.4 It may be noted that the BC treatment does not give a better agreement for the strong reflexions despite a more rigorous calculation. We think that the missing θ-dependence in the Z1 development partly counterbalances the Borrmann effect. It is seen that the last model corrects best for extinction even if the agreement is slightly worse than the overall R value for all 503 reflexions. Table 5 shows the parameters related to the Borrmann effect correction for the same 11 reflexions. It may be noted that the relevant factor for this correction $A_{+1}+A_{-1}/2A_0$ has a maximum value of 4·01.

Table 4. *Observed and calculated F^2 values for the strongest reflexions for different extinction models*

The observed values are expressed as $10^{-3}\,F_o^2/k^2y$.

	(Z1) without Borrmann effect Table 2·1		(BC) without Borrmann effect Table 2·3		(BC) with Borrmann effect Table 2·4	
$h\ k\ l$	F_o	F_c	F_o	F_c	F_o	F_c
4 0 0	558	574	554	575	600	575
4 2 0	556	527	547	528	517	527
4 4 4	703	564	719	566	629	564
6 4 0	608	590	628	591	646	589
8 0 0	1545	1232	1878	1237	1186	1230
8 4 2	265	271	256	272	261	271
8 8 0	832	751	882	753	770	750
8 8 8	605	540	620	542	589	539
16 0 0	349	349	353	351	342	348
16 8 0	357	353	364	356	357	351
16 8 8	273	267	280	271	275	266
$R(F^2)$	0·16		0·26		0·056	

Table 5. *Value of the Borrmann effect for some reflexions*

$h\ k\ l$	$r_B^*[10^{-4}$ cm] introduced into Borrmann effect	$r^*[10^{-4}$ cm]	$\bar{\kappa}_K$	$\frac{A_{+1}+A_{-1}}{2A_0}$
4 0 0	1·02	1·03	0·56	1·29
4 2 0	1·12	1·13	0·54	1·62
4 4 4	1·60	1·63	0·52	1·96
6 4 0	1·65	1·68	0·53	1·47
8 0 0	1·77	1·81	0·60	4·01
8 4 2	1·93	1·99	0·42	1·24
8 8 0	2·18	2·25	0·49	2·25
8 8 8	2·39	2·49	0·40	1·69
16 0 0	2·52	2·63	0·32	1·38
16 8 0	2·60	2·72	0·27	1·30
16 8 8	2·65	2·79	0·21	1·21

Table 6. *Previous refinements on yttrium iron garnet and gadolinium iron garnet* (GdIG)

(Standard deviations in parentheses)

Reference and substance	x	y	z	B_{Ox}	B_{FeO}	B_{FeT}	B_{T}
Geller & Gilleo (1957) YIG	−0·0274 (9)	0·0572 (9)	0·1492 (9)	2·05	0·631	0·631	0·161
Weidenborner (1961) GdIG	−0·0269 (7)	0·0550 (5)	0·1478 (5)	1·32	0·49	0·49	0·25
Batt & Post (1962) YIG	−0·0269 (1)	0·0581 (3)	0·1495 (1)				
Euler & Bruce (1965) YIG	−0·0270 (4)	0·0569 (5)	0·1505 (5)	0·66 (13)			
Present work YIG	−0·0271 (1)	0·0567 (1)	0·1504 (1)	0·42 (2)	0·35 (1)	0·34 (1)	0·30 (1)

The positional and isotropic thermal parameters are compared in Table 6 with previous results on YIG. Positional parameters, distances and angles are in close agreement with the work of Euler & Bruce (1965). These authors quoted, however, only the thermal parameter for oxygen as they worked on class (*a*) reflexions alone. The large discrepancy between the isotropic temperature factor of oxygen as given by Euler & Bruce on the one hand and Geller & Gilleo (on YIG) and Weidenborner (1961) (on GdIG) on the other was not acceptable for an appropriate correction of the polarized neutron data.

It should be noted that all these models are based on mathematical (Gaussian or Lorentzian distribution) or physical assumptions (mosaic blocks) which only give an image of the reality. The work of Schneider (1974, 1975) with γ-ray diffraction has in fact shown that the distribution cannot be described by simple mathematical distribution laws. Furthermore this author has shown that the inhomogeneity may play an important part in the extinction process for several samples. As already stated earlier a fairly homogeneous distribution has been found for another crystal of YIG which was however cut from the same specimen. The experimental value of the mosaic spread deduced from the γ-ray measurements is inferior to 10″ and a value of this order is calculated from the refined r^* parameter. But even if the model calculations do not describe the real situation we have shown that they are adequate in giving a good agreement between observed and calculated intensities.

Table 7 shows a comparison between interatomic distances and angles from Euler & Bruce (1965) and the present work.

Table 7. *Interatomic distances and angles*

(Standard deviations in parentheses)

		Euler & Bruce (1965)	Present work
Cation–anion			
	(tet) *d–h*	1·866 (5)	1·865 (1)
	(oct) *a–h*	2·019 (6)	2·017 (1)
	(dod) *c–h*	2·434 (6)	2·436 (1)
		2·356 (5)	2·357 (1)
Anion–anion			
shared	(tet, dod)	2·837 (12)	2·837 (2)
	(oct, dod)	2·692 (9)	2·692 (2)
	(dod, dod)	2·783 (12)	2·789 (2)
unshared	(tet)	3·148 (9)	3·146 (2)
	(oct)	3·010 (11)	3·005 (2)
	(dod)	2·975 (10)	2·976 (2)
Angles			
	a–h–d	125·8 (3)	125·9 (1)
	a–h–c	104·2 (2)	104·3 (1)
	a–h–c	101·5 (2)	101·5 (1)
	a–h–c	93·5 (2)	93·5 (1)
	d–h–c	123·0 (3)	123·0 (1)
	c–h–c	104·6 (2)	104·5 (1)

d: Fe^{3+} in 24 (*d*)
a: Fe^{3+} in 16(*a*)
c: Y^{3+} in 24 (*c*)
h: O^{2-} in 96(*h*)

A remark on thermal diffuse scattering (TDS)

We did not make a correction for TDS but made an estimation which shows that this effect is weak in our case. In fact we may represent the TDS by a factor α which gives

$$I_{\text{corr}} = I_B(1+\alpha) \qquad (26)$$

The error on the thermal parameters is in an isotropic approximation and for a spherical scan (Willis, 1972)

$$\Delta B = \frac{8\pi k_B T}{\lambda c}\left(\frac{2}{9}\,\frac{\omega\psi_1\psi_2}{\pi}\right)^{1/3} \qquad (27)$$

with k_B the Boltzmann constant, T the absolute temperature, λ the wavelength and c a function of the elastic constants. The experimental conditions are described by the scan range ω and the horizontal ψ_1 and vertical ψ_2 opening angles of the counter as seen from the sample ($\psi_1 \simeq \psi_2 \simeq 1°$). For a Bragg angle of $\theta = 45°$ we have a scan range of $\omega = 1°$. With the elastic constants measured by Nilsen, Comstock & Walker (1965) we estimated the error of the isotropic thermal parameter to be $\Delta B = 0{\cdot}01$ Å. This means that the error made by neglecting a TDS correction is of the order of a standard deviation.

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The Crystal and Molecular Structure of Benzoyl-DL-leucylglycine Ethyl Ester

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The crystal structure of the modified dipeptide benzoyl-DL-leucylglycine ethyl ester has been determined by direct methods and refined by full-matrix least-squares calculations to $R=0.0388$ for 2496 observed reflexions. The crystals are monoclinic, $P2_1/n$, $a=15.104$ (8), $b=16.631$ (9), $c=14.700$ (8) Å, $\beta=91.28$ (2)° with two molecules per asymmetric unit. These two molecules have slightly different conformations and pack in the crystal in a manner similar to a twisted parallel pleated sheet.

Introduction

The structure of benzoyl-DL-leucylglycine ethyl ester (Fig. 1) has been determined and compared with similar structures of heavy-atom derivatives (Rao, 1969; Chandrasekaran & Subramanian, 1969). The presence of two molecules in the asymmetric unit allows an internal check of molecular parameters and also a comparison with related structures.

Experimental

Transparent lath-shaped crystals were obtained from ethanol/benzene. Preliminary precession photographs indicated space group $P2_1/n$ and cell dimensions obtained by least-squares refinement of the θ values of 20 reflexions on a four-circle diffractometer were $a=15.104$ (8), $b=16.631$ (9), $c=14.700$ (8) Å, $\beta=91.28$ (2)°. The crystal density by flotation in aqueous KI solution was 1.151 g cm^{-3} indicating an asymmetric unit molecular weight of 640, *i.e.*, two molecules of $C_{17}H_{24}N_2O_4$ per asymmetric unit. The absorption

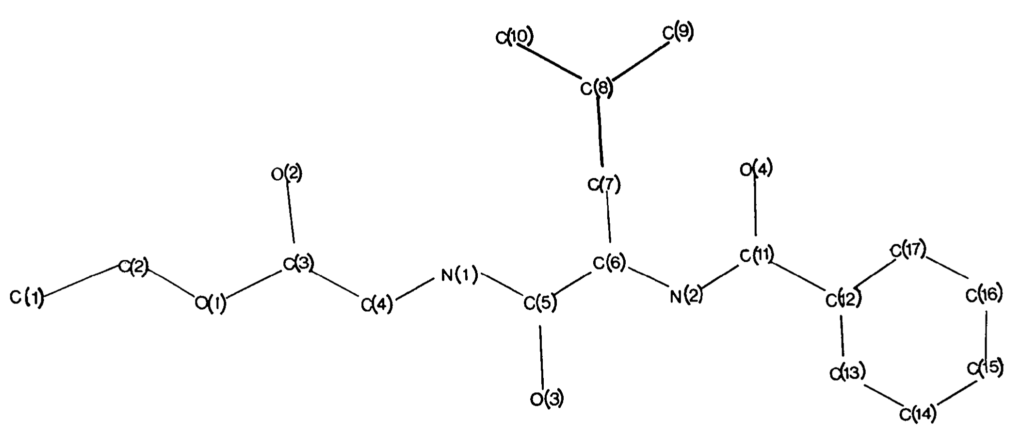

Fig. 1. Benzoylleucylglycine ethyl ester numbering scheme for non-H atoms.

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