1959) only the average-multiple test (Wilson, 1950) can be applied when the material consists of atoms of different weights. Moreover, the scope of the latter test is fairly restricted because it cannot be used to detect centres of symmetry — except, sometimes, indirectly — and because it involves types of reflexions which are frequently too small in number to give statistically significant results.

Wherever possible, moment tests — and, indeed, other statistical tests — should be performed with three-dimensional (hkl) reflexions rather than reflexions with one or two indices zero. The larger number of reflexions available permits more reliable statistical averaging; in addition, the results are less likely to be seriously influenced by hypersymmetry, by the overlap of atoms in projection and by the inadequate statistical averaging which may occur if a heavy atom happens to fall, in projection, near a special position.

When present, hypersymmetry invariably increases the moments of centrosymmetrical structures, but since statistical tests are usually made on unknown structures it is, in general, impossible to allow for hypersymmetry quantitatively.

Overlap may raise or lower moments, depending upon the space group, but the errors which it introduces are likely to be important only with one-dimensional data, or two-dimensional data from crystals with unit cells containing a small number of atoms or one very heavy atom.

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The Secondary Extinction Correction

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It is shown that Darwin's formula for the secondary extinction correction, which has been universally accepted and extensively used, contains an appreciable error in the X-ray diffraction case. The correct formula is derived.

As a first order correction for secondary extinction Darwin showed that one should use an effective absorption coefficient $\mu + gQ$ where an unpolarized incident beam is presumed. The new derivation shows that the effective absorption coefficient is $\mu + 2gQ(1 + \cos^4 2\theta)/(1 + \cos^2 2\theta)^2$, which gives $\mu + gQ$ at $\theta = 0°$ and $\theta = 90°$, but $\mu + 2gQ$ at $\theta = 45°$.

Darwin's theory remains valid when applied to neutron diffraction.

Introduction

The effect of secondary extinction on the integrated intensity of X-ray diffraction in mosaic crystals was first studied in detail by C. G. Darwin (1922), and the formulas derived by him have been used extensively throughout the last forty years.

Recently this writer found that the Darwin equations did not give agreement with precise intensity measurements. As a consequence a reexamination of the theory was undertaken. It was found that the polarization of the X-ray beams was incorrectly treated in Darwin's paper and in all subsequent theoretical work on secondary extinction. The correct formulas have been derived and have been found to give agreement with experiment. Since the new theoretical treatment of secondary extinction requires significant modifications of equations in general use, the results of the reexamination will be given in some detail in the present article.

1. The ideal mosaic crystal

It is convenient first to review well known results for X-ray diffraction in the ideal mosaic crystal. Throughout the article it will be assumed that all observations are made in the equator plane, *i.e.* the plane containing directions of incidence and diffraction.

If the incident beam is linearly polarized, one must specify the polarization angle φ which the electric vector makes with the normal to the equator plane. For general polarization one needs to know the intensity distribution $I_0(\varphi)d\varphi$, the integral over which gives the total incident intensity. It is permissible to resolve the electric vector into normal ($\varphi=0$) and parallel ($\varphi=\pi/2$) components and to set for the total incident intensity $I_0=I_0(0)+I_0(\pi/2)$.

When the incident beam is linearly polarized at angle φ, it follows that $I_0(0)=I_0\cos^2\varphi$ and $I_0(\pi/2)=I_0\sin^2\varphi$. For an unpolarized incident beam $I_0(0)=I_0(\pi/2)=\frac{1}{2}I_0$, and when the incident beam is produced by reflection under a glancing angle θ_0 from a monochromator crystal (in the same equator plane) one has

$$I_0(0)=I_0/(1+\cos^2 2\theta_0) \quad \text{and}$$
$$I_0(\pi/2)=I_0\cos^2 2\theta_0/(1+\cos^2 2\theta_0).$$

The total diffracted power, $\delta R(\varphi)$, due to a crystal of volume δV, so small that all power losses are negligible, is

$$\delta R_0(\varphi) = I_0(\varphi)Q(\varphi)\delta V$$
$$Q(\varphi) = Q(0)\{\cos^2\varphi+\sin^2\varphi\cos^2 2\theta\}$$
$$Q_0 = Q(0) = |Ne^2F/mc^2|\lambda^3/\sin 2\theta . \quad (1)$$

For an unpolarized incident beam equation (1) takes the form

$$\delta R_0 = I_0Q_0p_1\delta V$$
$$p_1 = (1+\cos^2 2\theta)/2 , \quad (1a)$$

and this equation will be valid also for monochromatized incident beams if p_1 is replaced by p_1', where

$$p_1' = (1+\cos^2 2\theta_0\cos^2 2\theta)/(1+\cos^2 2\theta_0) . \quad (1b)$$

Power losses due to diffraction are by definition negligible in the ideal mosaic crystal. Integrating equation (1) and taking account of ordinary absorption one finds

$$R_0(\varphi) = I_0(\varphi)Q(\varphi)VA(\mu)$$
$$A(\mu) = V^{-1}\int \exp[-\mu(T_1+T_2)]dV. \quad (2)$$

V is the irradiated volume of the crystal, and A is the transmission factor. For an unpolarized incident beam

$$R_0=I_0Q_0VAp_1 \quad (2a)$$

where p_1 must be replaced by p_1' if a monochromator is used.

It is useful to list the specific form of equation (2a) for symmetrical diffraction by a plane parallel plate

of thickness T_0 which completely covers the incident beam. These equations are:

Laue case

$$R_0=P_0Q_0p_1T\exp(-\mu T)$$
$$T = T_0/\cos\theta , \quad (2b)$$

Bragg case, $\mu T_0\gg 1$

$$R_0=P_0Q_0p_1/2\mu , \quad (2c)$$

where $P_0=SI_0$ is the total power of the incident beam, S being its cross section.

2. Secondary extinction

The equations given in § 1 are obviously approximations since the X-ray beams in traversing the crystal must lose some power through the diffraction process.

In part A of this section the exact solution to the diffraction problem in a plane parallel plate will be given, while in part B an approximate solution will be derived for the general case of arbitrary crystal shape.

Let $W(\varDelta)$ be the distribution function which characterizes the misalignment of the mosaic blocks in the crystal specimen, $\varDelta$ being the angular deviation from the mean. The considerations will be restricted to the case of small secondary extinction, implying that the width of W is large compared to the width of the diffraction peak for a single mosaic block.

Suppose that the incident direction makes a sharply defined glancing angle θ with the mean orientation of a lattice plane for which the ideal Bragg angle is θ_B. The expectation value for the power diffracted by a volume element is then

$$dP(\theta,\varphi)=I_0(\varphi)\sigma(\varphi,\theta)dV$$
$$\sigma(\varphi,\theta)=W(\theta_B-\theta)Q(\varphi) , \quad (3)$$

where P and I_0 are measured at the volume element.

2A. The plane parallel plate

The diffraction problem for the plane parallel plate was investigated and solved by C. G. Darwin (1922). A somewhat different derivation, which led to identical results, was later made by this writer (Zachariasen, 1945). However, both of these workers made the same error in taking account of the polarization of the incident beam.

The derivation to follow will adhere closely to that previously given by the writer, except that the error will be corrected and the notation modified. (The symbols $\gamma\sigma, T, P_0, P$ of the earlier work correspond to the quantities $\sigma(\varphi), \gamma T, P_0(\varphi), P(\varphi)$ as used in the present article. A prefix Z is used in references to equations given in the earlier publication.)

The equations which $P_0(\varphi, T)$ and $P(\varphi, T)$ must satisfy are (see $Z4\cdot21$)

$$dP_0=-[\mu+\sigma(\varphi)]P_0dT+\sigma(\varphi')PdT$$
$$dP = \mp[\mu+\sigma(\varphi')]PdT\pm\sigma(\varphi)P_0dT. \quad (4)$$

In these equations T is the distance of travel of the incident beam into the crystal. The upper sign refers to Laue and the lower sign to Bragg reflection. The terms involving $\sigma(\varphi')$ correspond to diffraction of the diffracted beam, so that φ and φ' are related as follows

$$\cos \varphi' = \cos \varphi/[\cos^2 \varphi + \sin^2 \varphi \cos^2 2\theta]^{\frac{1}{2}}. \quad (5)$$

Thus $\varphi' = \varphi$ only when $\varphi = 0$ or $\pi/2$, i.e. for normal or for parallel linear polarization of the incident beam.

Equations (5) have been solved exactly for the case $\varphi' = \varphi$ (see Z4·24–30), and these solutions are:

Laue case

$$P = P_0 \exp[-(\mu+\sigma)T] \sinh(\sigma T),$$
$$P = P_0 T \exp(-\mu T)[\sigma - \sigma^2 T + \tfrac{2}{3}\sigma^3 T^2 + \ldots],$$
$$T = T_0/\cos\theta, \quad (6)$$

Bragg case, $\mu T_0 \gg 1$

$$P = P_0[\mu + \sigma - \{(\mu+\sigma)^2 - \sigma^2\}^{\frac{1}{2}}]/\sigma,$$
$$P = P_0(2\mu)^{-1}[\sigma - \sigma^2/2\mu + 5\sigma^3/8\mu^2 + \ldots]. \quad (7)$$

It must be remembered that P, P_0, σ in equations (6) and (7) refer either all to $\varphi = 0$, or all to $\varphi = \pi/2$, and that σ is a function of θ, σ having appreciable value only for $\theta \approx \theta_B$.

It is convenient to use new symbols R, g_n, p_n and p_n' defined as follows

$$R = \int P\,d(\theta - \theta_B), \quad g_n = \int W^n d(\theta - \theta_B),$$
$$p_n = (1 + \cos^{2n} 2\theta)/2,$$
$$p_n' = (1 + \cos^2 2\theta_0 \cos^{2n} 2\theta)/(1 + \cos^2 2\theta_0) \quad (8)$$

where one notes that $g_1 = 1$, and that p_1 and p_1' agree with previous definitions.

Integration of equations (6) and (7) and addition of normal and parallel components give as result

$$R/P_0 = R_0/P_0[1 - \alpha_2(R_0/P_0) + \alpha_3(R_0/P_0)^2 + \ldots]. \quad (9)$$

R_0/P_0 are the quantities given by equations (2b) and (2c) while

	Laue case	Bragg case
$\alpha_2 =$	$g_2(p_2/p_1^2) \exp(\mu T)$	$2g_2(p_2/p_1^2)$
$\alpha_3 =$	$(\tfrac{2}{3})g_3(p_3/p_1^3) \exp(2\mu T)$	$5g_3(p_3/p_1^3)$. $\quad (9a)$

For the monochromator case p_n' everywhere replaces p_n in the above equations.

The previous treatments by Darwin and this writer gave the results of equation (9a) if one sets $p_2/p_1^2 = p_3/p_1^3 = 1$. However, this is not permissible for p_2/p_1^2 increases from 1 at $2\theta = 0$ to 2 at $2\theta = \pi/2$, p_3/p_1^3 from 1 to 4.

2B. Arbitrary crystal shape

In the following an approximate solution, good to the first order correction term, will be given for a crystal of any shape. The approximation to be made is this: for X-ray beams traversing the crystal power losses due to absorption and diffraction are considered, but power gains from double diffraction are neglected. It is thus assumed that

$$dP_0(\varphi) = -[\mu + \sigma(\varphi)]P_0 dT$$
$$dP(\varphi) = -[\mu + \sigma(\varphi')]P\,dT. \quad (10)$$

In other words terms in σ^2 are neglected.

If the considerations are restricted to either normal or parallel linear polarization, the integration of equations (10) gives

$$P = I_0 \sigma V A(\mu + \sigma). \quad (11)$$

In the X-ray case $\mu \gg \sigma$ so that

$$A(\mu + \sigma) \approx A + \sigma\,dA/d\mu. \quad (12)$$

where it is senseless to include quadratic terms since in equation (10) such terms were neglected.

Integration of equation (11) and addition of normal and parallel components give

$$R/I_0 \approx R_0/I_0[1 - \alpha R_0/I_0]$$
$$\alpha = S^{-1}\alpha_2 = g_2(p_2/p_1^2)V^{-1}dA^*/d\mu. \quad (13)$$

R_0/I_0 is given by equation (2a), $A^* = A^{-1}$ is the absorption factor, and S is the cross section of that part of the incident beam which falls on the crystal. Again p_n' replaces p_n if a monochromator is used.

It is readily verified that equation (13) correctly gives equations (9) (to the first order expansion terms) when applied to a plane parallel plate.

Letting $Q = Q_0 p_1$ equation (13) can be rewritten in the form

$$R = I_0 Q V A(\mu') \quad (13a)$$

$$\mu' = \mu + g_2(p_2/p_1^2)Q \quad (13b)$$

where equation (13b) is the correct form for the old Darwin relation $\mu' = \mu + g_2 Q$.

Since intensity measurements are usually made on relative rather than absolute scale, it is useful to use equation (13) in the form

$$F_{\text{corr}} \approx K F_{\text{obs}}[1 + \beta_{(2\theta)}C J_{\text{obs}}]. \quad (14)$$

F_{obs} is the observed structure factor, F_{corr} the value corrected for secondary extinction, and J_{obs} the observed integrated intensity on arbitrary scale. K and C are scale factors to be adjusted, while $\beta(2\theta)$ takes account of the angular variation of the extinction correction and is assumed to be normalized to unity at $2\theta = 0$.

For an unpolarized incident beam the expression for $\beta(2\theta)$ is

$$\beta(2\theta) = \frac{2(1 + \cos^4 2\theta)}{(1 + \cos^2 2\theta)^2} \cdot \frac{A^{*'}(2\theta)}{A^{*'}(0)} \quad (15)$$

where $A^{*'}(2\theta)$ is the value of $dA^*/d\mu$ at 2θ and $A^{*'}(0)$ the value at $2\theta = 0$.

When a monochromator is used the expression for $\beta(2\theta)$ becomes

$$\beta'(2\theta) = \frac{(1+\cos^2 2\theta_0)(1+\cos^2 2\theta_0 \cos^4 2\theta)}{(1+\cos^2 2\theta_0 \cos^2 2\theta)^2} \cdot \frac{A^{*\prime}(2\theta)}{A^{*\prime}(0)} .$$
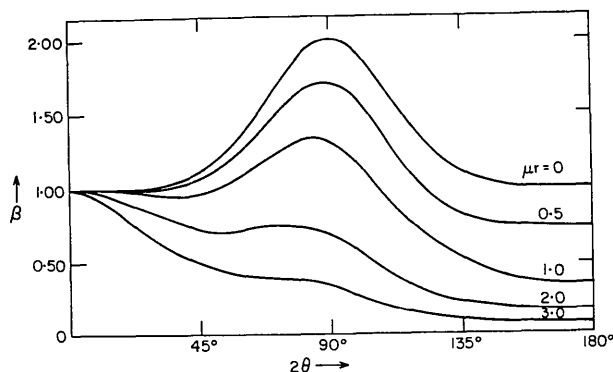
(15a)

Fig. 1. Variation of β with scattering angle for a crystal sphere of radius r, for selected values of μr.

Fig. 1 shows β as function of the scattering angle for a crystal sphere of radius r bathed in the incident beam for various values of μr. It is clearly illustrated that one cannot regard β as independent of scattering angle, as is usually assumed. For large values of μr for a crystal sphere one has $\beta(0)/\beta(\pi) = \frac{3}{2}(\mu r)^2$.

Equation (14) is probably a good approximation even for $\beta CJ \approx 1$, at small scattering angles and small values of μr or μT_0.

Consider the Laue and Bragg cases for which the second order correction terms have been given. Inversion of equation (9) gives

$$R_0/P_0 \approx R/P_0[1 + \alpha_2(R/P_0) + (2\alpha_2^2 - \alpha_3)(R/P_0)^2]. \quad (16)$$

Under the stated conditions one finds:

Laue case

$$R_0/P_0 \approx R/P_0[1 + g_2 R/P_0 + (2g_2^2 - \tfrac{2}{3}g_3)(R/P_0)^2]. \quad (17)$$

Bragg case

$$R_0/P_0 \approx R/P_0[1 + 2g_2 R/P_0 + (8g_2^2 - 5g_3)(R/P_0)^2]. \quad (18)$$

The approximation

$$F_{corr} \approx F_{obs}[1 + CJ] \quad (19)$$

(note that $\beta \approx 1$ for small 2θ and μT) is thus good to second order if the brackets on the right of equations (17) and (18) are perfect squares. This requires

Laue case	$g_3 = g_2^2 21/16 = 1\cdot31g_2^2$	
Bragg case	$g_3 = g_2^2 \ 7/5 \ = 1\cdot40g_2^2$.	(20)

It is reasonable to suppose that $W(\Delta)$ is an error function, and if so by equation (8), $g_3 = g_2^2 2(3)^{-\frac{1}{2}} = 1\cdot15g_2^2$. Thus the conditions of equation (20) are nearly fulfilled, and it appears that equation (19) can be used with some confidence even when $CJ \approx 1$.

Hamilton (1957) has made a detailed study of the effect of crystal shape on secondary extinction and

outlined a practical method for numerical solution of the problem. In the approximate solution of this paper the crystal shape effect is contained in the term $dA^*/d\mu$ of equation (13). Hamilton's results are valid for neutron diffraction; but in the case of X-ray diffraction the normal and parallel components must be considered separately and the components added at the end of the process. Thus the modifying factors p_n/p_1^n will again enter, although implicitly.

3. Experimental verification of the new formula

Experiments by the Manchester school of crystallographers during the nineteen twenties supposedly confirmed the Darwin formula for secondary extinction which is now known to be in error. (A good survey of this work is given by James, 1950.) However, in the Manchester experiments intensities were measured with adequate precision only at small scattering angles, so that no real test was made of a possible dependence of the extinction coefficient on scattering angle.

The new formula for secondary extinction derived in this paper ought to be checked by means of experiments carefully designed for this very purpose. This has not yet been done.

However, it was related in the introduction that the reexamination of the theory of secondary extinction was undertaken because discrepancy was observed between Darwin's formula and experimental results. The specific case of disagreement was the set of carefully measured integrated intensities for a crystal of $Be_2BO_3(OH)$, the mineral hambergite.

This crystal is of great hardness, so that the thermal intensity attenuation is small. The intensities were measured with a proportional counter, Cu $K\alpha$ radiation with unpolarized incident beam and a perfect crystal sphere for which $\mu r = 0\cdot69$. Under the circumstances strong reflections were observed over the entire scattering range. It was quickly apparent that there was considerable secondary extinction in the specimen in spite of surface grinding and thermal shock treatment in liquid nitrogen.

A very precise determination was made of the 24 positional degrees of freedom in the structure and of the 42 thermal parameters (the anisotropic coefficients for all but the hydrogen atoms) by means of least-square refinements based on the weak reflections for which secondary extinction is negligible. The structure factors corresponding to strong reflections, which were not used in the refinement, could thus be calculated with high accuracy. It was found, however, that the application of a secondary extinction correction to the strong reflections in accordance with the Darwin formula led to discrepancies of systematic nature.

Table 1 gives the observed integrated intensities (on arbitrary scale), the experimental and calculated

Table 1. *HK0 reflections*

| HK0	J_{obs}	F_{obs}	F_{corr}	KF_{calc}	HK0	J_{obs}	F_{obs}	F_{corr}	KF_{calc}
020	36	4·8	5·0	−4·6	4,10,0	20·8	9·7	10·0	−9·7
200	44	5·9	6·2	5·5	850	5·1	4·8	4·8	−4·5
210	458	20·0	30·1	−30·5	2,11,0	147	25·8	32·2	−35·1
220	976	32·0	66·3	−61·7	860	49	14·8	15·9	−16·0
230	1034	36·8	78·8	−74·1	690	2·0	3·0	3·0	2·7
040	489	25·7	39·5	−40·7	0,12,0	0·6	1·7	1·7	1·3
240	229	19·4	24·2	−23·8	4,11,0	1·1	2·2	2·2	−1·6
400	196	18·7	22·7	−22·3	870	64	16·5	18·1	−18·8
410	687	35·4	62·2	−62·1	2,12,0	0·1	0·7	0·7	0·3
420	97	13·8	15·2	−14·4	6,10,0	30·1	11·1	11·5	−11·9
250	314	25·4	34·2	−31·9	10,0,0	36·1	12·1	12·7	12·3
430	101	14·8	16·5	15·0	10,1,0	74	17·3	19·0	−19·0
060	211	21·8	26·9	25·9	10,2,0	54	14·6	15·7	15·9
440	316	27·9	37·7	37·0	880	0·2	0·9	0·9	0·8
260	46	10·8	11·3	10·4	10,3,0	1·0	2·0	2·0	1·3
450	445	35·3	54·3	51·9	4,12,0	4·7	4·2	4·2	−3·5
270	192	24·0	29·8	28·2	10,4,0	18·3	8·1	8·3	−8·0
600	106	18·0	20·4	20·5	2,13,0	19·7	8·3	8·5	−8·6
610	91	16·8	18·8	−18·3	6,11,0	13·4	6·8	6·9	6·4
620	109	18·7	21·3	−21·1	890	2·5	2·9	2·9	−2·2
460	64	14·4	15·6	14·8	10,5,0	44	12·0	12·5	12·5
080	314	32·3	45·8	−46·7	10,6,0	85	15·6	16·9	−17·0
630	72	15·6	17·1	16·2	4,13,0	85	15·4	16·7	−17·0
280	13·5	6·9	7·0	−6·1	0,14,0	376	32·0	43·1	−43·8
470	13·7	7·2	7·3	6·3	8,10,0	62	12·7	13·5	13·5
640	132	21·9	26·0	25·3	6,12,0	0·1	0·6	0·6	0·5
650	15·2	7·7	7·9	−7·2	2,14,0	43	10·3	10·7	−10·5
290	0·3	1·2	1·2	1·2	10,7,0	6·3	3·9	3·9	−3·4
480	172	26·6	33·8	−33·7	10,8,0	150	16·3	18·1	18·4
660	287	34·7	50·7	51·4	4,14,0	143	15·9	17·5	16·5
0,10,0	130	23·8	28·7	29·7	8,11,0	3·9	2·6	2·6	−1·6
800	0·6	1·6	1·6	1·9	6,13,0	5·3	2·9	2·9	2·7
810	50	14·9	16·1	16·4	12,0,0	71	10·6	11·1	11·3
820	12·8	7·5	7·7	−7·5	12,1,0	169	16·1	18·0	−18·5
670	272	34·8	50·9	−50·6	12,2,0	0	nil	nil	0·3
490	182	28·4	37·2	37·6	2,15,0	37	7·0	7·2	7·6
2,10,0	167	27·3	35·1	35·3	12,3,0	154	13·5	14·9	−15·0
830	129	24·1	29·4	30·9	10,9,0	258	16·3	19·0	18·9
840	71	17·9	20·1	−20·8	12,4,0	13·4	3·4	3·4	−3·6
680	99	21·3	24·9	−24·9					
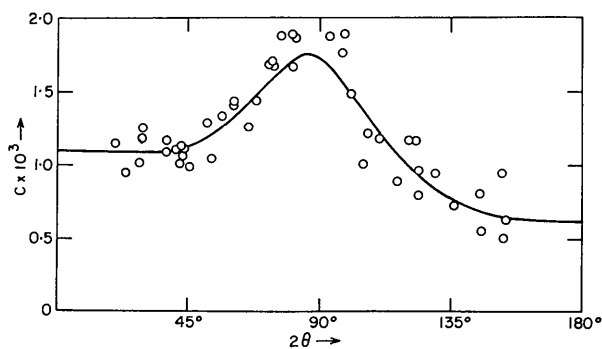
Fig. 2. Experimental values βC obtained with a sphere of hambergite for which $\mu r = 0.69$. The curve is the theoretical one, calculated with $C = 1.1 \times 10^{-3}$.

structure factors for all reflections $(HK0)$. It is seen that there is very good agreement for small structure factors, but that the calculated values are consistently higher for the strong reflections. Agreement for the latter cannot be obtained by means of the Darwin formula. Fig. 2 plots the actual values of $\beta(2\theta)C$ resulting from the data of Table 1 (and for other strong reflections from the three-dimensional set of data), while the curve in Fig. 2 is the theoretical curve calculated in accordance with equation (15), using the value $C = 1.1 \times 10^{-3}$. Conversely, the last column of Table 1 gives the corrected F values based on the use of equation (15) and the value of C given above.

A least-square refinement based on these corrected F values (for the full three-dimensional set of 437 reflections) gave the low conventional R value of 0·041.

The standard error for bond lengths attained in the last refinement was 0·004 Å for B–O and Be–O bonds, 0·04 Å for the H–O bond and 0·002 Å for O–O distances.

Note added in proof.— The writer regrets having overlooked a paper by Chandrasekhar (1960), in which it is correctly stated (equation 9) that the proper procedure for handling extinction is to take the mean integrated reflection for parallel and perpendicular components. Thus equation (9) gives the correct formula for the symmetrical Bragg case.

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The Structure and Birefringence of Hambergite, Be₂BO₃.OH

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Be₂BO₃(OH) is orthorhombic with four molecules in a cell of dimensions $a = 9\cdot755$ Å, $b = 12\cdot201$ Å, $c = 4\cdot426$ Å. The space group is *Pbca* with all atoms in general positions.
The structure has been redetermined with high precision ($R = 0\cdot04$). Bond lengths are:

$$\text{Be–4O} = 1\cdot633 \text{ Å}, \text{ B–3O} = 1\cdot367 \text{ Å}, \text{ H–O} = 0\cdot93 \text{ Å}, \text{ H}\cdots\text{O} = 2\cdot04 \text{ Å}.$$

Refractive indices calculated from the structure agree well with measured values.

Introduction

The approximate crystal structure of the mineral hambergite, Be₂BO₃(OH), was reported thirty years ago (Zachariasen, 1931). The original intensity data were crude. As a consequence the results as to bond lengths were quite inaccurate, and the position of the hydrogen atom was assumed rather than deduced from experiment.

It seemed desirable to make a precise determination of the hambergite structure using modern techniques to measure intensities. In the first place it was of interest to obtain accurate values for the Be–O and B–O bond lengths. Second, infrared studies had indicated a bond angle for hydrogen considerably smaller than the 180° usually found in the O–H $\cdots$ O bond. Third, an accurate knowledge of the structure could be used to calculate the birefringence of the crystal in a situation where the anisotropic components were not all parallel. The results of the refinement of the structure are presented in the following, together with results of a calculation of the refractive indices of the crystal from the refined structure.

The essential features of the 1931 structure determination have been confirmed; but there is considerable difference in detail.

The refinement of the structure

New values for the cell dimensions are

$$a = 9\cdot755 \pm 0\cdot001, \ b = 12\cdot201 \pm 0\cdot001,$$
$$c = 4\cdot426 \pm 0\cdot001 \text{ Å}.$$

The cell contains four molecules, the space group is *Pbca*, and all atoms are in general positions.

The intensities were measured with an incident beam of unpolarized Cu $K\alpha$ X-rays, a proportional counter, and a crystal (selected from the original Madagascar material) shaped into a perfect sphere of radius $r = 0\cdot0314$ cm, corresponding $\mu r = 0\cdot69$. All reflections *HK*0, *HK*1, *H*0*L*, *H*1*L*, *H*2*L*, 0*KL*, 1*KL* were measured.

It was quickly found there was considerable secondary extinction in the specimen, in spite of surface grinding and thermal shock treatment in liquid nitrogen. In the early refinement stages only the weak reflections were therefore used. Since one of the objects of the study was the direct location of the hydrogen atom, it became essential to make corrections for secondary extinction in subsequent refinements. It was then found that the commonly used correction formula was in error (Zachariasen, 1963), and the revised equation was used in the ultimate least-square refinement.

The Busing–Levi IBM-704 program was used with the f curves (for neutral atoms) given in the *International Tables for X-Ray Crystallography*. The initial atomic coordinates were those of the 1931 paper with the hydrogen atom placed midway between two O$_{\text{IV}}$ atoms. An isotropic temperature factor, with $B = 2\cdot0$ Å², was assumed for the hydrogen atom. In the last refinements all (24) position parameters, 42 anisotropic thermal parameters (for all but the hydrogen atoms) and 4 scale factors were varied simultaneously. Only the final refinement included extinction correction in accordance with the true