Acta Cryst. (1960). **13**, 588

An Experimental Method of Correcting for Extinction in Crystals

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(*Received* 12 *November* 1959)

The paper deals with an experimental method of correcting for extinction errors by the use of polarized X-rays. It involves an accurate study of the variation of the integrated reflection with angle of polarization. The theory and limits of applicability are discussed in detail. It is shown experimentally that the method is feasible when intensity measurements are made with high precision. The principal merit of the technique is that it accounts in certain circumstances for both primary and secondary extinction simultaneously in a crystal of any shape.

Introduction

Most crystals approximate more closely to the ideal mosaic than to the ideally perfect type in so far as their properties of reflecting X-rays are concerned. As a rule they exhibit a small amount of extinction which reduces the intensities of the strongest reflections by about 30%. Some crystals show more pronounced extinction effects, but usually such specimens may be rendered imperfect by grinding or by thermal shock produced by immersion in liquid air. Although it is possible to reduce extinction by such treatment, one can rarely be certain of having eliminated it altogether. Extinction is one of the major sources of error in the determination of a set of structure factors. In crystal analysis it is often found that in the final stages of refinement the calculated structure factors (F_c) for the strongest reflections tend to be greater than the corresponding observed values (F_o). It is generally assumed that this is caused by extinction. The usual procedure is to replace F_o by F_c for these reflections, or to weight the difference between them suitably, before completing the refinement. Such methods, which seek to correct for extinction by a comparison of F_o and F_c, may prove to be efficacious for obtaining the atomic coordinates, but in all of them it is taken for granted that the assumed scattering factors, which are based on the theoretical calculations for the free atom, are unaltered in the molecule or crystal. If, however, the object of the analysis is the accurate determination of the electron-density distribution and the outer electron configuration in the solid state, the expedient of replacing F_o by F_c is obviously unsatisfactory.

There have been very few attempts at making a direct experimental determination of extinction. The pioneering researches of W. L. Bragg, James and Bosanquet, and of others, on the secondary extinction in rock salt have been described in detail by James (1954; see also Cochran, 1953, for an extension of the method of Bragg *et al.* to small crystals). More recently, a method of correcting for primary extinction, which requires the measurement of the absolute integrated reflection for various wavelengths, has been applied by Weiss & De Marco (1958) to crystals of Cu, Ni, Co, Fe and Cr in order to determine their absolute scattering factors experimentally (see also Hume-Rothery, Brown, Forsyth & Taylor, 1958; Batterman, 1959; Weiss & De Marco, 1959). However, these methods are not satisfactory when both primary and secondary extinction exist in a crystal.

The influence of crystal perfection on the reflection of polarized X-rays has been investigated by Ramaseshan & Ramachandran (1953, 1954; see also Chandrasekaran, 1955, 1959). They studied the variation with angle of polarization of the integrated reflection from large crystals, first using the natural face and later after grinding it. They obtained the important result that the experimental variation for both the natural and the ground face lay between the theoretical curves for the ideally perfect crystal and the ideal mosaic respectively. The experimental points for the ground face lay close to the curve for the ideal mosaic, while those for the natural face were consistently higher, approaching the curve for the perfect crystal. They suggested that this fact could be used as a criterion for assessing the 'degree of perfection' of a crystal. The physical significance of this definition is, however, rather ambiguous. A high degree of perfection would seem to imply that the size of the perfect blocks constituting the mosaic is large (i.e. large primary extinction), whereas, as we shall see later, polarization measurements cannot in fact distinguish between primary and secondary extinction. Moreover, so far as the properties of reflecting X-rays are concerned, the degree of perfection of a crystal may vary a great deal from reflection to reflection. For instance, it is well known that a crystal may behave like an ideal mosaic for a very weak reflection and yet show considerable perfection (extinction) for a very strong one. This method of estimating the degree of perfection

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of a crystal is for this reason somewhat inconclusive.

In an earlier paper (1956), the author proposed a method of obtaining the true value of the structure factor in the presence of extinction by the use of polarized X-rays. The principal merit of this technique is that it accounts for both primary and secondary extinction simultaneously. In the present paper the theory and applicability of the method are discussed in greater detail. It is shown experimentally that the method is feasible when intensity measurements are made with high precision.

Theory

In X-ray analysis, the crystals employed are usually very small and completely bathed in the incident X-ray beam. We shall derive the theory for this particular experimental arrangement, but the equations may be readily modified for any other type of set up.

Let us assume in the first instance that the incident X-rays are polarized perpendicular to the plane of incidence, so that the polarization factor is unity. For a mosaic crystal of arbitrary shape and of volume V, completely bathed in the X-ray beam, the integrated reflection is given by

$$\varrho = AQV, \tag{1}$$

where

$$Q = \left(\frac{Ne^2}{mc^2}\right)^2 \frac{\lambda^3}{\sin 2\theta} |F|^2$$

(see, for instance, James, 1954, p. 41).

A is the absorption factor and may be expressed as

$$1/V \int \exp(-\mu r) dV,$$

where dV is a small element of volume in the crystal, r is the total path traversed by the beam in the crystal before and after reflection from the element of volume under consideration, and μ is the linear absorption coefficient for the wavelength λ. The integral can be evaluated by numerical methods if the shape of the crystal is known.

Let ϱ' be the integrated reflection in the presence of extinction. For primary extinction,

$$\varrho'/\varrho = 1-(A_0^2/3)\,, \tag{2}$$

to a first approximation, where

$$A_0 = \frac{Ne^2\lambda}{mc^2} \cdot \frac{t_0}{\gamma_0} \cdot |F|\,,$$

t_0/γ_0 being the effective thickness of the perfect blocks constituting the mosaic (see Chandrasekhar, 1956). Hence, we may write

$$\varrho' = \alpha|F|^2 - \beta|F|^4, \tag{3}$$

where α is known quantity, while β is unknown, since t_0/γ_0 is unknown.

If the crystal suffers from secondary extinction,

$$\begin{aligned}\varrho' &= Q \int \exp[-(\mu+gQ)r] dV \\ &= Q \int \exp(-\mu r) dV - gQ^2 \int r \exp(-\mu r) dV \end{aligned} \tag{4}$$

to a first approximation, where g is the secondary extinction coefficient. Again since $Q \propto |F|^2$, (4) may be expressed in the same form as (3), where, as before, α is known and β is unknown.

When both primary and secondary extinction exist simultaneously, it may be verified that, to a first approximation, the integrated reflection may still be represented by a formula of the type (3).

Therefore, whatever be the type of extinction present, the integrated reflection for normal polarization may be written as

$$\varrho'_{\perp} = \alpha|F|^2 - \beta|F|^4 \tag{5}$$

when the extinction is not large.* If, on the other hand, the incident beam is polarized parallel to the plane of incidence, the integrated reflection is obtained simply by replacing $|F|$ by $|F \cos 2\theta|$, since all other factors remain unchanged, and we have

$$\varrho'_{\parallel} = \alpha|F|^2 \cos^2 2\theta - \beta|F|^4 \cos^4 2\theta\,. \tag{6}$$

Eliminating β from (5) and (6), we get

$$|F|^2 = \frac{\varrho'_{\parallel} - \varrho'_{\perp} \cos^4 2\theta}{\alpha(\cos^2 2\theta - \cos^4 2\theta)}. \tag{7}$$

A measurement of the integrated reflection for X-rays polarized perpendicular and parallel to the plane of incidence should, therefore, enable one to eliminate extinction effects. Equation (7) was derived in the earlier paper for the symmetrical reflection from the face of a thick crystal and the symmetrical reflection through a plate of thickness T.

It is interesting to consider the problem from a slightly different standpoint. When the incident X-rays are unpolarized, the integrated reflection from an ideal mosaic may be written as

$$\begin{aligned}\varrho &= AV\left(\frac{Ne^2}{mc^2}\right)^2 \frac{\lambda^3}{\sin 2\theta} |F|^2 \left(\frac{1+\cos^2 2\theta}{2}\right) \\ &= R\left(\frac{1+\cos^2 2\theta}{2}\right), \text{ say}\,.\end{aligned}$$

If the incident X-rays are polarized at an angle φ with respect to the plane of incidence,

$$\varrho_{\varphi} = R\,(\sin^2\varphi + \cos^2\varphi \cos^2 2\theta)$$

(Ramaseshan & Ramachandran, 1954). For normal polarization ($\varphi = 90°$),

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* The same type of expression is valid for the integrated reflection from a crystal bathed in a neutron beam when the extinction (primary or secondary) is not large. The only difference in this case is that μ may be taken to be very nearly equal to zero (see Chandrasekhar & Weiss, 1957).

$$\varrho_\perp = R$$

$$\therefore \varrho_\varphi/\varrho_\perp = \sin^2\varphi + \cos^2\varphi\cos^2 2\theta\,. \tag{8}$$

Similarly, for an imperfect crystal exhibiting extinction, we have from (5) and (6)

$$\frac{\varrho'_\varphi}{\varrho'_\perp} = \frac{\{\alpha|F|^2(\sin^2\varphi+\cos^2\varphi\cos^2 2\theta) - \beta|F|^4(\sin^2\varphi+\cos^2\varphi\cos^4 2\theta)\}}{\{\alpha|F|^2-\beta|F|^4\}}\,. \tag{9}$$

Except for $2\theta=0°$, $90°$ and $180°$, (8) and (9) are different. Thus the ideal mosaic and the imperfect crystal exhibiting extinction may be expected to behave differently towards polarized X-rays. The variation of $\varrho'_\varphi/\varrho'_\perp$ with φ is shown in Figs. 1 and 2 for the 200 and 220 reflections of rock salt for $\lambda = 1{\cdot}5418$ Å (weighted mean of Cu $K\alpha_1$ and Cu $K\alpha_2$). The percentage of extinction in these curves is defined in terms of the reduction in intensity due to extinction for *normal* polarization; for example, the curve for 10% extinction is obtained by putting $\beta|F|^4 = 0{\cdot}1\alpha|F|^2$ in (9). These curves provide an alternative method of estimating extinction which involves the measurement of the variation of the integrated reflection with angle of polarization.

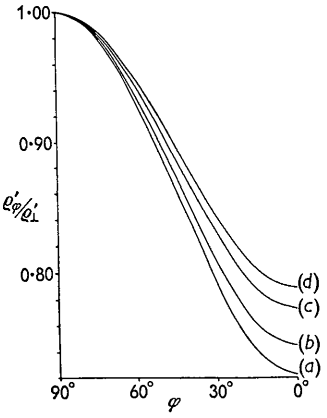

Fig. 1. $\varrho'_\varphi/\varrho'_\perp$ versus φ (theoretical) for 200 of rock salt ($2\theta = 31°\,48'$); (*a*) no extinction; (*b*) 10% extinction; (*c*) 20% extinction; (*d*) 25% extinction.

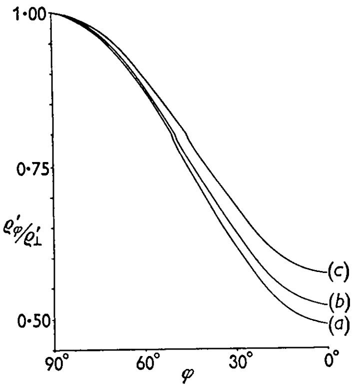

Fig. 2. $\varrho'_\varphi/\varrho'_\perp$ versus φ (theoretical) for 220 of rock salt ($2\theta = 45°\,34'$); (*a*) no extinction; (*b*) 10% extinction; (*c*) 25% extinction.

At first sight there appears to be no direct connection between our first approach to the problem (viz. equation (7)), and the work of Ramaseshan & Ramachandran (1954), but in the light of these theoretical curves, their experimental observations become significant. Although (7) provides a straightforward method of eliminating extinction and is theoretically simpler, the latter approach is superior from the point of view of experiment, since it requires the fitting of a theoretical curve through a *number* of observed points.

Accuracy of method

Since the theory makes use of the fact that the effective structure factor of a reflection is altered by varying the angle of polarization of the incident beam, the method will obviously be more powerful the greater the value of θ. This will be evident even from the curves in Figs. 1 and 2. For the 200 reflection, the presence of 25% extinction causes an increase in $\varrho_\parallel/\varrho_\perp$ of about 10% (of the mosaic value), whereas for the 220 reflection the increase is nearly 15%. For this reason the method will prove to be insensitive for very low Bragg angles, as can be judged from the curves in Figs. 3 and 4 for $2\theta = 20°$ and $10°$ respectively.

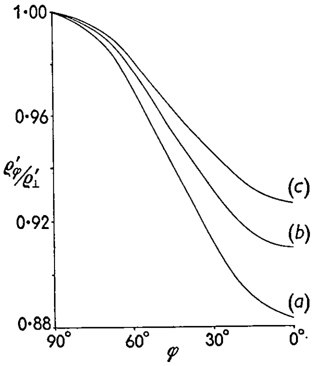

Fig. 3. $\varrho'_\varphi/\varrho'_\perp$ versus φ (theoretical) for $2\theta = 20°$: (*a*) no extinction; (*b*) 20% extinction; (*c*) 30% extinction.

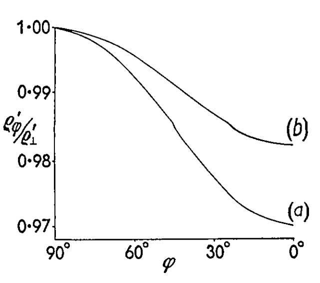

Fig. 4. $\varrho'_\varphi/\varrho'_\perp$ versus φ (theoretical) for $2\theta = 10°$; (*a*) no extinction; (*b*) 30% extinction.

It is also necessary to have an idea of the approximate limit to which (5) is valid. Let us first consider primary extinction. As remarked by Vand (1955), the formula for primary extinction for a crystal completely bathed in the incident X-ray beam will be that for the reflection through a thin plate, viz. Waller's formula. We shall accordingly consider the error involved in the approximation

$$\sum_{n=0}^{\infty} J_{2n+1}(2A_0)/A_0 \simeq 1-\tfrac{1}{3}A_0^2$$

used in (5). For small values of A_0,

$$\sum_{n=0}^{\infty} J_{2n+1}(2A_0)/A_0 = 1-\tfrac{1}{3}A_0^2+\tfrac{1}{20}A_0^4-\ldots,$$

but this series converges rather slowly for $A_0>1$. Hence to simplify computation we shall make use of the following approximation (Vand, 1955):

$$\sum J_{2n+1}(2A_0) \simeq A_0 \exp\left(-\tfrac{1}{3}A_0^2\right)$$

to a good accuracy over the range $0<A_0<2$. The numerical values are given in Table 1.

Table 1. *Primary extinction*

A_0	$\exp(-\frac{1}{3}A_0^2)$	$1-\frac{1}{3}A_0^2$
0·0	1·000	1·000
0·3	0·970	0·970
0·6	0·887	0·880
0·9	0·763	0·730
1·0	0·717	0·667
1·1	0·668	0·597
1·2	0·619	0·520
1·3	0·516	0·437

For about 25% extinction, the error in neglecting the higher terms is only about 4%; for 30% extinction it is about 7%.

For secondary extinction the approximation used is

$$\int \exp\left[-(\mu+gQ)r\right]dV \simeq \int \left[\exp(-\mu r)\right](1-gQr)\,dV \quad \text{(see (4))}.$$

If, for the sake of argument, we replace the integral by $\exp\left[-(\mu+gQ)r_{\text{eff.}}\right]V$, where $r_{\text{eff.}}$ is the effective path traversed by the beam in the crystal, it will be seen that the error in neglecting squares and higher powers of gQr in the expansion of $\exp(-gQr)$ is approximately of the same magnitude as in the previous case (Table 1). We may therefore conclude that the theory developed here is applicable to a fair degree of accuracy to extinction values of about 25–30%.

Experimental details

The 311 reflection of diamond ($2\theta \sim 91°\,30'$ for copper radiation) was used to obtain polarized X-rays. The diamond was in the form of a plate (approximately $8\times7\times2{\cdot}5$ mm.^{3}) whose faces were parallel to the (111) planes. It was mounted about a vertical axis in level with the window of the X-ray tube so that the reflected beam was horizontal with the electric vector polarized vertically. The plate could be set in two possible positions to get the reflection: in one setting the reflection was sharp and intense because of a focusing effect, and in the other (with the incident and reflected beam effectively reversed) the reflection was relatively broad and not so intense. As the aim was to make measurements on crystals completely bathed in the polarized beam, the latter setting was found to be more suitable. Perfect polarization may be achieved only if $2\theta=90°$, but the degree of polarization realised with this arrangement was reckoned to be adequate for the present purpose. (In passing, it may be mentioned that the 311 reflection of copper, $2\theta=90°\,12'$, gives almost perfectly polarized X-rays with copper radiation; see, for instance, Chandrasekaran, 1955).

A Geiger-counter diffractometer designed for three-dimensional X-ray work (Bones, 1956) was employed for the experiment. The apparatus was aligned first with the aid of a fluorescent screen (the polarized beam was of sufficient intensity to be seen on a fluorescent screen in a well darkened room) and then more accurately by means of photographs. The photographs also ensured the homogeneity of the beam through the collimator.

Different values of φ were obtained by means of a vertical circle, the axis of which was collinear with the axis of the collimator. The arcs with the crystal under investigation were mounted on this circle so that the plane of incidence could be rotated through any desired angle.

Intensity measurements were made with a Geiger counter (Mullard Type MX 118) and scaling unit (Ericsson Type 1221C). The dead-time correction for the counter was determined by the multiple-foil technique (Lonsdale, 1948) and also by measuring the absorption factor of a nickel foil over a wide range of incident intensities. In the latter method, the measured value of the absorption factor at higher intensities was less than that for weak intensities on account of the dead-time loss. Since the actual absorption factor is independent of the incident intensity, the dead-time loss of the counter could be estimated. This technique overcame any possible errors due to variations in the thickness of the foils in the multiple-foil technique, but both techniques yielded comparable results. However, with the present set up, the peak intensities of the reflections did not exceed about 150 counts/sec., so that the errors due to the non-linearity of the response of the counter were very small. The integrated intensities were measured by oscillating the crystal about a vertical axis, and therefore the appropriate Cox–Shaw factor had to be applied to each observation. The X-ray set was a North American Phillips Co., Inc., Type 12022; it was run at 36 kV. and 6 mA. with a Sorensen Voltage regulator (Sorensen and Co., Inc., Stamford, Connecticut). The X-ray output was fairly constant, and intensity measurements were generally accurate to about 3%.

Divergence of polarized beam

It was realised at the outset that as the experiment consisted of an accurate study of the variation of the integrated reflection with φ, the non-uniformity of the divergence of the diamond-reflected polarized beam might be a source of error in the measurements. An attempt was made to correct for this by means of a Soller slit, but the loss in intensity was found to be prohibitive. Consequently the following procedure was adopted to check whether any correction was necessary.

When the incident beam is polarized at an angle φ with respect to the plane of incidence, we have for an ideally perfect crystal with negligible absorption

$$\varrho_\varphi/\varrho = \sin^2\varphi + \cos^2\varphi|\cos 2\theta| \qquad (10)$$

(Ramaseshan & Ramachandran, 1954). The corresponding expressions for the ideal mosaic and the imperfect crystal exhibiting extinction are respectively given by (8) and (9). When $2\theta = 90°$, (8), (9) and (10) become identical, and thus, irrespective of the state of perfection of the crystal,

$$\varrho_\varphi/\varrho_\perp = \sin^2\varphi\ .$$

Any departure from the $\sin^2\varphi$ variation could only be due to the non-uniformity of the divergence and (or) the lack of perfection of polarization of the incident beam.

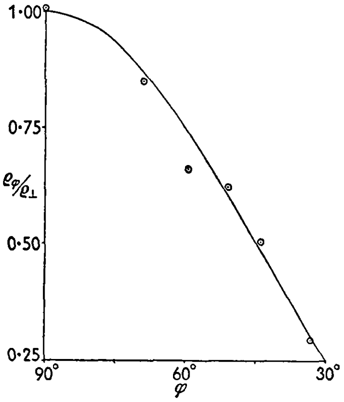

Fig. 5. $\varrho_\varphi/\varrho_\perp$ versus φ for the 311 reflection from a small specimen of diamond with theoretical curve for $2\theta = 90°$.

A small specimen of diamond (less than 1 mm. diameter) was used for the measurement. The experimental variation of $\varrho_\varphi/\varrho_\perp$ versus φ for the 311 reflection ($2\theta \sim 91° 30'$) is shown in Fig. 5. This was indeed a repetition of the early experiments of Barkla, Compton, and others which demonstrated that X-rays consist of electromagnetic waves (see Compton & Allison, 1935).

All the experimental points except one lie very close to the theoretical curve, indicating that the effect of the non-uniformity of the divergence was negligible in this set up. The large discrepancy for one reading is almost certainly caused by some sudden fluctuation in the X-ray output, which, despite the fact that a voltage regulator was used, occurred occasionally for short periods of time. For this reason, in all subsequent measurements each reading was repeated three times.

Measurements on rock salt

Measurements were carried out on rock salt to test the practical applicability of the method. Three small crystals were examined. The experimental data for two specimens, which serve to illustrate the kind of results obtained, are shown in Figs. 6–10. Details of the two specimens are given below.

Specimen I		
Grown from solution	Cube (about 1 mm.^{3})	Unground
Specimen II		
Cleaved from large crystal	Plate (0·93 × 0·93 × 0·221 mm.^{3})	Principal faces (as distinct from rim) ground on fine emery paper

As mentioned earlier, at each setting of φ the reading was repeated thrice, and the spread so obtained is shown in the graphs. In addition, the whole series of measurements on specimen II (Figs. 7–10) were checked by repetition using shorter counting times. It was concluded that while the individual readings may be in error by about 3%, the general trends of the values indicated in the graphs are accurate.

The main points which emerge from these results are:

(*a*) The 200 reflection from specimen I (unground) shows considerable extinction, as evidenced by the fact that the experimental values of $\varrho_\varphi/\varrho_\perp$ lie significantly above the theoretical curve for the ideal mosaic (Fig. 6), while that for specimen II (ground faces) shows hardly any extinction (Fig. 7). A similar observation has been made by Ramaseshan & Ramachandran (1954) on large crystals.

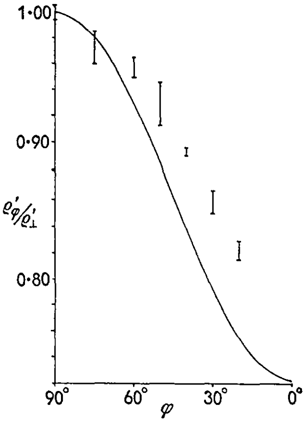

Fig. 6. $\varrho'_\varphi/\varrho'_\perp$ versus φ for the 200 reflection from specimen I with theoretical curve for no extinction.

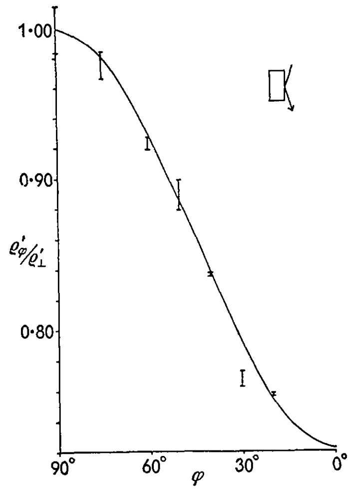

Fig. 7. $\varrho'_\varphi/\varrho'_\perp$ versus φ for the 200 reflection from specimen II with theoretical curve for no extinction.

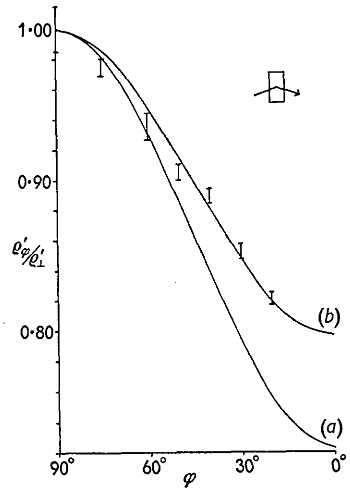

Fig. 8. $\varrho'_\varphi/\varrho'_\perp$ versus φ for the 200 reflection from specimen II with theoretical curves for (a) no extinction; (b) 27% extinction.

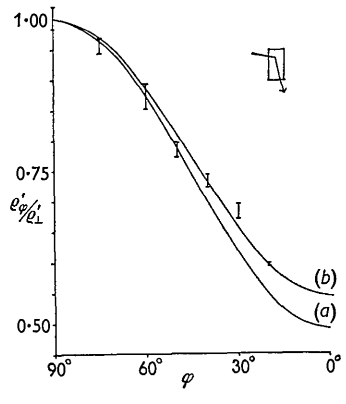

Fig. 9. $\varrho'_\varphi/\varrho'_\perp$ versus φ for the 220 reflection from specimen II with theoretical curves for (a) no extinction; (b) 18% extinction.

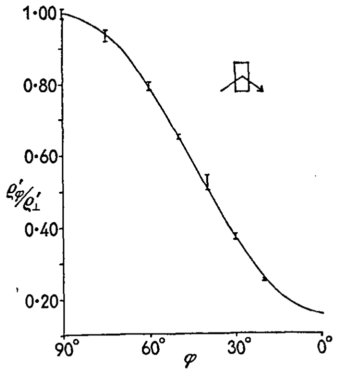

Fig. 10. $\varrho'_\varphi/\varrho'_\perp$ versus φ for the 400 reflection from specimen II ($2\theta = 66°26'$) with theoretical curve for no extinction.

(*b*) Similar reflections from the same crystal (specimen II) exhibit different amounts of extinction depending on whether the reflecting planes are parallel or perpendicular to the ground faces (Figs. 7 and 8). This is in fact to be expected since the state of the ground surface is scarcely representative of the interior of the crystal.

(*c*) By fitting the appropriate theoretical curve to the experimental data it is estimated that the 200 reflection (Fig. 8) has about 27% extinction, the 220 (Fig. 9) about 18% extinction and the 400 (Fig. 10) hardly any extinction. This agrees qualitatively with the well-known result that extinction is greater for the stronger reflections. (Caution is necessary in comparing extinction effects from different reflections, but in this case it would seem from the geometry of the reflections that such a comparison is justified). The next step was to verify whether these estimates are quantitatively correct. The relative values of the structure factors were calculated on the basis of the formula

$$\varrho'_\perp \propto \frac{AF_o^2}{\sin 2\theta}(100-\varepsilon)\,,$$

where $\varrho'_\perp$ is the observed integrated reflection in the presence of extinction, A the absorption factor, and ε the percentage of extinction as estimated from the experimental variation of $\varrho'_\varphi/\varrho'_\perp$. The values for the three reflections together with the absolute structure factors at room temperature, which have been determined to a very high precision by Renninger (1952)

Table 2. *Measurements on rock salt*

hkl	$\varrho'_\perp$ (arbitrary units)	A†	ε (%)	F'_o	F_o	F (Renninger) Cu $K\alpha$	F (Witte & Wölfel) Mo $K\alpha$
200	584	0·2337	27	17·4	20·4	20·55	20·19
220	252	0·1838	18	15·0	16·6	16·75*	—
400	180	0·2360	0	12·7	12·7	12·70	12·45

† Thanks are due to Dr M. Wells for kindly evaluating the absorption factors on EDSAC.

* Obtained from scattering factors at room temperature due to Renninger.

and Witte & Wölfel (1958), are given in Table 2. Here F'_o and F_o are respectively the observed structure factors before and after correcting for extinction. The values have been scaled so that $F_o(400)$, which has been found to have negligible extinction, is equal to the absolute value given by Renninger.

Concluding remarks

The results indicate that this method of correcting for extinction will work in practice. The main advantage of the method is that it accounts for both primary and secondary extinction in a crystal of any shape. It is applicable to a good accuracy when the extinction is not greater than 25%, but is unsatisfactory for low Bragg angles, say for $2\theta < 20°$, depending upon the accuracy of the intensity measurements.

The present experimental arrangement is defective in one respect. The axis of oscillation remaining vertical for all angles of φ prevents ϱ_φ from being measured over the whole range from $\varphi = 90°$ to 0°. (The Cox–Shaw factor becomes zero for $\varphi = 0°$). The most sensitive portion of the curve connecting $\varrho'_\varphi/\varrho'_\perp$ versus φ is between $\varphi = 20°$ and 0°, and hence the inability to make measurements in this range is a disadvantage. This can be overcome either by rotating the entire diffractometer about the polarized beam or by rotating the plane of polarization. An apparatus for accomplishing the latter, designed with a view to making the experimental procedure as efficient as possible, is now under construction at the Royal Institution.

I am indebted to Prof. Dame Kathleen Lonsdale for provision of facilities and for many helpful suggestions. I am also grateful to Dr H. J. Milledge for the loan of the diamonds and for discussions. Thanks are due to Mr E. Nave for his valuable help in setting up the apparatus. The work was carried out during the tenure of a D.S.I.R. Special Research Grant.

References

Batterman, B. W. (1959). *Phys. Rev.* Lett. **2**, 47.

Bones, R. (1956). *J. Sci. Instrum.* **33**, 241.

Chandrasekhar, S. (1956). *Acta Cryst.* **9**, 954.

Chandrasekhar, S. & Weiss, R. J. (1957). *Acta Cryst.* **10**, 598.

Chandrasekaran, K. S. (1955). *Acta Cryst.* **8**, 361.

Chandrasekaran, K. S. (1959). *Acta Cryst.* **12**, 916.

Cochran, W. (1953). *Acta Cryst.* **6**, 260.

Compton, A. H. & Allison, S. K. (1935). *X-rays in Theory and Experiment.* New York: Van Nostrand.

Hume-Rothery, W., Brown, P. J., Forsyth, J. B. & Taylor, W. H. (1958). *Phil. Mag.* **3**, 1466.

James, R. W. (1954). *The Optical Principles of Diffraction of X-rays.* London: Bell.

Lonsdale, K. (1948). *Acta Cryst.* **1**, 12.

Ramaseshan, S. & Ramachandran, G. N. (1953). *Acta Cryst.* **6**, 364.

Ramaseshan, S. & Ramachandran, G. N. (1954). *Proc. Indian Acad. Sc.* A, **39**, 20.

Renninger, M. (1952). *Acta Cryst.* **5**, 711.

Vand, V. (1955). *J. Appl. Phys.* **26**, 1191.

Weiss, R. J. & De Marco, J. J. (1958). *Rev. Mod. Phys.* **30**, 59.

Weiss, R. J. & De Marco, J. J. (1959). *Phys. Rev.* Lett. **2**, 148.

Witte, H. & Wölfel, E. (1958). *Rev. Mod. Phys.* **30**, 51.

Acta Cryst. (1960). **13**, 594

The Crystal Structure of *bis*-Biuret-Cadmium Chloride

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(*Received* 2 *December* 1959)

Bis-biuret-cadmium chloride, $CdCl_2 . 2\,C_2H_5N_3O_2$, is monoclinic ($P2_1/c$) with

$$a = 3{\cdot}704,\ b = 19{\cdot}96,\ c = 8{\cdot}20\ \text{Å};\ \beta = 111{\cdot}1°;\ Z = 2\,.$$

The crystal structure has been determined by Fourier methods using $0kl$, $1kl$ and $2kl$ reflections. The cadmium atom coordinates octahedrally with four Cl and two O atoms of two different biuret molecules (Cd–Cl = 2·55 and 2·62 Å, Cd–O = 2·34 Å). The biuret molecule is planar and has a 'trans' configuration.

1. Introduction

Biuret, $NH(CONH_2)_2 = Bu$, forms two kinds of coordination compounds with divalent metals. Among those which can be obtained in an alkaline medium, the potassium *bis*-biuret-cuprate tetrahydrate has recently been studied by Freeman, Smith & Taylor (1959), who found that two biuret molecules are coordinated as bidentate ligands, through the nitrogen atoms of the amino-groups, by a copper atom.

In a neutral medium, coordination compounds of