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A First-Order Correction for Extinction in Crystals

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A method of effecting a first-order correction for extinction in crystals is suggested. It involves an accurate measurement of the integrated intensity of a particular reflexion for X-rays polarized perpendicular and parallel respectively to the plane of incidence. The change of polarization alters the effective structure factor, and consequently the extinction, by a known quantity. It is shown that from the resulting two relations for the integrated intensity $|F|$ may be estimated without making any special assumptions as to the nature of the extinction, i.e. whether it is primary or secondary or both.

Introduction

Extinction is by far the greatest factor which limits the accuracy of determination of a set of structure factors. There have been numerous attempts in the past to estimate the influence of extinction on the intensities of X-ray reflexions from crystals. An excellent survey of the classical researches in this field has been made by James in *The Optical Principles of the Diffraction of X-rays* (1954) and a thorough treatment of the theoretical aspects of the problem may be found in Zachariasen's *Theory of X-ray Diffraction in Crystals* (1945). Some of the more recent investigations are due to McWeeny (1951), Weiss (1952), Lang (1953), Williamson & Smallman (1955) and Vand (1955). Different methods have been proposed by different authors, but there appears to be no satisfactory way of determining the true value of $|F|$ for any reflexion when the extinction is of a general type. Wooster & Macdonald (1948) have tried to estimate $|F|$ by measuring the integrated reflexion for two wavelengths for a number of crystals of varied texture. Gay (1952) has measured $|F|$ by studying the dependence of the integrated intensity on the asymmetry of the reflexion.

In the present note, a new method of effecting a first-order correction for extinction is suggested. It is shown that a reasonable value of $|F|$ can be obtained by measuring the integrated intensity of a particular reflection for X-rays polarized perpendicular and parallel respectively to the plane of incidence, without making any special assumptions as to the nature of the extinction, i.e. whether it is primary or secondary or both.

Primary extinction

First, it must be emphasized that unless otherwise stated the incident X-rays are assumed to be polarized perpendicular to the plane of incidence, so that the polarization factor is taken to be unity. Let ϱ' and ϱ denote the integrated reflexion with and without extinction respectively. For primary extinction (see Zachariasen (1945), equation (4·46)) we have

$$\varrho'/\varrho = f(A_0)\,, \tag{1}$$

where, for the Bragg case,*

$$f(A_0) = \tanh A_0/A_0 \tag{2}$$

and for the symmetrical Laue case*

$$f(A_0) = \sum_{n=0}^{\infty} \frac{J_{2n+1}(2A_0)}{A_0}\,, \tag{3}$$

where $A_0 = e^2\lambda|F|t/mc^2V$, t is the effective linear dimension of a perfect crystal block, V is the volume of the unit cell and the other symbols have their usual meanings.

For small values of A_0 we have

$$\tanh A_0/A_0 \quad = 1-\frac{A_0^2}{3}+\frac{2A_0^4}{15}-\ldots$$

and

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

so that, to a first approximation, for both cases

$$f(A_0) = 1-\frac{A_0^2}{3}\,.$$

Therefore

$$\frac{\varrho'}{\varrho} = 1-\frac{e^4\lambda^2t^2}{3m^2c^4V^2}|F|^2\,. \tag{4}$$

For a symmetrical reflexion from the incident side of a thick plate we have

$$\varrho = Q/2\mu\,, \tag{5}$$

while for a symmetrical reflexion through a plate of thickness D we have

$$\varrho = QD\sec\theta\exp(-\mu D\sec\theta)\,, \tag{6}$$

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* In this particular context, we are using the terms Bragg and Laue in the sense adopted by Zachariasen.

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

and μ is the normal linear absorption coefficient. Substituting for ϱ in (4), it is quite easy to see that when there is primary extinction, the integrated intensity could be written as

$$\varrho' = \alpha|F|^2-\beta|F|^4\,, \tag{7}$$

where α is a known quantity depending on the geometry of the reflexion while β is unknown since t, the effective thickness of the perfect blocks constituting the mosaic crystal, is unknown.

It has been pointed out by Weiss (1952) that for primary extinction the correct formula to be applied should be that for small spherical crystals and not that for thin blocks, as has been assumed in deriving (2) and (3). Ekstein (1951) has treated this problem and arrives at a correction term for the peak intensity which is essentially of the same type as (4) except for a numerical factor. The correction term for the integrated intensity in Ekstein's case has not been worked out, but, as pointed out by Lang (1953), it will differ from that for the peak intensity only by a numerical factor. So the integrated intensity can still be represented by a formula of the type (7).

Secondary extinction

For a symmetrical reflexion from the incident side of a thick plate which exhibits secondary extinction we have, to a first approximation,

$$\varrho' = \frac{Q}{2(\mu+gQ)} = \frac{Q}{2\mu} - \frac{gQ^2}{2\mu^2}\,, \tag{8}$$

where gQ is called the secondary extinction coefficient.

For a symmetrical reflexion through a plate of thickness D, we have to a first approximation

$$\begin{aligned}\varrho' &= QD\sec\theta\exp\left[-(\mu+gQ)D\sec\theta\right]\\ &= \left[D\sec\theta\exp(-\mu D\sec\theta)\right](Q-gDQ^2\sec\theta)\,. \end{aligned} \tag{9}$$

Again, since $Q\alpha|F|^2$, equations (8) and (9) could be expressed as
$$\varrho' = \alpha|F|^2-\beta|F|^4\,,$$

where α is known and β is unknown since g is unknown.

When both primary and secondary extinction are present, Q in (8) and (9) has to be replaced by $Q(1-\frac{1}{3}A_0^2)$. By simple substitution, it is quite easy to verify that to a first approximation, the integrated intensity will then be given by

$$\varrho' = \alpha|F|^2-(\beta_{\text{prim.}}+\beta_{\text{sec.}})|F|^4\,. \tag{10}$$

Evaluation of $|F|^2$

We have thus arrived at the interesting result that whatever be the type of extinction, the integrated intensity for normal polarization can be written as

$$\varrho'_{\perp} = \alpha|F|^2-\beta|F|^4\,. \tag{11}$$

If, on the other hand, the X-rays are polarized parallel to the plane of incidence, the integrated intensity for the same reflexion is obtained by simply replacing $|F|$ by $|F\cos 2\theta|$, since all other factors remain unchanged, and we have

$$\varrho'_{\parallel} = \alpha|F|^2\cos^2 2\theta-\beta|F|^4\cos^4 2\theta\,. \tag{12}$$

Eliminating β from (11) and (12), we get

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

The principle of the method can be stated physically as follows. Extinction, whether it is primary or secondary, is greater for the stronger spectra. By the present technique of using polarized X-rays we are artificially altering the effective structure factor, and consequently the extinction, for the same reflexion by a known quantity. From the resulting two relations for the integrated intensity we can eliminate the effect of extinction. Obviously, the more accurately ϱ' is determined, the more accurately can $|F|^2$ be estimated. As this is only a preliminary account, we shall not discuss in detail the dependence of the accuracy on the various factors involved.

In the foregoing discussion, we have treated only the cases of the symmetrical reflexion from the incident side of a thick crystal and the symmetrical reflexion through a plate of thickness D. It should be possible to extend the arguments to cases when the reflecting planes are neither parallel nor perpendicular to the surface of the crystal. It may be remarked that the experiment can be performed with a single crystal without altering its state of perfection (or imperfection) in any way.

It is proposed to test these ideas experimentally with a view to verifying whether the method will work in actual crystals. We shall reserve a full discussion of this aspect of the problem for a future report.

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The Crystal Structure of Oxy-mercuric-mercurous Chloride, $2HgO.Hg_2Cl_2$

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The crystal structure of the mercury oxychloride, known under the formula HgO.HgCl and identical with the mineral terlinguaite, has been determined. It follows from the structure that $2HgO.Hg_2Cl_2$ is the correct formula.

The crystals are monoclinic holosymmetric with the space group C_{2h}^6–$C2/c$. The unit cell, of dimensions

$$a = 19{\cdot}53,\quad b = 5{\cdot}92,\quad c = 9{\cdot}48\ \text{Å},\quad \beta = 144^\circ,$$

contains 4 formula units $2HgO.Hg_2Cl_2$. The atomic co-ordinates have been obtained with the help of vector and electron-density projections along [001] and [010]. Diffraction effect of the mercury atoms did not allow the co-ordinates of the light atoms to be determined with greater accuracy than $\pm 0{\cdot}05$ Å. The layer-type crystal structure is built up of mercuric oxide and mercurous chloride. The mercuric oxide forms zigzag chains ··· Hg–O–Hg–O–Hg ··· with the Hg–O distance 2·03 Å and the bond angles at the mercury atoms 180° and 168° alternately and 112° at the oxygen atom. The mercurous chloride molecules are deformed with a deflection of 19° from linearity; the distances Hg–Hg and Hg–Cl are 2·66 and 2·57 Å respectively.

Introduction

In connexion with the earlier investigations of the mercury oxychlorides (Šćavničar & Grdenić, 1955; Šćavničar, 1955) an attempt was made to determine the crystal structure of the synthetic oxychloride known by formula HgO.HgCl; the mineral terlinguaite is a natural product of the same composition (Bird, 1932; Dana & Dana, 1951). This oxychloride contains mercury atoms in the mercuric and mercurous state. The aim of our investigation was to investigate the bonds between mercury and oxygen atoms and their crystallochemical and stereochemical relations, as it was indicated earlier (Grdenić & Šćavničar, 1953).

Crystallographic data

The compound was prepared according to the known procedure (Fischer & v. Wartenberg, 1905). The homogeneous crystals were usually small (the average size was $0{\cdot}5 \times 0{\cdot}3 \times 0{\cdot}1$ mm.) and of honey yellow colour. The crystals were monoclinic holosymmetric and flattened on {001}. The observed forms were: {100}, {001}, {$\bar{1}$01}, {110}, {$\bar{1}$11}. All data in this paper refer to an axis sytem which is different from that of Dana and the matrix $\bar{1}0\bar{2}/0\bar{1}0/001$ serves for the transformation of our system to Dana's.

All the X-ray measurements were performed with Ni-filtered Cu K radiation. The dimensions of the unit cell, as obtained from the oscillation photographs, were

$$a = 19{\cdot}53,\quad b = 5{\cdot}92,\quad c = 9{\cdot}48\ \text{Å},\quad \beta = 144^\circ$$

and differed in average 2·2% from the Dana values for terlinguaite.

The picnometrically determined density is 9·27 g.cm.$^{-3}$ and the density calculated for 4 formula units $2HgO.Hg_2Cl_2$ is 9·31 g.cm.$^{-3}$. The systematically absent reflexions are hkl with $h+k = 2n+1$, $h0l$ with l odd, and $0k0$ with k odd, so that the space group is C_{2h}^6–$C2/c$.

Structure determination

The measurement of the relative intensities of the reflexions $hk0$ and $h0l$ and the corresponding corrections were performed in the manner described before (Šćavničar & Grdenić, 1955). In order to perform better correction for absorption ($\mu = 1909$ cm.$^{-1}$ for Cu K radiation) a suitable form was given to the specimen by grinding. The absorption corrections were made very carefully by using the formulae of the absorption factors for a single crystal of high absorbing power (Grdenić, 1952*).

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* It has been noticed that in this communication one of the formulae was misprinted. In the denominator of the formula $A(4)$ the sine fraction should be $\sin\varphi_2/\sin\psi_2$ instead of $\sin\psi_2/\sin\varphi_2$. For all corrections previously done the correct formula was applied from a manuscript copy used in the laboratory.