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The Derivation of Structural Information from Absorption Effects in X-ray Diffraction

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The results of the two-beam dynamical theory for the diffraction of X-rays in a crystal, taking absorption into account, have been expressed in such a way as to make clear the dependence on the Fourier coefficients, ψ''_H, of the imaginary part of the polarizability, ψ'', due to absorption. For thin crystals the transmitted beam profile has an antisymmetric part depending on the amplitude and sign of ψ''_H, relative to ψ'_H. This conclusion has been verified by double-crystal spectrometer measurements for two different reflections for calcite and for sodium nitrate. From such measurements or from measurement of the intensities of beams transmitted through thick perfect crystals, values of ψ''_H could be derived which could be of considerable value for purposes of structure analysis.

From measurements of fluorescence radiation given by atoms within a diffracting crystal, or from observation of the Kossel line patterns given when atoms within a crystal emit their characteristic radiation, it should be possible to derive information concerning the positions, in the unit cell, of the emitting atoms. This could be used to investigate the environments of impurity atoms present in relatively small quantities in a crystal lattice.

Introduction

The theory of the diffraction of X-rays, taking absorption into account, has been treated by a number of authors (*e.g.* Zachariasen, 1944; Hirsch, 1952; Kato, 1955). The results have been found in fair agreement with the experiments made on those substances of relatively simple structures for which good single crystals are now readily available. The theoretical treatments have been equally applicable to more complicated structures, since no restrictions have been placed on the Fourier coefficients, ψ_H, proportional to the structure factors except that, when convenient, a center of symmetry has been assumed. Because in both theory and experiment only simple structures have been examined in detail, the implications of the theoretical results relevant to more complicated structures have apparently been overlooked. One exception is provided by the recent work of Cole & Stemple (1962) who showed that observations of the discontinuity in absorption effects, occurring at the critical absorption wave-length, allowed a determination of the polarity in the non-centrosymmetric GaAs structure.

It is the purpose of this paper to point out some further implications of the X-ray diffraction theory and suggest additional ways in which diffraction experiments with X-rays and other radiations may be used to derive structural information concerning crystal lattices and their defects.

In the notation of Zachariasen (1944) and subsequent papers, the polarizability (multiplied by 4π) in a crystal is complex and denoted by $\psi'=\psi'+i\psi''$ Both the real and imaginary parts are periodic, with Fourier coefficients denoted by ψ'_H and ψ''_H respectively. The above-mentioned authors obtained expressions for the intensities of transmitted and diffracted beams and for the wave field in the crystal, which contain structure-sensitive terms involving both ψ'_H and ψ''_H. It should be possible to derive values for these terms from diffraction experiments.

When the real and imaginary parts of ψ represent scattering distributions which are not very different, as in the case of crystals containing only one kind of atom, the only new knowledge to be gained in this way is the magnitude and form of the imaginary part of the atomic scattering factors. For crystals containing more than one kind of atom, ψ'' may differ markedly from ψ', so that ψ'_H and ψ''_H may even be opposite in sign. Then from the diffraction effects ψ''_H may be deduced if ψ'_H is known, and *vice versa.*

The nature of the experiments which may be performed to provide this information is evident from an analysis of the scattering processes. When a well-collimated X-ray beam enters an absorbing crystal, the intensity of the wave field at the position of an absorbing atom varies with the angle of incidence. Hence, the distribution of absorbing atoms with respect to the scattering atoms will determine the variation, with angle of incidence, of the intensities of the transmitted and diffracted beams and also of the fluorescence radiation produced. Also, the fluorescence radiation from sources within a crystal, produced either by X-radiation or by electron bombardment, will give Kossell line patterns for which the intensity distribution will depend on the relative positions of absorbing atoms and also on the relative positions of the emitting atoms.

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In the following sections, expressions for the intensity distributions relevant to these experimental possibilities will be quoted or derived, where necessary, for the Laue case and the possibilities for deriving structural information will be discussed.

Transmitted and diffracted beams

According to Zachariasen (1944) and Kato (1955), the intensities of the diffracted wave, I_H, and the transmitted wave, I_T, for the Laue case, can be written as:

$$\frac{I_H}{I_0}=\frac{|b|}{1+y^2}\exp\left(-\mu_0 t\right)\left\{\sin^2(av)+\sinh^2(aw)\right\} \quad (1)$$

and

$$\begin{aligned}\frac{I_T}{I_0}&=\exp\left(-\mu_0 t\right)\left\{1+\left(\frac{1+2y^2}{1+y^2}\right)\sinh^2(aw)-\left(\frac{1}{1+y^2}\right)\right.\\ &\quad\left.\times\sin^2(av)+\left(\frac{y\sqrt{(1+y^2)}}{1+y^2}\right)\sinh(2aw)\right\}\\ &=\exp\left(-\mu_0 t\right)\left\{1+2\sinh^2(aw)+\frac{y}{\sqrt{(1+y^2)}}\right.\\ &\quad\left.\times\sinh(2aw)\right\}-\frac{1}{|b|}\frac{I_H}{I_0}\,. \end{aligned} \quad (2)$$

Here μ_0 is the mean absorption coefficient given by

$$\mu_0=-2\pi\psi_0''/\lambda\,, \quad (3)$$

and t is the effective thickness given by

$$t=\tfrac{1}{2}t_0\left(\frac{1}{\gamma_0}+\frac{1}{\gamma_H}\right), \quad (4)$$

where t_0 is the crystal thickness and γ_0 and γ_H are the direction cosines of the incident and diffracted beams relative to the normal to the crystal surface (Fig. 1).

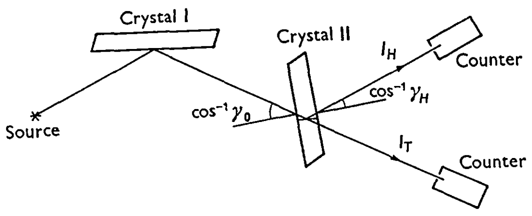

Fig. 1. Two-crystal spectrometer arrangement for measuring the transmitted intensity (I_T) and diffracted intensity (I_H) from crystal II.

The variable y, giving the deviation from the Bragg angle, is defined by

$$y=\{\tfrac{1}{2}(1-b)\psi_0'+\tfrac{1}{2}b\alpha\}/K|\psi_H'|\,.\,|b|^{\frac{1}{2}}, \quad (5)$$

where $b=\gamma_0/\gamma_H$, $\alpha=2(\theta_B-\theta)\sin 2\theta_B$ and K is the polarization factor (equal to 1 for the normal component and $|\cos 2\theta|$ for the parallel component).

We define

$$g=\tfrac{1}{2}(1-b)\psi_0''/K|\psi_H'|\,.\,|b|^{\frac{1}{2}}, \quad (6)$$

and

$$\varkappa=\{\psi_H\psi_{\bar{H}}-|\psi_H'|^2\}/2i|\psi_H'|^2. \quad (7)$$

When the crystal has a center of symmetry,

$$\varkappa=\psi_H''/\psi_H'\,.$$

Usually $|\varkappa|\ll 1$ and $|g|\ll 1$, and we may write

$$av\ =\ A\sqrt{(1+y^2)} \quad (8)$$

$$aw\ =\ A(\varkappa+gy)/\sqrt{(1+y^2)}\,, \quad (9)$$

where

$$a=\pi t_0/\lambda\gamma_0 \quad\text{and}\quad A=a|b|^{\frac{1}{2}}K|\psi_H|\,.$$

From (1) it is seen that the profile of the reflected beam is made up of terms essentially positive and symmetric with a small asymmetry introduced if $b\neq 1$, so that $g\neq 0$. The magnitude of the intensity peak depends on $|aw|$ and so is independent of the sign of $(\varkappa+yg)$. On the other hand, (2) shows that the transmitted beam has an antisymmetric component depending on both the magnitude and sign of aw. For the case $b=1$, $g=0$, corresponding to the symmetrical arrangement of incident and diffracted beams, it is readily seen that the familiar black-white asymmetry of the transmitted beam will be inverted if ψ_H'' and ψ_H' are opposite in sign.

The magnitude and detectability of such effects are more readily appreciated for the limiting cases of very thin and very thick crystals. For very thin crystals, for which we can assume $|aw|\ll 1$, we put $\sin aw\simeq\sinh aw\simeq aw$. Then ignoring higher order terms in aw, equations (1) and (2) become, respectively,

$$\frac{I_H}{I_0}\simeq\frac{|b|\,.\,A^2\exp\left(-\mu_0 t\right)}{1+y^2}\left[\sin^2 A(1+y^2)+\frac{(\varkappa+yg)^2}{1+y^2}\right], \quad (10)$$

and

$$\frac{I_T}{I_0}\simeq\exp\left(-\mu_0 t\right)\left[1+2Ag-\frac{2\mathrm{A}g}{1+y^2}+\frac{2A\varkappa y}{1+y^2}\right]-\frac{I_H}{I_0}\cdot\frac{1}{|b|}\,. \quad (11)$$

From equation (10) it is seen that the influence of the imaginary part of the structure factor on the intensity of the diffracted beam is always small. For $g=0$ the maximum contribution is of the order of $|\psi_H''/\psi_H'|^2$ times the contribution from the real part of the structure factor.

The intensity of the transmitted beam, on the other hand, contains terms in the first power of $\varkappa$ and g, and so is much more sensitive to the values of ψ_0'' and ψ_H'. The effects of these absorption terms is shown up more clearly by considering the sum of the transmitted intensity and $1/|b|$ times the reflected intensity. If the intensity profile for this sum is resolved into symmetric and antisymmetric parts, corresponding to the last two terms of the bracket in equation (11), the symmetric part gives the value of g and so of ψ_0''. The antisymmetric part has a magnitude proportional to ψ_H'' and has the same sign as ψ_H''/ψ_H'.

By making an appropriate choice of the crystal thickness, t_0, it should be possible to obtain these values with considerable accuracy.

For very thick crystals it is possible to ignore the sine terms of equations (1) and (2) and replace sinh aw by $\pm\exp(a|w|)$, the choice of sign depending on the sign of w. Then

$$\frac{I_H}{I_0} \simeq \frac{b}{4(1+y^2)} \exp(-\mu_0 t + 2a|w|) \tag{12}$$

and

$$\frac{I_T}{I_0} \simeq \exp(-\mu_0 t + 2a|w|) \frac{(y \pm \sqrt{(1+y^2)})^2}{1+y^2} . \tag{13}$$

Since the value of $a|w|$ is assumed to be large, the intensity profile in each case will be determined almost entirely by the exponential term. For $g \neq 0$ there will be an asymmetry of the peak, depending on the relative magnitude of ψ_0'' and ψ_H'', but for the most part the asymmetry will be slight and will correspond to a small shift in peak position. For the transmitted beam the function of y multiplying the exponential also introduces an asymmetry, which will result in a small shift of the peak in a direction depending on the sign of w.

The maximum intensity given by equations (12) and (13) for $g=0$ will be a very sensitive function of ψ_H'' and for some crystals the absolute intensity measurements which would be necessary may be made to give accurate values for ψ_H''. The need for absolute intensity measurements is avoided and additional information is obtained by varying a further parameter, the wave-length. In passing through the critical absorption wave-length for one of the elements present, both μ_0 and $|w|$ will change. The change in μ_0 alone is given by the change in transmission when no reflection takes place. From the change in $\exp(2a|w|)$ relative to this background value, it should be possible to deduce the change in the contribution to ψ_H'' of those atoms whose absorption has changed. If this contribution is small compared with the value of ψ_H'' corresponding to all atoms present, both its amplitude and sign will be given. Thus in favorable cases it should be possible to deduce the contribution to ψ_H, and hence the position relative to other atoms, of absorbing atoms present only in very small concentrations in the crystal lattice.

Since it is easier to measure intensities integrated over the angle of incidence, Kato (1955) has obtained expressions for integrated reflecting power and transmitting power and derived expressions appropriate to the limiting cases of very thin and very thick crystals. For thin crystals, integrating over y gives

$$R_H^y = \exp(-\mu_0 t) \cdot \frac{\pi}{2} \left\{ 1 + \frac{h^2}{4} + \frac{h^4}{64} + \dots \right\} , \tag{14}$$

$$R_T^y = \exp(-\mu_0 t) . \pi \{ -(\cos\beta) . h - \tfrac{1}{2}(\cos 2\beta) . h^2 + \dots \} - R_H^y , \tag{15}$$

where

$$h = 2A\sqrt{(\varkappa^2+g^2)} \quad \text{and} \quad \beta = \tan^{-1}(\varkappa/g) .$$

For thick crystals

$$R_H^y = \exp(-\mu_0 t) \cdot \frac{\pi}{2} \frac{e^h}{\sqrt{(2\pi h)}} \left\{ 1 + \frac{1}{8h} + \dots \right\} , \tag{16}$$

$$R_T^y = \exp(-\mu_0 t) . \pi \frac{e^h}{\sqrt{(2\pi h)}} \left\{ D_0 + \frac{D_1}{h} + \frac{D_2}{h^2} + \dots \right\} - R_H^y , \tag{17}$$

where D_0, D_1, D_2 are functions of $\cos\beta = g/\sqrt{(\varkappa^2+g^2)}$.

It is seen that, in taking the integrated value, the possibilities for direct determination of ψ_H'' and ψ_0'' from the transmission from thin crystals has been lost. For thick crystals the slight asymmetries depending on the relative signs and magnitudes of ψ_0'' and ψ_H'' are not observed, but the practical value of these effects is, in any case, doubtful. The possibilities for deducing information from accurate intensity measurements or from wave-length variation exist as for the case of resolved intensity profiles. Experiments involving the wave-length variation of integrated reflection intensities in the Bragg case have been made by Cole & Stemple (1962) for reflections from the germanium and gallium arsenide.

The crystal wave-field: fluorescence radiation

The intensity of fluorescence radiation emitted by an atom in a crystal is proportional to the intensity of the wave field at the position of the atom. The total intensity of fluorescence radiation observed will be given by summing the contributions from all atoms emitting radiation to which the detector responds.

From Zachariasen (1944) we see that the total wave field in the crystal is given by adding the transmitted and diffracted waves:

$$\begin{aligned} \Psi = {} & \exp(iw_0 t - 2\pi i \mathbf{k}_0^e . \mathbf{r}) \\ & \times [\exp(-i\varphi_1 t) D_0' \{1 + x_1 \exp(-2\pi i \mathbf{B}_H . \mathbf{r})\} \\ & + \exp(-i\varphi_2 t) D_0'' \{1 + x_2 \exp(-2\pi i \mathbf{B}_H . \mathbf{r})\}] , \end{aligned} \tag{18}$$

where

$$\varphi_1 = 2\pi k_0 \delta_0' / \gamma_0, \quad \varphi_2 = 2\pi k_0 \delta_0'' / \gamma_0 . \tag{19}$$

Here, $\mathbf{k}_0^e$ and $\mathbf{k}_0$ are the internal and external wave vectors, $\mathbf{B}_H$ is the reciprocal lattice vector,

$$\left. \begin{matrix} \delta_0' \\ \delta_0'' \end{matrix} \right\} = \tfrac{1}{2}(\psi_0 - z \pm \sqrt{(q+z^2)}) , \tag{20}$$

$$\left. \begin{matrix} x_1 \\ x_2 \end{matrix} \right\} = (-z \pm \sqrt{(q+z^2)}) / \psi_{\bar{H}} , \tag{21}$$

where

$$q = K^2 b \psi_H \psi_{\bar{H}} \quad \text{and} \quad z = \tfrac{1}{2}(1-b)\psi_0 + \tfrac{1}{2} b \alpha ,$$

so that

$$\sqrt{(q+z^2)} = v + iw .$$

For the Laue case

$$D_0' = \frac{x_2}{x_2 - x_1} \cdot E_0 \quad \text{and} \quad D_0'' = \frac{-x_1}{x_2 - x_1} \cdot E_0$$

where E_0 is the amplitude of the incident wave outside the crystal.

Then, omitting an exponential term of modulus unity,

$$\Psi = \frac{E_0}{(v+iw)}\Big[(v+iw)\cos a(v+iw)$$
$$-i\Big\{z+\frac{q}{K\psi_{\bar{H}}}\cdot\exp(-2\pi i\mathbf{B}_H.\mathbf{r})\Big\}\sin a(v+iw)\Big]. \quad (22)$$

If the term in the brackets $\{\ldots\}$ is put equal to $\chi=\chi'+i\chi''$, so that, for a crystal with a center of symmetry,

$$\chi' = \frac{1-b}{2}\,\psi_0'+\frac{b\alpha}{2}+Kb\psi_H'\cos 2\pi\mathbf{B}_H.\mathbf{r}$$
$$+Kb\psi_H''\sin 2\pi\mathbf{B}_H.\mathbf{r}\,, \quad (23)$$

and

$$\chi'' = \frac{1-b}{2}\,\psi_0''+Kb\psi_H''\cos 2\pi\mathbf{B}_H.\mathbf{r}-Kb\psi_H'\sin 2\pi\mathbf{B}_H.\mathbf{r}, \quad (24)$$

then the intensity at a point in the crystal defined by the vector $\mathbf{r}$ is given by

$$\mathscr{I}(\mathbf{r}) = \Psi.\Psi^* = \exp(-\mu_0 t).E_0^2$$
$$\times[1+1/(v^2+w^2)\{(|\chi|^2-(v^2+w^2))\sin^2(av)$$
$$+(|\chi|^2+v^2+w^2)\sinh^2(aw)+(v\chi''-w\chi')\sin 2av$$
$$+(v\chi'+w\chi'')\sinh 2aw\}]\,. \quad (25)$$

The total fluorescence intensity, given by points at positions $\mathbf{r}$ in the unit cell, will be obtained by summing equation (25) for all unit cells, *i.e.* by integrating (25) over the thickness parameter a.

$$\int_0^{a_0}\mathscr{I}(\mathbf{r})da = \frac{\exp(-\mu_0 t)E_0^2}{2(v^2+w^2)}\Big[\{v^2+w^2-|\chi|^2\}\frac{\sin 2a_0v}{2v}$$
$$+\{v^2+w^2+|\chi|^2\}\frac{\sinh 2a_0w}{2w}$$
$$+\Big\{\Big(\frac{w^2-v^2}{vw}\Big)\chi'-2\chi''\Big\}+\Big(\frac{v\chi''-w\chi'}{v}\Big)\cos 2a_0v$$
$$+\Big(\frac{v\chi'+w\chi''}{w}\Big)\cosh 2a_0w\Big]\,. \quad (26)$$

The fluorescence radiation produced may contain a number of different wave-lengths, which may be recorded with different sensitivity by the detecting system. For any particular detector we may define a function, say $\eta(\mathbf{r})$, which describes the distribution in the unit cell of points giving fluorescence radiation to which the detector responds. Then $\eta(\mathbf{r})$ will be a periodic function

$$\eta(\mathbf{r}) = \sum_H \eta_H\exp(-2\pi i\mathbf{B}_H\mathbf{r})\,,$$

and the total intensity of fluorescence radiation recorded will be

$$F(\alpha) = \int_0^{a_0}\int\mathscr{I}(\mathbf{r}).\eta(\mathbf{r})d\mathbf{r}.da\,. \quad (27)$$

The integral over $\mathbf{r}$ is readily carried out since, if there is a center of symmetry,

$$\int\chi'(\mathbf{r}).\eta(\mathbf{r})d\mathbf{r} = \Big\{\Big(\frac{1-b}{2}\Big)\psi_0'+\frac{b\alpha}{2}\Big\}\eta_0+Kb\psi_H'\eta_H\,,$$

and

$$\int\chi''(\mathbf{r})\eta(\mathbf{r})d\mathbf{r} = \Big(\frac{1-b}{2}\Big)\psi_0''\eta_0+Kb\psi_H''\eta_H\,.$$

The general expression for equation (27) is too complicated for the form of the result to be appreciated readily. However, for the limiting cases of very thin or very thick crystals, there is considerable simplification.

For very thin crystals with $Ay \ll 1$, equation (26) becomes

$$\int\mathscr{I}(\mathbf{r})da = \exp(-\mu_0 t).E_0^2a_0[1+a_0w\chi'/v]$$

and

$$F(\alpha) \propto \Big[\eta_0+\frac{a_0w}{v}\{|\psi_H'|.|b|^{\frac{1}{2}}.\eta_0y+Kb\psi_H'\eta_H\}\Big], \quad (28)$$

where

$$\frac{w}{v} = \frac{\varkappa+gy}{1+y^2}\,.$$

For the symmetrical-beam case, $b=1$, and a crystal with a center of symmetry,

$$F(\alpha) \propto \Big[\eta_0+\frac{K^2a_0\psi_H'\psi_H''}{2(K^2\psi_H'^2+\alpha^2/4)}\{\tfrac{1}{2}\alpha.\eta_0+K\psi_H'.\eta_H\}\Big]\,. \quad (29)$$

For thick crystals, putting $\cosh 2a_0w$ equal to $\exp(2a_0|w|)$ and $\sinh 2a_0w$ equal to $\pm\exp(2a_0|w|)$, as before, we obtain

$$\int_0^{a_0}\mathscr{I}(\mathbf{r})da = \frac{\exp(-\mu_0 t+2a_0|w|)E_0^2}{8|w|(v^2+w^2)}$$
$$\times[(v\pm\chi')^2+(w\pm\chi'')^2]\,,$$

and for the special case of $b=1$ and a center of symmetry,

$$F(\alpha) \propto \frac{\exp(-\mu_0 t+2a_0|w|)}{8K^2\psi_H'^2\psi_H''^2}$$
$$\times\Big[|\psi_H'\psi_H''|\eta_0+\frac{(K^2\psi_H'^2+\alpha^2/4)}{\psi_H'\psi_H''}\{\tfrac{1}{2}\alpha\eta_0+K\psi_H'\eta_H\}\Big]\,. \quad (30)$$

From equation (29) it is seen that for thin crystals the intensity profile contains symmetric and antisymmetric terms. The antisymmetric part is proportional to $\psi_H'\psi_H''$ and so gives ψ_H'' uniquely in terms of ψ_H'. The symmetric part of the profile depends on the product $\psi_H''.\eta_H$. If this can be measured, its magnitude and sign will give information on the distribution of the fluorescing atoms relative to the distribution of absorbing atoms.

Thus, if the fluorescing atoms are also responsible for the major part of the absorption, their distribution will be given approximately by ψ'' and information regarding their positions is given by the antisymmetric terms. If the fluorescing atoms constitute only a very small part of the absorbing matter and ψ'' is similar to ψ', information on the relative positions of fluorescing atoms is obtained from the symmetric terms. For thick crystals the part of equation (30) in square brackets is much the same as the corresponding part of equation (29), but the angular dependence will be determined almost entirely by the factor $\exp\{-\mu_0 t+2a_0|w|\}/|\psi'_H\psi''_H|$ which is independent of η_H and so of the positions of the fluorescing atoms, but depends on the angular variables, in much the same way as the integrated intensities, equations (16) and (17).

Batterman (1962) has recently demonstrated the variation of fluorescence with angle of incidence for a thick crystal of germanium giving the 220 reflection for Mo $K\alpha$ radiation.

Kossel lines

The theory of the formation of Kossel lines from radiation diverging from points within a crystal, neglecting absorption, was given by Laue (1935), who made use of the reciprocity law concerning the interchange of sources and sinks of radiation. For our present purposes this may be said to imply that the intensity at a point B outside a crystal due to a point source at A inside the crystal is equal to the intensity at A due to a point source at B. Hence, the intensity in a direction defined by α due to radiation from a point at a position in the crystal defined by $\mathbf{r}$ is given by equation (25), which expresses the intensity at a point $\mathbf{r}$ as a function of α, which defines the direction of incident radiation.

The total radiation in direction α from all points $\mathbf{r}$ throughout the crystal is then given by equation (26). The production of Kossel lines is thus the complete inverse of the production of fluorescence radiation by a crystal wave field and the expressions for the intensity are completely analogous.

If we denote the distribution of emitting points by

$$\xi(\mathbf{r}) = \sum_H \xi_H \exp(-2\pi i\mathbf{B}.\mathbf{r})\,,$$

then the intensity observed in the Kossel line pattern will be given by

$$K(\alpha) = \int_0^{a_0}\int \mathscr{I}(\mathbf{r}).\,\xi(\mathbf{r})\,dr.da\,. \tag{31}$$

Then for thin crystals, in analogy with equation (28),

$$K(\alpha) \propto \left[\xi_0+\frac{aw}{v}\left\{\frac{1-b}{2}\,\psi'_0\xi_0+\frac{b\alpha}{2}\,\xi_0+Kb\psi'_H\xi_H\right\}\right]\,, \tag{32}$$

or, for the symmetrical-beam case,

$$K(\alpha) \propto \left[\xi_0+\frac{K^2a_0\,\psi'_H\psi''_H}{2(K^2\psi'^2_H+\alpha^2/4)}\{\xi_0\tfrac{1}{2}\alpha+K\psi'_H\,\xi_H\}\right]\,,$$

and there is a corresponding expression, analogous to equation (30), for thick crystals.

For thin crystals the intensity distribution of the Kossel line, if resolved, will show a black-white asymmetry.* When separated out, the antisymmetric part, depending on the product $\psi'_H\psi''_H$, will give information on the relative distributions of absorbing and normally scattering atoms. The symmetric part, depending on the product $\psi'_H\xi_H$ will give information on the distribution of emitting atoms relative to other atoms.

Experimental considerations

For the detailed verification of the expressions derived in the preceding sections, it would be necessary to use diffraction equipment of high angular resolving power. The interesting part of the intensity profile in each case is contained within a few units of y; *i.e.* within a range of α of the order of $|\psi'_H|$. For most crystals and radiations used this angular range is thus about 10^{-5} radian, or a few seconds of arc. Similarly the mosaic spread of the crystal used should not exceed a few seconds of arc. Suitable crystals are readily obtained for only a few substances in cases where the 'thick-crystal' approximations apply (for thicknesses of the order of 1 mm or more), but are much more common when the 'thin-crystal approximations' may be valid (thicknesses of a few microns or tens of microns).

In the more usual diffraction experiments, including the usual Kossel line observations, the angular resolution is of the order of 10^{-3} radian. This is determined either by the geometry of the equipment or by the mosaic spread of the crystals used. If the mosaic spread is of this order and the individual perfect crystal regions are very small, the intensity excess or defect of a reflection profile is given by integrating the thin-crystal formulas over the angle of incidence. The averaging over orientation will then wipe out the antisymmetric component, and only the symmetric component of the ideal profile will contribute.

For the intensity of fluorescence radiation given by atoms within a diffracting crystal and for the Kossel lines given by emitting atoms within a crystal, it is this symmetric component which is proportional to the Fourier coefficient of the distribution of fluorescing or emitting points. Relatively low resolution patterns could therefore be used to obtain information concerning the relative positions of fluorescing or emitting atoms within a crystal.

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* This asymmetry is not to be confused with the black-white asymmetry on a larger scale, observed by many workers (*e.g.* Borrmann, 1936; Lonsdale, 1947) and arising from the separation of the effective source-points of transmitted and diffracted beams.

For thick perfect-crystal regions, angular integration of the intensity profiles in all cases gives an expression in which the most important term is of the form exp $(-\mu_0 t+h)$, (see equations (16) and (17)). Then if all the relevant variables can be adequately controlled, any of these low-resolution measurements on thick crystals may be used to derive values for $h=2A\sqrt{(\varkappa^2+g^2)}$, and if such measurements can be made for several different wave-lengths or for several different b values, it should be possible to deduce ψ_0'' and ψ_H'' separately in terms of ψ_H'.

For very thin crystals, the only information derivable from the low-resolution measurement of transmitted intensities is the value of ψ_0'', or the average absorption coefficient. However, high-resolution studies may be made fairly easily by use of a double-crystal spectrometer, or, preferably, a three-crystal spectrometer arrangement.

The form of the intensity profile for transmitted and diffracted beams has been verified by several authors for monatomic crystals and by Brogren & Adell (1953) and Brogren & Nordling (1962) for one plane, the cleavage plane, of calcite. In order to demonstrate the variation of the profiles with the lattice plane involved for non-simple crystals, and to show the dependence of the anti-symmetric component on the sign as well as the magnitude of ψ_H'', some preliminary tests of the thin-crystal

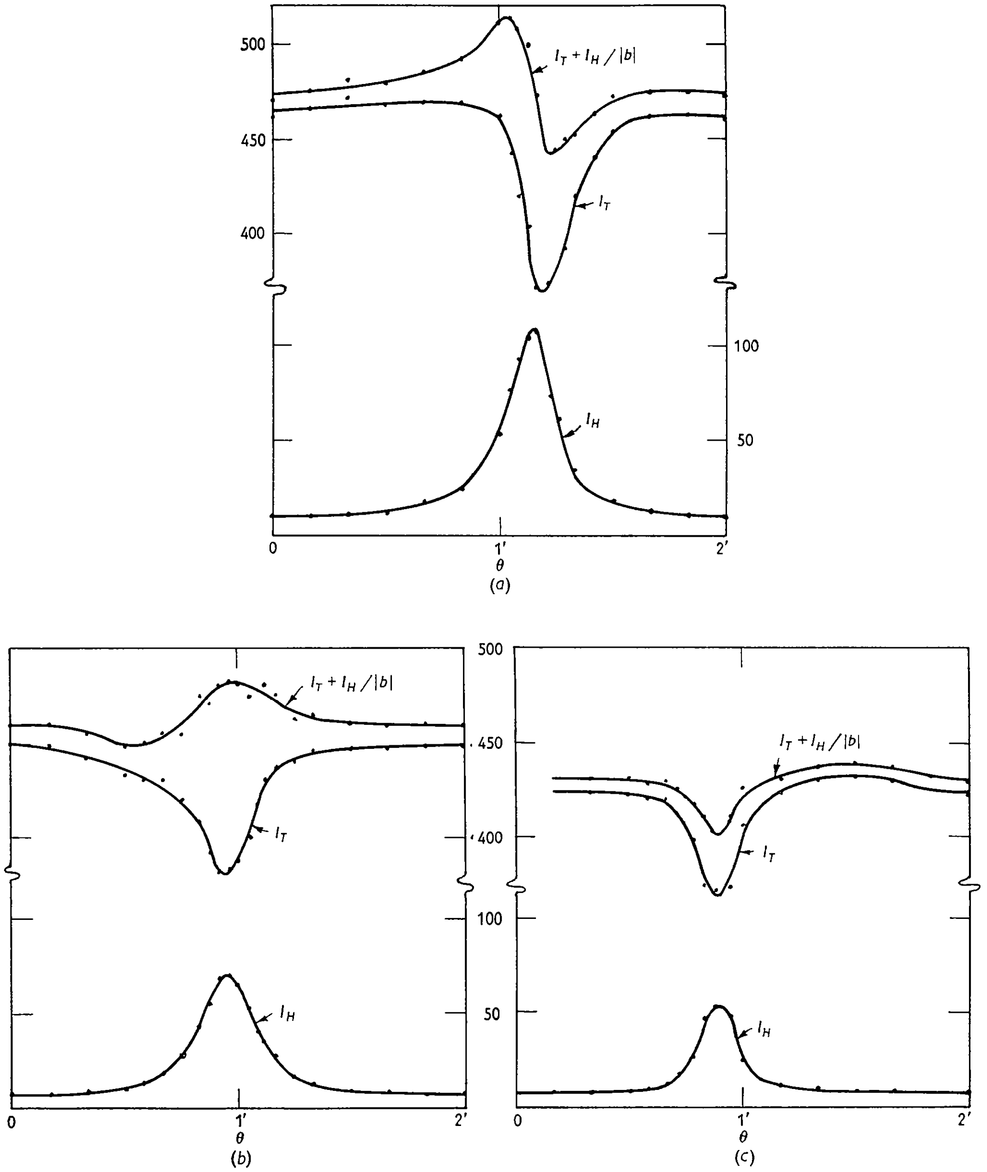

Fig. 2. Transmitted and diffracted intensities for a calcite crystal, thickness 0·7 mm, with Mo $K\alpha$ radiation. Horizontal scale in minutes of arc. Vertical scale in number of counts divided by 32. (*a*) 211 reflection, with $b=1{\cdot}065$; (*b*) 222 reflection with $b=0{\cdot}78$; (*c*) 222 reflection with $b=1{\cdot}46$.

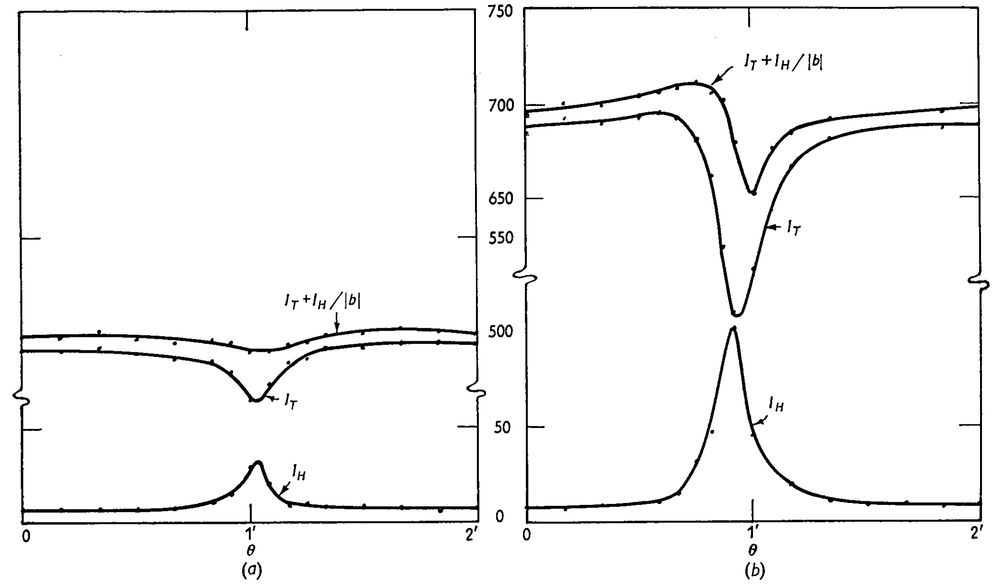

Fig. 3. Transmitted and diffracted intensities for a sodium nitrate crystal of thickness 0·8 mm with Mo $K\alpha$ radiation. Scales as for Fig. 2. (*a*) 110 reflection with $b = 0{\cdot}96$; (*b*) 211 reflection with $b = 1{\cdot}08$

formula, equation (11), have been made with a standard double-crystal spectrometer, with the second crystal set for transmission as in Fig. 1. The first crystal was, in each case, a large calcite crystal set to give a first-order reflection from the cleavage face, the (211) plane, with Mo $K\alpha$ radiation. The second crystal, the crystal under investigation, was set with the desired plane approximately anti-parallel to the reflecting plane of the first. Reflections were chosen with Bragg angles close to that of the (211) calcite plane so that the wave-length dispersion of the two-crystal arrangement would be small. Intensity measurements were made on the directly transmitted and the diffracted beams at small intervals of rotation of the second crystal. Values of these intensities, I_T and I_H, and of the sum, $I_T + I_H/|b|$, are plotted in Figs. 2 and 3 for the (211) and (222) planes of calcite, and for the (211) and (110) planes of sodium nitrate, which is isomorphous with calcite.

For the (211) planes in each crystal, all atoms scatter in phase, so that both ψ'_H and ψ''_H are negative (F'_H and F''_H are positive). For the (222) planes of calcite, the structure factor is $F_{222} = -2f_{\text{Ca}} + 2f_{\text{C}} + 6f_{\text{O}}$. For the real part, the atomic scattering factor for calcium is less than the sum of the scattering factors for the lighter elements so that F'_H is positive. For the imaginary part, the effective atomic scattering factor increases much more rapidly with atomic number (proportional to Z^4) so that the calcium scattering predominates and F''_H is negative. Similarly for the 110 reflection of $NaNO_3$, we have $F_{110} = -2f_{\text{Na}} + 2f_{\text{N}} + 2f_{\text{O}}$ and because of the much greater contribution of the sodium scattering to the imaginary component, ψ''_H is positive while ψ'_H is negative.

From Figs. 2 and 3 it can be seen that there is at least qualitative agreement with the predictions of equations (10) and (11). The curve for $I_T + I_H/|b|$ shows an antisymmetric component which is of opposite sign for the calcite 211 and 222 reflections, being negative (maximum at low θ values) for ψ'_H and ψ''_H of the same sign and positive if they have the opposite sign. The same difference is seen for the 211 and 110 reflections of $NaNO_3$. There is also a symmetric component which is positive for $b < 1$ (g negative), as in Fig. 2(*b*), and negative for $b > 1$, as in Fig. 2(*c*).

The relative magnitudes of the symmetric and antisymmetric components are approximately in agreement with the theoretical predictions, but accurate comparison would involve detailed calculation of the effects of instrumental broadening and mosaic spread on the profile shapes. It is clear that these factors contribute a major part to the observed half-widths of the reflections (all in the range of 10 to 20 seconds).

The asymmetry of the diffracted beam profile due to absorption effects is visible for the calcite 211, Fig. 2(*a*), but for the weaker reflections the accuracy of the data is not sufficient to show the effect clearly.

Discussion

If we overlook, for the moment, the considerable, but not insuperable, experimental difficulties which may be involved, we may conclude from our analysis of the theoretical results that observations of the effects of absorption on X-ray diffraction processes should provide useful additional information concerning the structures of crystals and of their defects. From the measurement of intensity profiles for the transmission of X-rays through thin crystals, or from measurements of intensities of X-rays transmitted by near-perfect thick crystals, it should be possible to deduce the Fourier coefficients, ψ''_H. In the absence of absorption edges, the imaginary component of the atomic scattering factors increases very much more rapidly with Z than the real part. In the process of the structure analysis of crystals containing atoms of differing atomic number, the measurement of the coefficients, ψ''_H, would be equivalent to, and as useful as, good isomorphous replacement data, and in favorable cases could lead to the unambiguous determination of crystal structures.

When medium-weight atoms are involved, large differences in absorption coefficient for small differences in atomic number may be realized by choosing the appropriate radiation relative to the absorption edges of the atoms. The use of the absorption Fourier coefficients would then allow ready separation of atoms of almost equal weight in structure analyses.

For radiations other than X-rays, diffracted by crystals, the theoretical considerations apply equally well. In neutron diffraction experiments advantage could be taken of the widely, and erratically, varying inelastic-scattering cross-sections of the elements. However, for neutrons perfect crystals large enough for the application of the 'thick-crystal' formulas are difficult to obtain, and the instrumental resolution required to get useful information from the 'thin-crystal' formulas is also difficult. For electrons the situation is more complicated because the two-beam approximation to the dynamical theory, from which all the above formulas were derived, is not usually valid.

High-resolution measurements of fluorescence radiation or Kossel line profiles would contain the same information on the distribution of absorbing atoms and could be used in the same way for purposes of crystal structure analysis. In addition they would contain information on the distribution of emitting atoms in the unit cell, and for this, high resolution conditions are not necessarily required.

The detection of radiation from particular kinds of atom in a crystal can be made highly selective. The characteristic radiation associated with one element may be detected when the element is present in only small proportions. The possibility therefore exists that by observation of fluorescence radiation emitted when X-rays of a suitable wave-length are diffracted by a crystal, or by observing the Kossel line pattern produced by characteristic radiation from atoms within a crystal, the location of relatively small numbers of impurity atoms may be determined with respect to the unit cell of the host crystal.

For radiations other than X-rays the situation is even more favorable for some special cases. Some very specific nuclear reactions may occur when slow neutrons are diffracted by a crystal, giving secondary radiation which may be detected readily. Knowles (1956) has performed an experiment along these lines. Also gamma radiation from nuclear reactions or from fluorescence excitation (Mössbauer effect) could give rise to Kossel line patterns. By the use of such techniques, methods could be evolved for determining the environment of impurity atoms present in very small concentrations.

The variation of the intensity of characteristic X-rays emitted when an electron beam is diffracted in a crystal has been observed by Duncumb (1962), and such observations could be used in a similar way. For electrons of the usual energies, however, the sensitivity to low concentrations of impurities would be limited because the total number of atoms in the very small crystals employed is relatively small.

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