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Extinction Correction in White X-ray and Neutron Diffraction

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Abstract

Extinction effects in white-beam X-ray and neutron diffraction are considered following the formulation developed for monochromatic-beam diffraction by Becker & Coppens [*Acta Cryst.* (1974), A**30**, 129–147]. In white-beam diffraction, a small deviation of the wavelength from the Bragg condition $\Delta\lambda$ is a variable which represents the line profile of the diffraction peaks, so that by using the new parameter $\Delta\lambda$ the theory is converted to one in white-beam diffraction. It is shown that for a convex crystal, primary extinction y_p agrees with the results calculated already for monochromatic diffraction. The same relation is shown to hold in secondary extinction y_s. It is concluded that extinction theory derived for monochromatic diffraction is applicable without any modification in white-beam diffraction.

1. Introduction

Recently, crystal-structure studies using the white-beam diffraction method have taken a more and more important place because of the advance in energy-dispersive solid-state X-ray detectors in X-ray diffraction, and the increase in available pulsed-neutron sources in neutron diffraction. In order to obtain the structure factor $|F|$ from the original data in white-beam diffraction, it is necessary to make wavelength-dependent corrections for the incident spectrum $\mathscr{I}_0(\lambda)$, absorption and extinction. Although the correction methods of the former two terms seem to be established so far, there has not been much discussion about the extinction effect. As demonstrated by Niimura, Tomiyoshi, Takahashi & Harada (1975), however, the extinction effect is very important in white-beam diffraction because a wide range of wavelengths of the incident radiation, sometimes more than 1 Å, is often used and, due to a λ^4 dependence of the integrated intensity, wavelength variation of the extinction effect is very large.

The extinction theories proposed hitherto have been developed by assuming a monochromatic incident beam and there has not been much discussion about the application of the theories to a white-beam radiation experiment. The purpose of the present paper is to clarify this point. As the theory of extinction, the formulation developed by Zachariasen (1967) is widely used but it includes a mathematical mistake. Becker &

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Coppen's (1974 – hereafter referred to as BC) treatments of extinction, which have basically the same formulation as that of Zachariasen, eliminate the mistake. For this reason, we tried to transform BC theory to white-beam diffraction.

The symbols used in this paper are the same as those used in BC, in which they were summarized in the glossary, so we often use the symbols without any definition. We also use the suffix w for each quantity in white-beam diffraction to distinguish it from that used in monochromatic diffraction.

2. The features of white-beam diffraction

We now summarize the kinematical theory of diffraction with the white-beam method. Let $\mathbf{u}_0^0$ and $\mathbf{u}^0$ be unit vectors along the incident and diffracted beams respectively in the case when the Bragg condition is exactly fulfilled (when the Bragg condition is not fulfilled the corresponding vectors are $\mathbf{u}_0$ and $\mathbf{u}$ respectively). The Bragg condition is described by

$$(1/\lambda)(\mathbf{u}_0^0 - \mathbf{u}^0) = \mathbf{H}, \quad (1)$$

where $\mathbf{H}$ is the reciprocal-lattice vector corresponding to a given reflection. In white-beam diffraction, the parameter by which the reciprocal space is scanned is the wavelength of the incident radiation, so we increase the wavelength from the Bragg wavelength λ to $\lambda + \Delta\lambda$ and keep $\mathbf{u}_0^0$ and $\mathbf{u}^0$ vectors fixed. The diffraction vector $\mathbf{S}$ shown in Fig. 1 is then defined by

$$\mathbf{S} = \frac{1}{\lambda + \Delta\lambda}(\mathbf{u}_0^0 - \mathbf{u}^0) = \mathbf{H} + \frac{1}{\lambda}\,\varepsilon_\lambda, \quad (2)$$

where $\varepsilon_\lambda/\lambda$ is the deviation of the scattering vector from $\mathbf{H}$ due to a small increase of the wavelength $\Delta\lambda$; its direction is along $\mathbf{H}$ and its magnitude is given by

$$|\varepsilon_\lambda| = \Delta\lambda|\mathbf{H}| = \Delta\lambda\, 2\sin\theta/\lambda, \quad (3)$$

where θ is the Bragg angle.

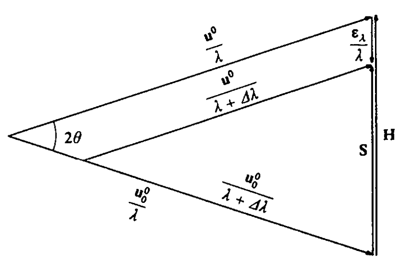

Fig. 1. Bragg scattering in reciprocal space. When the wavelength, $\lambda = 2d\sin\theta$, is increased to $\lambda + \Delta\lambda$ the scattering vector $\mathbf{S}$ varies along the reciprocal-lattice vector $\mathbf{H}$.

In white-beam diffraction a unit vector $\boldsymbol{\tau}_\lambda$ is defined in the $-\mathbf{H}$ direction, so $\boldsymbol{\varepsilon}$ in general is defined by

$$\boldsymbol{\varepsilon} = \varepsilon_\lambda \boldsymbol{\tau}_\lambda + \varepsilon_2 \boldsymbol{\tau}_2 + \varepsilon_2 \boldsymbol{\tau}_3, \quad (4)$$

where ε_2 is a divergence angle of the diffracted beam from $\mathbf{u}^0$ in the diffraction plane, and ε_3 is that perpendicular to the diffraction plane, and the definitions of ε_2, ε_3 are the same as defined in BC.

The differences between the monochromatic- and white-beam diffractions appear only in the $\boldsymbol{\tau}_1$ (or $\boldsymbol{\tau}_\lambda$) term without any other relations changed, so in the following we consider only the transformation of the parameter ε_λ from ε_1 in the theory of BC.

The intensity of radiation scattered in the direction $\mathbf{u}$ is given by

$$I_k(\boldsymbol{\varepsilon}) = \mathscr{I}_0(\lambda)\left|\frac{aFK}{R_0}\right|^2 \left|\sum_L \exp(2\pi i\lambda^{-1}\boldsymbol{\varepsilon}.\mathbf{L})\right|^2, \quad (5)\ (\text{BC. }2)$$

where $\mathscr{I}_0(\lambda)$ is a wavelength-dependent incident radiation spectrum but we assume that $\mathscr{I}_0(\lambda)$ is constant in the vicinity of the Bragg wavelength λ, a is the scattering amplitude, F is the structure factor, K is the polarization factor, R_0 is the distance from crystal to counter and $\mathbf{L}$ is a lattice vector in the crystal.

The power recorded in the counter $P_k(\Delta\lambda)$ which depends only on the deviation of the wavelength from λ, $\Delta\lambda$, is given by

$$P_k(\Delta\lambda) = R_0^2 \int\int I_k(\boldsymbol{\varepsilon})\,\mathrm{d}\varepsilon_2\,\mathrm{d}\varepsilon_3. \quad (6)\ (\text{BC. }3)$$

The diffracting cross section per unit volume and unit intensity is defined by

$$\sigma_w(\Delta\lambda) = \mathscr{I}_0^{-1}(\lambda)v^{-1}P_k(\Delta\lambda), \quad (7)\ (\text{BC. }4)$$

where w denotes the quantity in white-beam diffraction and v the volume of the sample crystal. Q, the average scattering cross section per unit volume of the crystal, is obtained by integration of $\sigma_w(\Delta\lambda)$ over $\Delta\lambda$:

$$Q_w = \int \sigma_w(\Delta\lambda)\,\mathrm{d}\Delta\lambda = \left|\frac{aFK}{V}\right|^2 \frac{\lambda^4}{2\sin^2\theta}. \quad (8)$$

Q in monochromatic diffraction is given by

$$Q = \left|\frac{aFK}{V}\right|^2 \frac{\lambda^3}{\sin 2\theta}. \quad (9)\ (\text{BC. }5)$$

The last factors of (8) and (9) are known as the Lorentz factor.

The extinction factor y is written as usual by

$$\mathscr{P} = \mathscr{P}_k y, \quad (10)\ (\text{BC. }7)$$

and

$$\mathscr{P}_k = \int \mathscr{P}_k(\Delta\lambda)\,\mathrm{d}\Delta\lambda = \mathscr{I}_0(\lambda)\,vQ, \quad (11)\ (\text{BC. }6)$$

where $\mathscr{P}$ and $\mathscr{P}_k$ are integrated intensities in the real crystal and in the kinematical theory, respectively.

3. Calculation of σ

The basic quantity to evaluate extinction effects is σ, the diffracting cross section per unit volume and unit intensity. We now calculate this quantity in white-beam diffraction following the method given in Appendix C of BC assuming convex crystals:

$$\sigma_w(\Delta\lambda) = Q_w(V^2/v)(2\sin^2\theta/\lambda^4)A(\Delta\lambda), \quad (12)\ (\text{BC. } C1)$$

$$A(\Delta\lambda) = \int\int \mathrm{d}\varepsilon_2\,\mathrm{d}\varepsilon_3 \sum_{\mathbf{L}} \left|\exp(2\pi i\boldsymbol{\varepsilon}.\mathbf{L}/\lambda)\right|^2, \quad (13)\ (\text{BC. } C2)$$

where V is the unit-cell volume.

Summation over the lattice points is replaced by the integral over the volume of the crystal. The axes $\{\omega_1, \omega_2, \omega_3\}$ in real space are defined by the reciprocal frame $\{\boldsymbol{\tau}_\lambda, \boldsymbol{\tau}_2, \boldsymbol{\tau}_3\}$ as shown in Fig. 2 which is different in a few aspects from Fig. 14 of BC. Thus $A(\Delta\lambda)$ transforms to

$$A = \frac{1}{V^2}\int_v\int_v \mathrm{d}v\,\mathrm{d}v' \exp[2\pi i\varepsilon_\lambda(r_1 - r_1')\sin\theta/\lambda] \times \int_{-\infty}^{+\infty} \exp[2\pi i\varepsilon_2(r_2 - r_2')\sin\theta/\lambda]\,\mathrm{d}\varepsilon_2 \times \int_{-\infty}^{+\infty} \exp[2\pi i\varepsilon_3(r_3 - r_3')/\lambda]\,\mathrm{d}\varepsilon_3. \quad (14)$$

This integration is calculated according to the treatments of Appendix C of BC and as a final result, $\sigma_w(\Delta\lambda)$ is obtained as

$$\sigma_w(\Delta\lambda) = \frac{Q_w}{v}\int \mathrm{d}v\,\alpha_w \frac{\sin^2\pi\Delta\lambda\alpha_w}{(\pi\Delta\lambda\alpha_w)^2}, \quad (15)$$

where α_w is defined by

$$\alpha_w = 2l\sin^2\theta/\lambda^2, \quad (16)$$

where l is the thickness of the crystal parallel to the diffraction beam. $\sigma(\varepsilon_1)$ in monochromatic-beam diffraction is given by

$$\sigma(\varepsilon_1) = \frac{Q}{v}\int \mathrm{d}v\alpha \frac{\sin^2\pi\varepsilon_1\alpha}{(\pi\varepsilon_1\alpha)^2}, \quad (17)\ (\text{BC. } 19a)$$

where

$$\alpha = l\sin 2\theta/\lambda. \quad (18)\ (\text{BC. } 19b)$$

The comparison of the above expressions with those of BC shows that σ is written in the identical form by replacing the corresponding quantities. $\sigma_w(\Delta\lambda)$ is also easily derived from $\sigma(\varepsilon_1)$ by using the relation $\Delta\lambda/\lambda = \varepsilon_1\cot\theta$. It is easily shown that $\sigma(\varepsilon_1 = 0) = \sigma_w(\Delta\lambda = 0)$, which shows that when the Bragg condition is exactly fulfilled, the diffraction cross section has the same value at its peak point in each case. For a spherical crystal with radius r, $\sigma_w(\Delta\lambda)$ is calculated by using (15):

$$\sigma_w(\Delta\lambda) = \tfrac{3}{4}Q_w\beta_w[(\pi\Delta\lambda\beta_w)^2 - (\pi\Delta\lambda\beta_w)\sin(2\pi\Delta\lambda\beta_w) + \sin^2(\pi\Delta\lambda\beta_w)]/(\pi\Delta\lambda\beta_w)^4, \quad (19)\ (\text{BC. } 29)$$

where

$$\beta_w = 2r\times 2\sin^2\theta/\lambda^2. \quad (20)$$

Equation (29) of BC has the same expression as the above formula.

4. Primary extinction

Primary extinction y_p in white-beam diffraction is defined by equation (14) of BC:

$$y_p = \frac{1}{Q_w}\int \sigma_w(\Delta\lambda)\varphi[\sigma_w(\Delta\lambda)]\,\mathrm{d}\Delta\lambda. \quad (21)\ (\text{BC. } 14)$$

We now calculate y_p for a perfect spherical crystal with radius r, in which $\varphi(\sigma_w)$ is a function of $\sigma_w r$ as shown in BC. From (19), $\sigma_w(\Delta\lambda)$ is defined as

$$\sigma_w(\Delta\lambda) = \sigma_w(0)f(\eta_w), \quad (22)$$

where

$$\eta_w = \pi\Delta\lambda\beta_w. \quad (23)$$

The quantity x defined in equation (35) of BC is given as

$$x = \sigma_w(0)r = \tfrac{2}{3}Q_w\bar{\alpha}_w\bar{t}, \quad (24)\ (\text{BC. } 35a)$$

where

$$\bar{\alpha}_w = \tfrac{3}{2}r\times 2\sin^2\theta/\lambda^2. \quad (25)\ (\text{BC. } 35b)$$

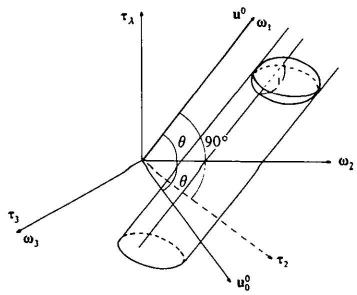

Fig. 2. The relationship between axes in reciprocal space $\{\boldsymbol{\tau}_\lambda, \boldsymbol{\tau}_2, \boldsymbol{\tau}_3\}$ and the corresponding ones in real space $(\boldsymbol{\omega}_1, \boldsymbol{\omega}_2, \boldsymbol{\omega}_3)$. $\boldsymbol{\tau}_\lambda$ is a unit vector along the $-\mathbf{H}$ direction. $\boldsymbol{\tau}_2$ is a unit vector perpendicular to the scattering beam in the diffraction plane, and $\boldsymbol{\tau}_3$ is one vertical to the diffraction plane. Projection of the crystal parallel to the diffraction beam onto the $\boldsymbol{\omega}_2$–$\boldsymbol{\omega}_3$ plane are shown. l is the length of the sample parallel to the diffracted beam.

y_p is then written as

$$y_p = \frac{3}{4\pi} \int_{-\infty}^{+\infty} f(\eta_w)\varphi[xf(\eta_w)]\, d\eta_w. \qquad (26) \quad (BC. 36)$$

The expression of this integral which is identical to that of equation (36) of BC is only dependent on x for a given value of θ, so if x given in (24) is shown to be identical for each case, primary extinction y_p will be proved to be equivalent for the two diffraction methods. Equation (24) can be written as

$$x = \frac{2}{3}\left|\frac{aFK}{V}\right|^2 \lambda^2\, 2r^2. \qquad (27)$$

Also, equation (35a) of BC is written in an identical form to (27). Therefore, we can conclude that, for spherical perfect crystals, primary extinction $y_p(x)$ becomes identical for both monochromatic- and white-beam diffraction. Next, we consider whether this equivalence is valid for a more general sample shape using a series expansion of $\varphi(\sigma)$. For a convex-shape crystal, $\varphi(\sigma)$ can be expressed in terms of a power series in σ as in equations (18a) and (18b) of BC by

$$\varphi(\sigma) = \sum_{n=0}^{\infty} (-1)^n \frac{\sigma^n}{n!} \overline{t^{(n)}} \qquad (28) \quad (BC. 18a)$$

with

$$\overline{t^{(n)}} = \sum_{n=0}^{n} \binom{n}{j}^2 v^{-1} \int_v dv\, t_1^j\, t_2'^{\,n-j}. \qquad (29) \quad (BC. 18b)$$

The symbols used have the same meanings as given in the glossary of BC. $\overline{t^{(n)}}$ does not include the variable ε_1, so this term is independent of the diffraction methods. The extinction factor y_p is given by using this series expansion in monochromatic diffraction and is expressed as follows:

$$y_p = \frac{1}{Q}\int \sigma\varphi(\sigma)\, d\varepsilon_1 = \sum_{n=0}^{\infty} (-1)^n \frac{\overline{t^{(n)}}}{n!} \int \frac{\sigma^{n+1}}{Q}\, d\varepsilon_1. \qquad (30)$$

We use (17) for $\sigma(\varepsilon_1)$ which is valid for a convex crystal; then

$$y_p = \sum_{n=0}^{\infty} (-1)^n \frac{\overline{t^{(n)}}}{n!} \frac{1}{v^{n+1}} \int dv_1 \ldots \int dv_{n+1} \int \frac{Q^{n+1}}{Q} \alpha^{n+1} \times \frac{\sin^{2n+2}(\pi\varepsilon_1\alpha)}{(\pi\varepsilon_1\alpha)^{2n+2}}\, d\varepsilon_1$$

$$= \sum_{n=0}^{\infty} (-1)^n \frac{\overline{t^{(n)}}}{n!} \frac{1}{v^{n+1}} \int dv_1 \ldots \int dv_{n+1} A_{2n+1} (Q\alpha)^n, \qquad (31)$$

where

$$A_n = \frac{2}{2^n(n-1)!} \sum_{r=0}^{p} (-1)^r \binom{n}{r} (n-2r)^{n-1} \qquad (32)$$

[for n odd, $p=(n-1)/2$, for n even, $p = n/2 - 1$].

When $\sigma_w(\Delta\lambda)$ in (15) is used in white-beam diffraction, then the final result is given by the replacement of $Q\alpha$ by $Q_w\alpha_w$ in (31). However,

$$Q\alpha = Q_w\alpha_w = |aFK/V|^2 \lambda^2 l, \qquad (33)$$

and volume integration over l is common for the two methods.

So y_p expressed in terms of a power series in Q is identical for both monochromatic and white-beam diffraction. A very important conclusion is that the combined quantity $Q\alpha$ which is a parameter to express extinction is independent of the diffraction methods although Q and α individually have different forms in monochromatic- and white-beam diffraction.

5. Secondary extinction

Consider the Bragg reflection by the mosaic blocks. Fig. 3 shows two blocks of crystal which make a very small misorientation angle ζ. It is assumed that for block 1 the Bragg condition $\lambda = 2d \sin\theta$ is fulfilled for a particular λ and θ. For block 2, the same incident radiation is diffracted with deviation angle 2ζ from the first one. The increase of the wavelength $\Delta\lambda$ from λ due to the variation of the scattering angle is determined by the well known formula:

$$\cot\theta \times \zeta = \Delta\lambda/\lambda. \qquad (34)$$

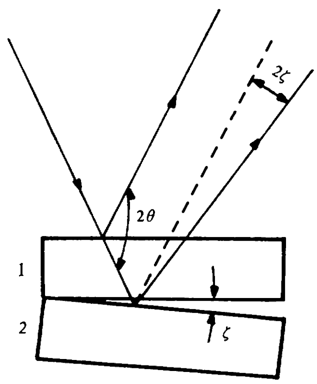

Fig. 3. Bragg reflection by two mosaic blocks which make a small misorientation angle ζ with each other.

Then, σ_w for block 2 is written as $\sigma_w(\Delta\lambda + \lambda \cot \theta \times \zeta)$ if we take block 1 as a standard. Therefore, the mean diffracting cross section for mosaic distribution $W(\zeta)$ is written as

$$\bar{\sigma}_w(\Delta\lambda) = \int \sigma_w(\Delta\lambda + \lambda \cot \theta \times \zeta)\, W(\zeta)\, d\zeta. \quad (35)$$

As an example of the mosaic distributions, consider the Lorentzian $W_L(\zeta)$:

$$W_L(\zeta) = 2g/(1 + 4\pi^2 \zeta^2 g^2), \quad (36)$$

where g is the width parameter of the mosaic distribution. From (34), $W_L(\zeta)$ is written as

$$W_L(\Delta\lambda) = 2g_w/[\tan \theta(1 + 4\pi^2 \Delta\lambda^2 g_w^2)/\lambda], \quad (37)$$

where

$$g_w = g \tan \theta/\lambda. \quad (38)$$

g_w expresses the nominal width of the mosaic distribution in the white-beam diffraction. With the use of the $\Delta\lambda$-dependent Lorentzian distribution, (37), $\bar{\sigma}_w(\Delta\lambda)$, the average diffracting cross section in a mosaic crystal, is written as

$$\bar{\sigma}_w(\Delta\lambda) = \int \sigma_w(\Delta\lambda + \Lambda)\, W_L(\Lambda)\, d\Lambda, \quad (39)$$

where Λ is the Bragg wavelength of a mosaic block with small misorientation angle ζ. This expression is the same as the one given in equation (21) of BC, and shows that $\Delta\lambda$ can be treated in the same manner as ε_1 of the mosaic crystal of BC. We can easily show by using (16) and (38) that $x = 2/3Q\alpha\bar{T}$ (where $\bar{T}$ is the mean path length through the crystals) becomes identical for both diffraction methods, so secondary extinction y_s as a function of x is identical for the two diffraction methods, as we have shown for y_p in § 4.

6. Discussion

We have tried in the present paper to calculate extinction effects in white-beam diffraction following the formulation developed by BC and it has been shown that, within the framework of their theory, extinction correction in white-beam diffraction agrees with that in monochromatic-beam diffraction.

Definition of x in (24) [equation (35a) of BC] shows that x has a value of $\sigma_w(\Delta\lambda)$ at $\Delta\lambda = 0$, when the Bragg condition is exactly fulfilled, so x does not depend on whether the parameter is ε_1 or $\Delta\lambda$. The extinction factor y is a function of the parameters x and θ, so we can say more generally that extinction does not depend on the method of diffraction.

The results given by Niimura, Takahashi & Harada (1974) for type I and type II crystals agree with the present one; however, their conclusion is derived from some simple assumption of σ for Zachariasen's theory, and the validity of their assumption is not fully proved.

The extinction theories given by Zachariasen (1967) and Cooper & Rouse (1970) are applicable without any modification in white-beam diffraction, since the expression of x as a function of F^2, λ, sin 2θ and other quantities is invariant for the two diffraction methods.

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