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Extinction and Borrmann Effect in Mosaic Crystals

By W. H. Zachariasen

Department of Physics, The University of Chicago, Chicago, Illinois 60637, *U.S.A.*

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The theory of X-ray diffraction in mosaic crystals is modified to include the Borrmann effect. The equations show that the Borrmann effect becomes important for strong reflections in type II mosaic crystals if the domain size is of the order of 10^{-4} cm or larger and if $\mu_0\bar{T}\geq 1$. Under these circumstances the integrated intensity may be enhanced by as much as a factor of two with a corresponding apparent decrease in the extinction effect.

Introduction

In a recent paper (Zachariasen, 1967, henceforth to be referred to as reference 1) it was shown that extinction in a mosaic crystal reduces the integrated intensity of X-ray diffraction by a factor y_K, the extinction factor, as compared with the prediction of the kinematical theory. The expression for the extinction factor is

$$\begin{aligned} y_K &= (1+2x_K)^{-1/2}\,, \\ x_K &= r^* K^2 Q_0 \lambda^{-1} \bar{T}\,, \\ r^* &= r/\sqrt{1+(r/\lambda g)^2}\,, \\ Q_0\lambda^{-1} &= \left|\frac{e^2\lambda F_H}{mc^2 V}\right|^2 \Big/ \sin 2\theta\,, \\ \bar{T} &= -A^{-1}dA/d\mu\,. \end{aligned} \tag{1}$$

r is the mean radius of a perfect crystal domain in the specimen, and $A(\mu)$ is the transmission factor. It is assumed that the observations are made in the plane of incidence, that $r \ll \bar{T}$ and that the misalignment of the domains obeys an isotropic Gaussian distribution law, $W(\Delta)=\sqrt{2g}\exp(-2\pi g^2\Delta^2)$, where Δ is the angular deviation from the mean orientation.

The quantity $K=1$ for the normal and $K=|\cos 2\theta|$ for the parallel component of polarization. The appropriate expression for y, when the incident beam is unpolarized, accordingly becomes

$$y=(y_1+K^2y_K)/(1+K^2)\,, \tag{2}$$

where the subscript specifies the value of K.

This intensity formula has been used successfully to interpret experimental data obtained with small crystal spheres showing high extinction, but small absorption effects (Zachariasen, 1968).

In deriving and using equations (1) and (2) it was tacitly assumed that the effective absorption coefficient μ was given by $\mu=\mu_0=V^{-1}\sum_j \mu_{aj}$, where μ_{aj} is the atomic absorption coefficient of the jth atom in the unit cell. This assumption implies that the Borrmann effect (Borrmann, 1941) is negligible, and the supposition is not valid when the extinction is high and simultaneously $\mu_0\bar{T}>1$. Accordingly equations (1) and (2) need to be modified to include the Borrmann effect.

The basic equations of the theory do not predict the value of the absorption coefficient μ. The first task of this article is therefore to find the correct expression for μ, and the next section is devoted to this problem.

The absorption coefficient

The propagation of an electromagnetic wave field of X-ray frequency in an absorbing perfect crystal will be discussed in this section. The problem is precisely that of the dynamical theory of X-ray diffraction to which different approaches have been given by Darwin (1914*a*,*b*), by Ewald (1916*a*,*b*, 1917) and by Laue (1931). Absorption phenomena were neglected in the original formulations. However, Prins (1930) modified the Darwin theory to include absorption, and so did Kohler (1933) for the Laue theory.

The Darwin–Prins and the Laue–Kohler treatments dealt specifically with crystals in the shape of infinite plane parallel plates. The boundary conditions appropriate for this crystal shape were applied, and the results for the diffraction pattern were given in terms of the deviation from the Bragg angle as observed outside the crystal plate.

For the present purpose of finding the expression for the absorption coefficient it will not be necessary to consider boundary conditions, and the variation of μ with scattering angle will be given in terms of the deviation from the Bragg angle as it would appear inside the medium. Except for the omission of boundary conditions and the use of an internal rather than an external variable the presentation of this section follows the Laue–Kohler formulation of the dynamical theory. As a consequence there will be considerable duplication of results already presented in an earlier treatment (Zachariasen, 1945).

In the X-ray frequency range the polarizability per unit volume is $\psi/4\pi$ where ψ is given by

$$\psi = -\frac{e^2\lambda^2}{\pi mc^2}\sum_k [1+\xi_k+i\eta_k]\Omega_k\,. \tag{3}$$

Ω_k is the electron density function and $\xi_k+i\eta_k$ the anomalous dispersion correction for electrons of type k. Since ψ is periodic in space, it may be expanded in a Fourier series, yielding

$$\begin{aligned}\psi &= \sum_H \psi_H \exp[-i2\pi\mathbf{H}\cdot\mathbf{r}]\\ \psi_H &= -\frac{e^2\lambda^2 F_H}{\pi mc^2 V}\\ F_H &= \sum_j (f_j+\Delta_j'+i\Delta_j'')\exp[i2\pi\mathbf{H}\cdot\mathbf{r}_j - M_j]\,.\end{aligned} \tag{4}$$

$\mathbf{H}$ is a reciprocal lattice vector, $\Delta_j'+i\Delta_j''$ the anomalous dispersion correction and $\exp(-M_j)$ the temperature factor for the jth atom in the unit cell.

It is convenient to set

$$\begin{aligned}&\psi_H=\psi_H'+i\psi_H'',\quad F_H=F_H'+iF_H''\\ &F_H'=\sum_j (f_j+\Delta_j')\exp[i2\pi\mathbf{H}\cdot\mathbf{r}_j-M_j]\\ &F_H''=\sum_j \Delta_j''\exp[i2\pi\mathbf{H}\cdot\mathbf{r}_j-M_j]\,.\end{aligned} \tag{5}$$

If the crystal has an inversion center at the origin, $\psi_H=\psi_{\bar H}$, $F_H=F_{\bar H}$, and all four quantities $\psi_H', \psi_H'', F_H', F_H''$ will be real. Since $\Delta_j''\ll(f_j+\Delta_j')$ it is usually, but not necessarily, true that $|F_H''|\ll|F_H'|$.

Because $|\psi|\ll 1$, the expression for the dielectric 'constant' can be taken to be $1+\psi$ with terms in higher powers of ψ neglected. The relationship between field $\mathscr{E}$ and displacement $\mathscr{D}$ accordingly becomes $\mathscr{D}=1(+\psi)\mathscr{E}$ or $\mathscr{E}=(1-\psi)\mathscr{D}$.

The Maxwell equations for a non-magnetic dielectric ($\mathscr{H}=\mathscr{B}$, $\nabla\cdot\mathscr{D}=0$) give the following self-consistency condition for $\mathscr{D}$,

$$\nabla\times[\nabla\times(1-\psi)\mathscr{D}] = -c^{-2}\partial^2\mathscr{D}/\partial t^2\,. \tag{6}$$

A solution of the form $\mathscr{D}=\mathbf{D}(\mathbf{r})\exp[i\omega_0 t-i2\pi\boldsymbol{\beta}_0\cdot\mathbf{r}]$ represents a wave with wave vector $\boldsymbol{\beta}_0$ and an amplitude $\mathbf{D}$ varying with position. If $\mathbf{D}$ is required to have the periodicity of the lattice, Fourier expansion gives

$$\begin{aligned}&\mathscr{D}=\sum \mathbf{D}_H\exp[i\omega_0 t-i2\pi\boldsymbol{\beta}_H\cdot\mathbf{r}]\,,\\ &\boldsymbol{\beta}_H=\boldsymbol{\beta}_0+\mathbf{H}\,,\\ &\boldsymbol{\beta}_H\cdot\mathbf{D}_H=0\,.\end{aligned} \tag{7}$$

Thus the displacement field is represented as a superposition of plane waves with coupled wave vectors $\boldsymbol{\beta}_H$. The third condition of equation (7) is a direct consequence of the requirement that $\nabla\cdot\mathscr{D}$ be identically zero.

Substitution of equations (4) and (7) in (6) gives

$$\sum_L \psi_{H-L}\boldsymbol{\beta}_H\times(\boldsymbol{\beta}_H\times\mathbf{D}_L)=(k_0^2-\beta_H^2)\mathbf{D}_H \tag{8}$$

where $k_0=\lambda^{-1}$. Upon scalar multiplication with $\mathbf{D}_0/D_0$ equation (8) simplifies to

$$(\beta_H^2-k_0^2)D_H-\sum_L \psi_{H-L}\beta_H^2\chi_{HL}D_L=0\,, \tag{9}$$

where $\chi_{HL}=\chi_{LH}=\mathbf{D}_H\cdot\mathbf{D}_L/D_HD_L$ is cosine of the angle between $\mathbf{D}_H$ and $\mathbf{D}_L$.

Since all quantities $|\psi_{H-L}|\ll 1$, it follows that $\beta_H\simeq k_0$, and one may set $\beta_H=k_0[1+\delta_H]$ with $|\delta_H|\ll 1$. The expression $1+\delta_H$ is the complex refractive index $n=n_r+in_i$ for the wave. Equation (9) can now be rewritten in the form

$$2\delta_H D_H-\sum_L \psi_{H-L}\chi_{HL}D_L=0\,. \tag{10}$$

Suppose that there is a single plane wave in the medium, *i.e.* that $D_0\neq 0$ and $D_L=0$ for $\mathbf{L}\neq 0$. In this case equation (10) reduces to

$$\begin{aligned}&(2\delta_0-\psi_0)D_0=0\\ &n_r=1+\tfrac{1}{2}\psi_0'\,,\quad n_i=\tfrac{1}{2}\psi_0''\,.\end{aligned} \tag{11}$$

The presence of an imaginary term for the refractive index implies absorption with an absorption coefficient μ given by $\mu=-4\pi\lambda^{-1}n_i$. Hence, one has for a single plane wave

$$\begin{aligned}&\mu=\mu_0=V^{-1}\sum_j \mu_{aj}\\ &\mu_{aj}=\frac{2e^2\lambda}{mc^2}\Delta_j''\,,\end{aligned} \tag{12}$$

which is the well known result.

If the wave vector $\boldsymbol{\beta}_0$ has a direction so as exactly or very nearly to satisfy the Laue–Bragg equation for one, and only one, lattice plane, one expects a wave field consisting of two plane waves. Accordingly, let $D_0\neq 0$ and $D_H\neq 0$ with all other Fourier components D_L equal to zero. The set of equations (10) then becomes

$$\begin{aligned}&(2\delta_0-\psi_0)D_0-\psi_{\bar H}\chi_{0H}D_H=0\\ &-\psi_H\chi_{0H}D_0+(2\delta_H-\psi_0)D_H=0\end{aligned} \tag{13}$$

and the eigenvalues are determined by the roots of the secular equation

$$(2\delta_0-\psi_0)(2\delta_H-\psi_0)=\chi_{0H}{}^2\psi_H\psi_{\bar H}\,. \tag{14}$$

Imagine that the internal Laue–Bragg equation is exactly satisfied when $\boldsymbol{\beta}_0=\boldsymbol{\beta}_0^0$. Then $\boldsymbol{\beta}_H=\boldsymbol{\beta}_H^0=\boldsymbol{\beta}_0^0+\mathbf{H}$, and $|\beta_H^0|=|\boldsymbol{\beta}_0^0+\mathbf{H}|=|\beta_0^0|$. Hence, $\delta_H^0=\delta_0^0$, and equation (14) gives

$$n=1+\tfrac{1}{2}\{\psi_0\pm K|'\psi_H\psi_{\bar H}\} \tag{15}$$

with $K=1$ for the normal and $K=|\cos 2\theta|$ for the parallel component. Henceforth, a centrosymmetric crystal will be assumed, implying $\psi_H=\psi_{\bar H}$. If the Laue–Bragg equation is exactly fulfilled, one has thus

$$\begin{aligned}&\mu=\mu_0\pm K\mu_H\,,\\ &\mu_H=V^{-1}\sum_j \mu_{aj}\exp[i2\pi\mathbf{H}\cdot\mathbf{r}_j-M_j]\,.\end{aligned} \tag{16}$$

When the Laue–Bragg equation is approximately satisfied, one sets $\boldsymbol{\beta}_0=\boldsymbol{\beta}_0^0+\varepsilon_1\beta_0^0\boldsymbol{\tau}$, where $\boldsymbol{\tau}$ is a unit vector such that $\boldsymbol{\tau}\cdot\boldsymbol{\beta}_0^0=0$, while ε_1 is a small angular deviation from the ideal Bragg angle. Since $\boldsymbol{\beta}_H=\boldsymbol{\beta}_0+\mathbf{H}$,

it follows that $\delta_H=\delta_0+\varepsilon_1\sin 2\theta$, and equation (14) gives

$$\delta_0=\tfrac{1}{2}\{\psi_0-\varepsilon_1\sin 2\theta\pm\sqrt{\psi_H^2K^2+(\varepsilon_1\sin 2\theta)^2}\} \quad (17)$$
$$\delta_H=\tfrac{1}{2}\{\psi_0+\varepsilon_1\sin 2\theta\pm\sqrt{\psi_H^2K^2+(\varepsilon_1\sin 2\theta)^2}\}\,.$$

Upon separation of real and imaginary parts one finds

$$\mu=\mu_0\pm K\mu_H\kappa_K \quad (18)$$
$$\kappa_K=(1+a^2\varepsilon_1^2)^{-1/2}$$
$$a=\sin 2\theta/K|\psi_H|\,.$$

When the Bragg equation is exactly or nearly satisfied, μ is accordingly given by equation (18), while the value $\mu=\mu_0$ is applicable only if there is no diffraction.

The extinction factor

The basic equations for a mosaic crystal as given in reference 1 are

$$\frac{\partial I_0'}{\partial T_1}=-(\mu+\bar\sigma)I_0'+\bar\sigma I'$$
$$\frac{\partial I'}{\partial T_2}=-(\mu+\bar\sigma)I'+\bar\sigma I_0'\,. \quad (19)$$

I_0' and I' are the intensities of the incident and diffracted beams, T_1 and T_2 the distances of travel of the two beams in the crystal. The boundary conditions are: $I_0'=J_0$ at $T_1=0$ and $I'=0$ at $T_2=0$ where J_0 is the incident intensity at the crystal surface.

$\bar\sigma(\varepsilon_1)$ is the diffracting power per unit volume of the mosaic crystal, and, as shown in reference 1, the approximate expression for $\bar\sigma$ for spherical domains of radius r is

$$\bar\sigma=2K^2Q_0\lambda^{-1}r^*/(1+b^2\varepsilon_1^2) \quad (20)$$
$$b=2\pi r^*\lambda^{-1}$$
$$r^*=r/\sqrt{1+(r/\lambda g)^2}\,.$$

The solution of equation (19) is $I_0'=I_0\exp[-\mu(T_1+T_2)]$ and $I'=I\exp[-\mu(T_1+T_2)]$ where I_0 and I are the solutions for $\mu=0$.

The integrated intensity of the diffracted beam is obtained by integrating I' over the crystal surface and with respect to ε_1.

The quantity $K\mu_K\kappa_K$ of equation (18) is in general small compared with $\bar\sigma$, and it becomes justifiable to replace κ_K with its mean value, $\bar\kappa_K$, over the diffracting power $\bar\sigma$.

One has

$$\bar\kappa_K=\int_{-\infty}^{\infty}\frac{d\varepsilon_1}{\sqrt{1+a^2\varepsilon_1^2(1+b^2\varepsilon_1^2)}}\Bigg/\int_{-\infty}^{\infty}\frac{d\varepsilon_1}{1+b^2\varepsilon_1^2}\,. \quad (21)$$

This integral can be evaluated, and the result (for $b\le a$) is

$$\bar\kappa_K=\frac{z}{\pi\sqrt{1-z^2}}\log e\,\frac{1+\sqrt{1-z^2}}{1-\sqrt{1-z^2}}$$
$$z=b/a=2r^*K|F_H|e^2\lambda/mc^2V\sin 2\theta\,. \quad (22)$$

Values of $z>1$ may occur when r^* and $|F_H|/V$ are unusually large. However, these represent physically impossible situations which arise because of the approximate character of equation (20). According to the dynamical theory the maximum value of b is precisely a, and hence the maximum value of $\bar\kappa_K$ is $2/\pi$.

Table 1 gives $\bar\kappa_K$ as function of the parameter z.

Table 1. *Relation of $\bar\kappa_K$ to z*

z	κ_K	z	κ_K
0	0	0·6	0·525
0·05	0·118	0·7	0·559
0·1	0·192	0·8	0·588
0·2	0·298	0·9	0·614
0·3	0·375	1·0	$2/\pi=0{\cdot}637$
0·4	0·435	>1·0	$2/\pi$
0·5	0·484		

As a second reasonable approximation let the exponential term in the solution $I'=I\exp[-\mu(T_1+T_2)]$ be replaced by its mean value over the crystal. The result is

$$I'=I(T_1,T_2)A(\mu_0\pm\mu_HK\bar\kappa_K)\,, \quad (23)$$

where A is the transmission factor. The integration required to yield the integrated intensity can now be performed, and the result for the extinction factor y becomes

$$y=A_{\pm K}y_{\pm K}/A_0 \quad (24)$$
$$y_{\pm K}=[1+2x_{\pm K}]^{-1/2}$$
$$x_{\pm K}=r^*K^2Q_0\lambda^{-1}\bar T_{\pm K}\,,$$

where subscripts refer to the value of K and of the absorption coefficient as follows

Subscript	μ
0	μ_0
+1	$\mu_0+\mu_H\bar\kappa_1$
−1	$\mu_0-\mu_H\bar\kappa_1$
$+K$	$\mu_0+K\mu_H\bar\kappa_K$
$-K$	$\mu_0-K\mu_H\bar\kappa_K$.

(25)

The two values for μ of $\mu_0+K\mu_H\bar\kappa_K$ and $\mu_0-K\mu_H\bar\kappa_K$ are equally probable. The detailed form of equation (24) for an unpolarized incident beam is accordingly

$$y=[A_{+1}y_{+1}+A_{-1}y_{-1}+K^2(A_{+K}y_{+K}+A_{-K}y_{-K})]/2A_0(1+K^2)\,. \quad (26)$$

When $\bar\kappa_K=0$, one has $A_{\pm K}=A_0$, $y_{\pm K}=y_K$ and equation (26) reduces to equation (2) which was given in reference 1.

Discussion

In discussing the final expression for the extinction factor y as given in equation (26) it will suffice to deal only with the normal polarization component for which $K=1$.

A necessary (but not a sufficient) condition for the observance of the Borrmann effect is that $\bar{\kappa}$ and hence z be significantly different from zero. A comparison of the expressions for the parameters x and z [equations (1) and (22)] shows that appreciable values of z can occur only when extinction is high. For a strong reflection ($|F_H|/V \simeq 0{\cdot}3 \times 10^{24}$ cm^{-3}) and reasonable experimental conditions ($\lambda = 1$ Å, $\theta = 15°$) one finds $z \simeq 0{\cdot}3r^* \times 10^4$ cm^{-1}. Hence, the Borrmann effect is negligible unless r^* is at least of the order of 10^{-4} cm.

In reference 1 a crystal was defined as being of type I if $r/\lambda g \gg 1$ and of type II if $r/\lambda g \ll 1$. Thus, the effect will be mainly confined to type II crystals for which $r \geq 10^{-4}$ cm.

The expression for μ_H, as given in equation (16), shows that $\mu_H < \mu_0$, but that μ_H is comparable to μ_0 for strong reflections. Suppose that $\mu_H \kappa \simeq \frac{1}{2}\mu_0$ (which is a reasonable assumption for strong reflections of type II crystals with $r \geq 10^{-4}$ cm). If one neglects the relatively small difference between y_{+1} and y_{-1}, it is seen from equation (26) that the magnitude of the Borrmann effect is predominantly determined by the ratio $(A_{+1}+A_{-1})/2A_0$. The value of this quantity (with $\mu = \mu_0 \pm \frac{1}{2}\mu_0$, $\theta = 15°$) for a spherical crystal of radius R as function of $\mu_0 R$ is shown in Table 2.

As illustrated by the numbers in Table 2 it becomes necessary under the stated conditions to take the Borrmann effect into account even when $\mu_0 R \simeq 0{\cdot}5$. For $\mu_0 R > 2$ the effect produces an intensity enhancement amounting to a factor of two or more.

Table 2. *Influence of absorption and crystal radius on the Borrmann effect*

$\mu_0 R$	$(A_{+1}+A_{-1})/2A_0$
0	1·00
0·5	1·06
1·0	1·25
2·0	1·77
4·0	2·44
6·0	2·36

The pure extinction depends upon the parameter x of equation (1), and it is of interest to consider the effect of wave length on the magnitude of the extinction for a given reflection of a given crystal specimen. For small scattering angles one has $x \propto \lambda \bar{T}$. If absorption effects are small over the entire wave length range under consideration, $\bar{T}$ is approximately constant; and hence extinction will increase with the wave length. However, for heavily absorbing crystals $\bar{T} \propto \mu^{-1}$. In a wave length region much shorter than any critical absorption edge, one has $\mu \propto \lambda^{2{\cdot}8}$ and accordingly $x \propto \lambda^{-1{\cdot}8}$. Extinction does in other words decrease with increasing λ in heavily absorbing crystals. When the Borrmann effect is also taken into account, the net result is that the extinction factor y as given by equation (26) has a much higher value for the longer wave length.

These and other consequences of the theory are well illustrated by experimental data obtained with a small sphere of calcium fluoride using both Mo $K\alpha$ and Cu $K\alpha$ radiation.

The detailed quantitative interpretation of the calcium fluoride data will be given in the following article.

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