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Extinction Theory for a Plane-Parallel Mosaic Crystal in Transmission

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Abstract

The reflecting and transmitting powers of a plane-parallel crystal composed of mosaic blocks of varying orientation and thickness are derived from dynamical theory in the symmetrical transmission case. The assumptions necessary to arrive at results coinciding with those obtained from Darwin's transfer equations are discussed in detail. The influence of a secondary reflexion is studied by solving the Darwin equations in the three-beam case. Numerical criteria to estimate the conditions under which the effect of secondary reflexion is negligible are presented.

Introduction

The conversion of measured integrated intensities to structure factor values requires the knowledge of the formulas describing the diffraction process in a real crystal. The mathematical difficulties associated with a correct description of the electromagnetic field in a crystal containing a number of imperfections are, however, so severe that no general formulas of practical use have yet been derived. Only for a perfect plane-parallel crystal of infinite extent has an exact and complete solution of the problem been obtained by Zachariasen (1945).

For the other cases, one has at hand only the kinematical description of the diffraction process, which is known to be correct only in the limit of vanishingly small diffracted intensity, and entirely unapplicable when the diffracted intensity is comparable to the transmitted one. To overcome this difficulty, a different approach has been first employed by Zachariasen (1967) and then further pursued by a number of other authors. The essence of the method is to use the Darwin transfer equations, written for the intensities, to describe the interaction of the diffracted and transmitted beam and to lump together in a single correction factor the difference between the actually diffracted intensity and that calculated from kinematical theory. Although this approach has the advantage of being applicable to a variety of diffraction geometries it is of a rather crude nature and it rests upon premises whose degree of accuracy is very difficult to assess. In any case, it may be remarked that, if structure factors of the highest attainable accuracy are not required, this approach leads, in general, to reasonably approximate expressions.

If, however, one is interested in obtaining highly accurate structure factors, as required for the testing of theories of charge redistribution in solids, this correction is not adequate and another approach must be used, both in the choice of the experimental conditions and in the theoretical description of the diffraction process. This approach, also, has been suggested by Zachariasen (1945) who derived formulas for imperfect plane-parallel crystals using the Darwin mosaic model and the results of dynamical theory. An application of Zachariasen formulas to correct for secondary extinction has been proposed by De Marco (1967) and since then extensively used.

The aim of the present paper is to examine carefully the theory of extinction in plane-parallel mosaic crystals in transmission in order to define as precisely as possible the conditions under which formulas expressing realistically the crystal reflectivity can be derived. Since this geometry seems to be one of the very few for which a detailed description of the diffraction process is possible, one expects to be able to assess with some confidence the reliability of the results of this investigation.

Two-beam case

In what follows, we will restrict our attention to the usual two-beam case postponing the discussion of multiple Bragg scattering to the next section. We will consider a plane-parallel crystal composed of platelets each individually perfect. The platelets will be of varying thickness and orientation. The angular distribution $W(\Delta)$ and the thickness distribution $U(t)$ will be assumed to be independent of each other, so that the fraction of platelets having an orientation between Δ and $\Delta + \mathrm{d}\Delta$ and a thickness between t and $t + \mathrm{d}t$ will be

$$\mathrm{d}n = W(\Delta)\, U(t)\, \mathrm{d}\Delta\, \mathrm{d}t. \qquad (1)$$

The results obtained from plane-wave dynamical theory of X-ray diffraction in the small-imaginary-part approximation will be used to calculate the reflecting

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power of each platelet and, in turn, the average power of the diffracted and transmitted beam after passing each layer of blocks in the crystal, following closely the steps of Zachariasen. Before actually doing so, however, we have to examine the paradox pointed out by Schneider (1975). Schneider shows that if one divides in two parts, with a plane perpendicular to the scattering vector, the portion of crystal bathed by the X-ray beam, the calculated reflectivity of the crystal is different from that calculated considering the crystal as a whole. The only condition for which the two reflectivities are equal is that the angular distributions $W_1(\Delta)$ and $W_2(\Delta)$ in the two portions of crystal are the same. Since this subdivision can be repeated indefinitely, it turns out that the angular distribution of the blocks must be the same at each point of the crystal, which in other words has to be a perfect one and not a mosaic. The origin of the difference in the calculated reflectivities, of course, arises from the fact that after passing a thickness T or a layer of blocks, the distribution of intensity in the incident and transmitted beams will not be the same as that at the crystal surface. This is because, in addition to absorption, there will be a different decrease (or increase) of intensity at different points over the X-ray beam cross section, depending on the orientation of the blocks just traversed. The subsequent average of the intensity over the beam cross section, by smearing out these differences, introduces an error. In order that this error be negligible, it is necessary that these differences remain small as the X-ray beam proceeds inside the crystal. This requires not so much that the orientation distribution function be the same all over the crystal but, rather, that, as one proceeds inside the crystal starting from different points on its surface, the orientations of the rows of blocks which are encountered are, statistically, sufficiently similar to ensure that the diffracted and transmitted intensities are nearly constant over the beam cross section.

With the nomenclature introduced by Zachariasen (1945), the integrated reflecting and transmitting powers for a plane-parallel mosaic block of thickness t have been obtained by Kato (1955) as follows, up to terms in A^2k^2:

$$R_H^y \simeq \exp(-\mu t/\gamma_0)\left[(R_H^y)_{\mu=0} + \frac{\pi}{2}A^2k^2\right], \quad (2)$$

$$R_H^y \simeq \exp(-\mu t/\gamma_0)[1 + \tfrac{3}{2}A^2k^2 - (R_H^y)_{\mu=0}], \quad (3)$$

where A is the primary extinction parameter, k the ratio of the imaginary part to the real part of the structure factor, γ_0 the direction cosine of the incident beam, μ the linear absorption coefficient, R_T^y and R_H^y the integrated power of the transmitted and diffracted beam on the y scale and the subscript $\mu = 0$ denotes the same quantities calculated in the case of zero absorption. In the small-imaginary-part approximation ($k < 0{\cdot}1$), and restricting ourselves to the case $A < 1$, the terms in A^2k^2 are negligible with respect to $(R_H^y)_{\mu=0}$. Passing to the θ scale, we therefore have

$$R_H^\theta \simeq \exp(-\mu t/\gamma_o)(R_H^\theta)_{\mu=0}, \quad (4)$$

$$R_T^\theta \simeq \exp(-\mu t/\gamma_0)[1 - (R_H^\theta)_{\mu=0}]. \quad (5)$$

Let us suppose that the whole crystal, of thickness T_0, is composed of n layers of blocks and that each layer contains a large number of blocks of variable orientation and thickness. We shall call $U_i(t)$ and $W_i(\Delta)$ the distribution functions of the ith layer and $\langle t\rangle_i = \int_i U(t)\,dt$ the average thickness of the blocks of the ith layer. The integrated reflecting power of the first layer of blocks will then be the average over t and Δ of the reflecting power P_H/P_0 of a single block:

$$\sigma_1\langle t\rangle_1 = \int_1 U_1(t)\,dt \int_1 W_1(\Delta)\,\frac{P_H}{P_0}(t, \theta - \theta_B + \Delta)\,d\Delta \quad (6)$$

where the subscript 1 means that we are referring to the first layer and σ_1, defined by (6), is the reflectivity per unit thickness of the first layer of blocks. If the half-width of the distribution function $W_1(\Delta)$ is large compared with the half-width of P_H/P_0, then $W_1(\Delta)$ can be treated as a constant, since P_H/P_0 is different from zero only in a narrow interval around $\theta - \theta_B + \Delta = 0$. Therefore,

$$\begin{aligned}\sigma_1\langle t\rangle_1 &\simeq W_1(\theta_B - \theta)\int_1 U_1(t)\,dt \\ &\quad\times \int_1 \frac{P_H}{P_0}(t, \theta - \theta_B + \Delta)\,d\Delta \\ &= W_1(\theta_B - \theta)\int_1 U_1(t)\,R_H^\theta(t)\,dt \\ &= W_1(\theta_B - \theta)\,\langle R_H^\theta\rangle_1. \end{aligned} \quad (7)$$

If $\mathscr{P}_T^{(1)}$ and $\mathscr{P}_H^{(1)}$ are respectively the power of the transmitted and diffracted beams after passing the first layer of blocks and $\mathscr{P}_0$ is the power of the incident beam at the crystal surface, we have

$$\begin{aligned}\mathscr{P}_T^{(1)}/\mathscr{P}_0 &= \int_1 \exp(-\mu t/\gamma_0)\,U_1(t)\,dt - \int_1 U_1(t)\,dt \\ &\quad\times \int_1 W_1(\Delta)\,\frac{P_T}{\mathscr{P}_0}(t, \theta - \theta_B + \Delta)\,d\Delta \\ &= \langle \exp(-\mu t/\gamma_0)\rangle_1 - W_1(\theta_B - \theta)\langle R_H^\theta\rangle_1, \end{aligned} \quad (8)$$

and similarly

$$\mathscr{P}_H^{(1)}/\mathscr{P}_0 = W_1(\theta_B - \theta)\langle R_H^\theta\rangle_1. \quad (9)$$

For a thickness such that $\mu t/\gamma_0 \ll 1$, we have

$$\begin{aligned}\langle \exp(-\mu t/\gamma_0)\rangle &\simeq 1 - \mu\langle t\rangle/\gamma_0 \\ &\simeq \exp(-\mu\langle t\rangle/\gamma_0).\end{aligned}$$

Having defined

$$\alpha_i = \exp(-\mu\langle t\rangle_i/\gamma_0);$$
$$\omega_i = W_i(\theta_B - \theta)\langle R_H^\theta\rangle_i = \sigma_i\langle t\rangle_i,$$

we have, after the first layer of blocks,

$$\mathscr{P}_T^{(1)} = (\alpha_1 - \omega_1)\,\mathscr{P}_0; \quad \mathscr{P}_H^{(1)} = \omega_1\,\mathscr{P}_0.$$

After the ith layer of blocks the finite difference equations will be

$$\mathscr{P}_T^{(i)} = (\alpha_i - \omega_i)\,\mathscr{P}_T^{(i-1)} + \omega_i\,\mathscr{P}_H^{(i-1)} \tag{10}$$

$$\mathscr{P}_H^{(i)} = (\alpha_i - \omega_i)\,\mathscr{P}_H^{(i-1)} + \omega_i\,\mathscr{P}_T^{(i-1)}. \tag{11}$$

This system of equations can be solved easily only if α_i and ω_i are such that the ratio α_i/ω_i does not vary passing from one layer to the next. Admitting therefore that $\alpha_i/\omega_i = \alpha/\omega$ = constant, we have

$$\mathscr{P}_T^{(n)}/\mathscr{P}_0 = \left[\prod_{i=1}^{n}\alpha_i\right]\sum_{k=0}^{[n/2]}\binom{n}{2k}\left(1-\frac{\omega}{\alpha}\right)^{n-2k}\left(\frac{\omega}{\alpha}\right)^{2k}$$
$$= \exp(-\mu T_0/\gamma_0)\sum_{k=0}^{[n/2]}\sum_{s=0}^{n-2k}(-1)^s \times \frac{n!}{(2k)!s!(n-2k-s)!}\left(\frac{\omega}{\alpha}\right)^{2k+s}, \tag{12}$$

$$\mathscr{P}_H^{(n)}/\mathscr{P}_0 = \exp(-\mu T_0/\gamma_0)\sum_{k=0}^{[(n-1)/2]}\sum_{s=0}^{n-2k-1}(-1)^s \times \frac{n!}{(2n+1)!s!(n-2k-s-1)!} \times \left(\frac{\omega}{\alpha}\right)^{2k+s+1}, \tag{13}$$

where $T_0 = \sum_i \langle t\rangle_i$ and $[n/2]$ and $[(n-1)/2]$ are the largest integers $\leq n/2$ and $(n-1)/2$ respectively. Simpler expressions are obtained expanding (12) and (13) in powers of ω/α. We have

$$\mathscr{P}_T^{(n)}/\mathscr{P}_0 = \exp(-\mu T_0/\gamma_0) \times \left[1 - n\frac{\omega}{\alpha} + n(n-1)\frac{\omega^2}{\alpha^2} - \tfrac{2}{3}n(n-1)(n-2)\frac{\omega^3}{\alpha^3}\right], \tag{14}$$

$$\mathscr{P}_H^{(n)}/\mathscr{P}_0 = \exp(-\mu T_0/\gamma_0)\, n\frac{\omega}{\alpha} \times \left[1 - (n-1)\frac{\omega}{\alpha} + \tfrac{2}{3}(n-1)(n-2)\frac{\omega^2}{\alpha^2} - \tfrac{1}{3}(n-1)(n-2)(n-3)\frac{\omega^3}{\alpha^3}\right] \tag{15}$$

plus higher terms in ω/α.

It is possible to show that (14) and (15) coincide with the solution obtained by Zachariasen employing differential equations instead of the finite difference approach, if the number of layers is so large that $(n-1)$, $(n-2)$ and so on can be approximated with n. In fact, from (4) and the definition of ω and α, we have

$$\frac{\omega}{\alpha} = W(\theta_B - \theta)\int \exp[-\mu(t - \langle t\rangle)/\gamma_0] \times (R_H^\theta)_{\mu=0}\,U(t)\,dt, \tag{16}$$

written without any index since this quantity is by hypothesis constant. Since the exponential is a quantity very near to 1 and has 1 as its average value, we can neglect it. Therefore,

$$\frac{\omega}{\alpha} \simeq W(\theta_B - \theta)\,\langle(R_H^\theta)_{\mu=0}\rangle. \tag{17}$$

If we call t_0 the average block thickness over the whole crystal then $n = T_0/t_0$ and

$$n\frac{\omega}{\alpha} \simeq \frac{T_0}{t_0}W(\theta_B - \theta)\,\langle(R_H^\theta)_{\mu=0}\rangle = (\sigma T_0)_{\text{Zachariasen}}. \tag{18}$$

If (18) is substituted in (14) and (15) and the number of layers is supposed to be very large, we have

$$\mathscr{P}_T^{(n)}/\mathscr{P}_0 = \exp(-\mu T_0/\gamma_0)[1 - \sigma T_0 + \sigma^2 T_0^2 - \tfrac{2}{3}\sigma^3 T_0^3 + \ldots], \tag{19}$$

$$\mathscr{P}_H^{(n)}/\mathscr{P}_0 = \exp(-\mu T_0/\gamma_0)[1 - \sigma T_0 + \tfrac{2}{3}\sigma^2 T_0^2 - \tfrac{1}{3}\sigma^3 T_0^3 + \ldots]\,\sigma T_0, \tag{20}$$

which coincide with Zachariasen expressions and are the starting point of the De Marco point-by-point method to correct for secondary extinction. In fact, from (19) and (20), one obtains

$$\sigma T_0 = \frac{\mathscr{P}_H^{(n)}}{\mathscr{P}_0\exp(-\mu T_0/\gamma_0)}\left\{1 + \frac{\mathscr{P}_H^{(n)}}{\mathscr{P}_T^{(n)}} + \tfrac{1}{3}\left[\frac{\mathscr{P}_H^{(n)}}{\mathscr{P}_T^{(n)}}\right]^2 + \left[\frac{\mathscr{P}_H^{(n)}}{\mathscr{P}_T^{(n)}}\right]^3 + \ldots\right\}. \tag{21}$$

Equation (21) therefore allows one to obtain from measurable quantities the value of σT_0 for each point of the diffraction profile.

It is now possible to consider in detail the many conditions the crystal has to fulfil in order that (19) and (20) can be obtained: (*a*) each block must be such that $A < 1$ and $\mu t \lesssim 5 \times 10^{-2}$. This corresponds to a thickness which, for iron-group metals studied with Ag $K\alpha$ radiation, ranges from about 2 to 10 μm; (*b*) the distribution functions of orientation and thickness must be entirely uncorrelated; (*c*) the energy distribution in the wave-front at any crystal depth must be about the

same as at the crystal surface. This requires that different rows of blocks along the crystal thickness have approximately the same orientation distribution function; (*d*) the distribution function $W(\Delta)$, for each layer, must have a half-width large compared to the natural half-width of the diffraction profile of each block; (*e*) the number of layers in the crystal must be of the order of 50 or more; (*f*) the quantity $\omega/\alpha = W(\theta_B - \theta)\exp(-\mu\langle t\rangle/\gamma_0)$ times $\langle R_H^\theta\rangle$ must be the same for all layers in the crystal (for all values of θ). This last condition deserves further attention. As we go from a layer with average thickness $\langle t\rangle_l$ to one with average thickness $\langle t\rangle_k$ the factor $\exp(-\mu\langle t\rangle/\gamma_0)$ times $\langle R_H^\theta\rangle$ will change and, since the function $W(\theta_B - \theta)$ is normalized to 1, it will be impossible for it to vary in such a way to compensate this change for all values of θ. Actually, $W(\theta_B - \theta)$ will increase for some values of θ and will decrease for others. As such, we conclude that the only way for ω/α to stay constant in different layers is, from a physical point of view, that both $\langle R_H^\theta\rangle$ and $W(\theta_B - \theta)$ stay constant. We therefore find that both the thickness distribution function and the orientation distribution function have to be the same in different layers. This is probably the most severe limitation of the secondary extinction theory in a mosaic crystal if we note that, examining different crystal spots, as a rule, one finds large variations in the shape of the diffracted peak.

In order that conditions (*c*) and (*f*) be satisfied we conclude that the crystal must be 'homogeneous' both vertically and horizontally, not in a point-wise manner, but from an average point of view, as explained so far. Only when conditions (*a*) to (*f*) are fulfilled is it possible to obtain (19) and (20) and, therefore, to deduce the value of σT_0 for each point of the diffraction profile.

For primary extinction, we know that, for a plane-parallel block of thickness t,

$$(R_H^\theta)_{\mu=0} = \frac{Qt}{\gamma_0}\left(1 - \sum_{m=1}^{\infty} K_m t^{2m}\right), \tag{22}$$

where the K_m's are suitable numerical coefficients. Then,

$$\begin{aligned}\sigma T_0 &= (T_0/t_0)W(\theta_B - \theta)\langle(R_H^\theta)_{\mu=0}\rangle \\ &= (T_0/t_0)\,W(\theta_B - \theta) \\ &\quad \times \int \frac{Qt}{\gamma_0}\left(1 - \sum_{m=1}^{\infty} K_m t^{2m}\right) U(t)\,\mathrm{d}t \\ &= (Q/\gamma_0)(T_0/t_0)W(\theta_B - \theta) \\ &\quad \times \left(t_0 - \sum_{m=1}^{\infty} K_m \langle t^{2m+1}\rangle\right),\end{aligned} \tag{23}$$

and $\langle t^{2m+1}\rangle = \int t^{2m+1}\,U(t)\,\mathrm{d}t$. The total integrated reflecting power of the crystal will then be (having corrected for secondary extinction)

$$\begin{aligned}\mathscr{R}_H^\theta &= \int(\mathscr{P}_H^{(n)}/\mathscr{P}_0)\,\mathrm{d}\theta = \exp(-\mu T_0/\gamma_0)\int\sigma T_0\,\mathrm{d}\theta \\ &= \exp(-\mu T_0/\gamma_0)(QT_0/\gamma_0) \\ &\quad \times \left[1 - \left(\sum_{m=1}^{\infty} K_m\langle t^{2m+1}\rangle\right)/t_0\right].\end{aligned} \tag{24}$$

Also, in this case, we have not specified the index of the layer since the thickness distribution function (and therefore all its moments) are the same for all layers. In any case, (24) in principle allows one to obtain Q from the (corrected) diffraction profile. For this purpose, however, it is necessary to know the $\langle t^{2m+1}\rangle$ values for the crystal spot under consideration. Since these values are obviously unknown, an extrapolation procedure to zero thickness coupled with the use of different wavelengths seems to be the only way to reduce the uncertainty due to primary extinction to the same order of magnitude as other errors.

All the considerations presented so far have ignored the fact that a real crystal is known to have a structure far more complicated than a mosaic composed of plane-parallel platelets. Actually, a more realistic model would imply the existence of irregularly shaped domains of coherence separated by a material almost non-crystalline. Even if the amount of this material is considered to be negligible, the question arises whether (4) (5) and (22) describe correctly the diffracted and transmitted intensity in a perfect crystal of irregular shape.

For calculating the integrated reflecting power of a single crystal it is well known that for a sphere it is possible to write an expression having the same functional dependence between the integrated reflecting power and the radius of the sphere, as in (22) with regard to platelet thickness. It is therefore presumable that the integrated reflecting power for an irregular crystal will be described by an expression similar to (22), with the substitution of a suitable path length in place of the platelet thickness. As for secondary extinction, we note that the results of this section show that, given conditions (*a*) to (*f*), the intensity of the diffracted and transmitted beam can be correctly derived from the solution of a system of differential equations which do not explicitly rely on the results of dynamical theory. If the irregular domains of coherence have the same statistical and dimensional properties discussed for the platelets, it is possible to set up a system of equations for a layer of thickness $\mathrm{d}T$ no matter what the shape of the crystallites. We conclude that, although the results obtained in this section can be derived from dynamical theory only for plane-parallel mosaic blocks, it is very likely that they should be correct also for a more realistic crystal model.

Three-beam case

The theory developed so far has ignored the frequent occurrence of multiple Bragg scattering. In order to study the phenomenon of extinction in this case, it would be necessary as a first step to solve the equations of the electromagnetic field inside a perfect crystal when more than two reciprocal-lattice points lie near the surface of the sphere of reflection. Unfortunately, as no such solution exists, we are able to calculate the reflecting power of the transmitted beams only in the kinematical approximation. In an actual experiment, however, the measurement of the integrated reflecting power from a plane-parallel crystal in symmetrical transmission is performed only when no detectable spurious dips are present in the transmitted beam. We are therefore concerned with secondary reflexions which have a reflecting power such that it can be considered a small perturbation of the two-beam case. This perturbation may arise either from a weak reflexion or from a strong one whose reciprocal-lattice point passes near but not quite through the sphere of reflection. In essence, the situation is not dissimilar from that described at the end of the preceding section: it is possible to set up a system of differential equations containing a set of parameters which we shall call reflectivities per unit thickness but whose physical meaning can only be approximately defined and have a precise expression only in the kinematical approximation. If these reflectivities are treated as constants the system of equations can, at least in principle, be solved.

In what follows, we will restrict ourselves to the case of three beams. Our aim will be to ascertain under what conditions a secondary extinction correction, as described by (21), is possible. The equations to be solved for the symmetrical transmission case are, in the notation of Moon & Shull (1964),

$$\mathrm{d}P_0/\mathrm{d}t = -(P_0/\gamma_0)(\mu + r_{10} + r_{20}) + (P_1/\gamma_0)r_{10} + (P_2/\gamma_2)r_{20}, \quad (25a)$$

$$\mathrm{d}P_1/\mathrm{d}t = -(P_1/\gamma_0)(\mu + r_{10} + r_{12}) + (P_0/\gamma_0)r_{10} + (P_2/\gamma_2)r_{12}, \quad (25b)$$

$$\mathrm{d}P_2/\mathrm{d}t = -(P_2/\gamma_2)(\mu + r_{20} + r_{12}) + (P_0/\gamma_0)r_{20} + (P_1/\gamma_0)r_{12}, \quad (25c)$$

with the boundary conditions $P_0(0) = P$, $P_1(0) = P_2(0) = 0$, and where γ_l is the direction cosine of the lth beam and $r_{lj} = r_{jl}$ is the cosine-independent part of the reflectivity per unit thickness relative to diffraction from the lth to the jth beam. Dividing each r_{lj} by the appropriate cosine allows for the volume of crystal which is effectively diffracting. This system of equations can be solved by the Laplace transform method and it leads to the search of the roots of a cubic equation in s, the variable of the Laplace transforms of P_0, P_1 and P_2. The extreme complexity of the coefficients of the cubic equation makes an analytical solution of the problem almost unmanageable. Simpler expressions are obtained setting $\gamma_2 = \gamma_0$. Although this position may look arbitrary, it is of immediate interest in the case where multiple Bragg scattering occurs more frequently, that is when a very short wavelength is used. In particular, it describes accurately the situation encountered in γ-ray diffractometry. In the case of X-rays, it is obviously a reasonable approximation if the modulus of the scattering vector of the secondary reflexion is not very different from that of the primary one. In addition, if the primary reflexion is a low-angle one with a high value of the reflectivity while the secondary one is a high-angle reflexion with low reflectivity, it is immediately seen that the terms $(P_2/\gamma_2)r_{20}$ and $(P_2/\gamma_2)r_{12}$ in (25a) and (25b) are small with respect to the other terms. This means that if they were neglected altogether we would obtain a first-order approximation to P_0 and P_1. Including these terms with the position $\gamma_2 = \gamma_0$ is therefore a second-order approximation. Moreover, since in this case $\gamma_0 > \gamma_2$, we have from (25c) that the value of $\mathrm{d}P_2/\mathrm{d}t$ calculated in this approximation is larger than its true value and therefore that the approximate value of P_2 is larger than the true P_2. Therefore, both the numerator and the denominator of the terms under examination are replaced by values which deviate in the same direction with a resulting partial cancellation of errors. On the other hand, the value of P_2 which is obtained in this approximation is not reliable but this is of no importance since our main interest is centered upon obtaining an accurate solution for P_0 and P_1, which are experimentally measurable quantities. This approximation therefore is particularly appropriate the shorter the wavelength and when studying a low-angle reflexion with high reflectivity.

With the position $\gamma_2 = \gamma_0$, it is possible to show that the roots s_1, s_2 and s_3 of the cubic equation are always real. The solutions for $P_0(t)$ and $P_1(t)$ are

$$P_0(t) = \frac{P\exp(-Dt/3)}{(s_2 - s_1)(s_3 - s_1)(s_3 - s_2)} \times \{(Xs_3 - Ys_2 s_1)[\exp(s_1 t) - \exp(s_2 t)] + (Xs_2 - Ys_1 s_3)[\exp(s_3 t) - \exp(s_1 t)] + (Xs_1 - Ys_2 s_3)[\exp(s_2 t) - \exp(s_3 t)] + s_1^2(s_3 - s_2)\exp(s_1 t) + s_2^2(s_1 - s_3)\exp(s_2 t) + s_3^2(s_2 - s_1)\exp(s_3 t)\}, \quad (26)$$

$$P_1(t) = \frac{P\exp(-Dt/3)}{(s_2-s_1)(s_3-s_1)(s_3-s_2)} \times \left\{\left(Zs_3 - \frac{r_{10}}{\gamma_0}s_1 s_2\right)[\exp(s_1 t) - \exp(s_2 t)] + \left(Zs_2 - \frac{r_{10}}{\gamma_0}s_3 s_1\right)[\exp(s_3 t) - \exp(s_1 t)] + \left(Zs_1 - \frac{r_{10}}{\gamma_0}s_2 s_3\right)[\exp(s_2 t) - \exp(s_3 t)]\right\}, \quad (27)$$

where D, X, Y and Z are coefficients detailed in the Appendix together with s_1, s_2 and s_3. The expressions for P_0 and P_1 are such that any investigation of the effect of a secondary reflexion must be performed numerically. As such, we have computed P_0 and P_1 with $\mu = 1/t$ and for a range of secondary extinction (as revealed by the transmitted beam) not exceeding ~25%, which is a value very seldom exceeded in an actual experiment. In order to obtain results applicable both to X-ray and γ-ray diffractometry we have let t range between 0·05 and 10 mm, and the reflectivities were varied within the limits imposed by the above mentioned restriction on the primary beam attenuation.

The applicability of (21) turns out to be strongly dependent on crystal thickness. We have therefore distinguished two cases:

case (*a*) $t \leq 0{\cdot}1$ mm (typical of X-ray thicknesses);
case (*b*) $t \leq 10$ mm (typical of γ-ray thicknesses).

The amount of extinction in the transmitted and diffracted beams depends in a complex manner on the relative values of the reflectivities while it is independent of μ. As an example, we have listed, for several values of r_{10}/γ_0, the maximum value of the ratio r_{20}/r_{10} for which (21) applies within 1%:

$r_{10}/\gamma_0 =$	0·01;	0·1;	1;	10	
$r_{20}/r_{10} \leq$	10;	2;	1;	0·2	case (*a*)
$r_{20}/r_{10} \leq$	1;	0·5;	0·2;	0·1	case (*b*).

For case (*a*), it is possible to state a useful rule of thumb: (21) applies within 1% when the sum of P_0 and P_1 on each point of the diffraction profile is equal, within 1%, to the value of P_0 when no diffraction is occurring.

The use of approximate values for $(P_2/\gamma_2)r_{20}$ and $(P_2/\gamma_2)r_{12}$ is not adequate when the primary reflexion is not much stronger than the secondary one. This is particularly true in anisotropy measurements of charge density from high-angle reflexions having a low reflectivity. Also in this case, though, a record of the transmitted intensity allows one to discard those cases in which a strong secondary reflexion is present, so that the perturbation on the transmitted beam due to a secondary reflexion must necessarily be small. The integration of system (25) can then be performed neglecting the last two terms on the right-hand side of (25*a*), since, by hypothesis, they are small second-order effects. The integration of (25*a*) can be performed at once:

$$P_0(t) = P\exp[(-\mu - r_{10} - r_{20})t/\gamma_0]. \quad (28)$$

With the help of (28), one obtains for P_1 the following expression:

$$P_1(t) = P\exp(-ut)\{[(c-u)w + r_{10}/\gamma_0][\sinh(vt)]/v - w\cosh(vt) + w\exp[(u-c)t]\}, \quad (29)$$

where u, v, w and c are coefficients detailed in the Appendix.

As in the previous case the values of P_0 and P_1 have been computed numerically. The ratio γ_0/γ_2 has been varied between 0·5 and 2, the reflectivities were chosen such that the total effect of diffraction on the primary beam was less than 1% and we have only considered X-ray thicknesses, that is $\leq 0{\cdot}1$ mm. A comparison of P_1 calculated from (29) with $\gamma_0 = \gamma_2$, and P_1 calculated exactly from (27) shows that the approximations which have lead to (29), for the above specified range of variables, introduce an error of the order of 0·01%. Since for low values of the reflectivity the reflecting power of the primary diffracted beam is calculated in the kinematical approximation, we have examined the conditions for which this procedure is still valid within 1%, even in the presence of a secondary reflexion. We found the following:

(i) the higher the value of the ratio γ_0/γ_2, the larger the difference between the true value of P_1 and that calculated in the kinematical approximation;

(ii) an increase of r_{20} must be accompanied by a decrease of r_{12}. For (21) to hold, the product $r_{20}r_{12}$ must be approximately $\leq r_{10}$;

(iii) no simple way to ascertain the influence of a secondary reflexion from a record of the diffracted and transmitted beam exists, so that in an actual experiment it is advisable to perform measurements at different azimuthal angles and then check that the results are compatible among themselves, within their statistical uncertainty.

Conclusion

The present analysis shows the difficulties of an exact calculation of secondary extinction even in the simple case of a plane-parallel mosaic crystal. The stringent requirement on the homogeneity of coherent blocks in the crystal is probably the most severe source of error when applying (21) in order to obtain from the diffraction profile the true reflectivity per unit thickness of the crystal. For multiple Bragg scattering, it seems possible to control its influence on the crystal reflec-

tivity if the reflexion studied is much stronger than the secondary ones. For thicknesses typical of X-ray diffraction, in fact, the criterion of energy conservation affords a simple way of checking that the experimental values are truly representative of the reflectivity of the crystal planes under consideration. On the other hand, when one is measuring a reflexion of low reflectivity it is very difficult to make an *a priori* estimate of the reflectivity of the secondary reflexion, mostly because the appropriate value of the angular distribution function, which determines the reflectivity of the secondary reflexion, is unknown. Since any calculation of the influence of a secondary reflexion requires the knowledge of its reflectivity, the quantitative criterion ($r_{20}\, r_{12} \leq r_{10}$) which can be derived from the solution of system (25) is, in actual practice, of little help.

Note added in proof: It may be worth remarking that the theory developed in the two-beam case applies to an X-ray beam composed of a single wavelength. In the general case one should perform the convolution of the orientation distribution function with the spectral distribution function. In the common case of crystal-monochromated $K\alpha$ radiation, the wavelength distribution function is the sum of two narrow functions ($K\alpha_1$ and $K\alpha_2$) whose relative weights have to be determined experimentally. When the angles of diffraction from the sample of the two δ-like functions differ by an amount which is negligible with respect to the half-width of $W(\Delta)$, the present theory applies as it is and no difficulty arises in order to perform the point-by-point correction of the experimental diffraction profile. When the above condition is not met, the two components of the incident beam have to be considered separately and, although the present theory applies to each of them, in general it will be impossible to perform a point-by-point correction since each point of the diffraction profile will be the sum in unknown proportions of the diffraction profiles of the two components. Only when the diffraction profiles of two components are entirely separated is the correction possible. In this last case, of course, the amount of secondary extinction has to be related to the decrease of the transmitted intensity of the appropriate component and not to the decrease of the transmitted intensity of the total incident beam.

APPENDIX

The expressions for the coefficients appearing in equations (26) and (27) are:

$$X = K - H\,D/3 + D^2/9$$

$$Y = H - 2D/3$$

$$Z = M - r_{10}\,D/3\;\gamma_0$$

$$s_1 = 2(-R/3)^{1/2}\cos(\theta/3)$$

$$s_2 = 2(-R/3)^{1/2}\cos[(\theta + 2\pi)/3]$$

$$s_3 = 2(-R/3)^{1/2}\cos[(\theta - 2\pi)/3]$$

$$\theta = \cos^{-1}[(3N/2R)(-3/R)^{1/2}]$$

$$R = (9T - 4G^2)/3$$

$$N = (16G^2 - 54TG)/27$$

$$K = (\mu^2 + \mu G + \mu r_{12} + T)/\gamma_0^2$$

$$H = (2\mu + r_{12} + G)/\gamma_0$$

$$D = (3\mu + 2G)/\gamma_0$$

$$M = (\mu r_{10} + T)/\gamma_0^2$$

$$T = (r_{10}\,r_{20} + r_{10}\,r_{12} + r_{20}\,r_{12})$$

$$G = r_{10} + r_{20} + r_{12}.$$

The expressions for the coefficients appearing in equation (29) are:

$$u = (a + b\Gamma)/2$$

$$v = [(a - b\Gamma)^2 + 4\Gamma r_{10}^2/\gamma_0^2]^{1/2}/2$$

$$w = [(b\Gamma - c)r_{10}/\gamma_0 + \Gamma r_{12}\,r_{20}/\gamma_0^2] \times [c^2 - (a + b\Gamma)\,c + ab\Gamma - \Gamma r_{12}^2/\gamma_0^2]^{-1}$$

$$c = (\mu + r_{10} + r_{20})/\gamma_0$$

$$a = (\mu + r_{10} + r_{12})/\gamma_0$$

$$b = (\mu + r_{20} + r_{12})/\gamma_0$$

$$\Gamma = \gamma_0/\gamma_2.$$

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