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The Theoretical Models of Extinction. Their Domain of Applicability*

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The various theoretical models of extinction are critically reviewed. It is shown that the Darwin energy transfer equations are valid as long as the mean coherence distance in the sample is smaller than the extinction length, as demonstrated recently by Kato. The available solution is correct when the entrance and exit surface do not overlap and the approximation is seen to be reasonable for more complicated cases. The correlation between primary and secondary extinction is discussed. It is emphasized, in practical applications, that many tests, both theoretical and experimental (when possible) of the correctness of the correction should be made. Only samples that fit a given diffraction theory should be used for accurate studies like charge density determination.

I. Introduction

The problem of extinction is one of the major obstacles to the accuracy of coherent X-ray or neutron diffraction experiments. Various methods of correction have been proposed, both experimental and theoretical. Those methods have been all criticized in the literature and many crystallographers may be believe that no serious progress has been made in this field.

In the present article, a review is given of the basic physical assumptions used in the extinction theories. Several tests are described that tell whether an extinction correction can be applied to a given data set. The main purpose of this article is to give some confidence in the actual correction of extinction.

There exist two theories of the diffraction of X-rays or neutrons:

(*a*) The kinematical theory is based on the Born approximation which is supposed to be applicable to the whole sample under diffraction. It is therefore assumed that the interaction between radiation and matter is small enough for the incident beam not to be perturbed (except in a classical absorption process) within the sample.

This theory is believed to be valid for the diffraction by gaseous molecules but the translational symmetry of a crystal does impose constraints on the structure of the waves that can travel inside the crystal. The kinematical theory is only valid in the limit of thin crystals.

(*b*) The dynamical theory is the study of the waves that are compatible with the periodic nature of the crystal. It can be developed with 'quasi-geometrical' arguments, taking into account all the possible rescatterings of the incident and diffracted beams (Darwin, 1914; James, 1957; Warren, 1969). The problem can be formulated in a more general way, in terms of the electromagnetic theory (James, 1963; Batterman & Cole, 1964; Authier, 1970; Kato, 1974), in either the plane-wave or the spherical-wave approximation. A major difficulty comes from the boundary conditions: no general solution has been found that is valid for every diffraction geometry.

The dynamical theory leads to the kinematical theory in the limit of thin crystals. The frontier can be calculated from

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diffraction conditions and is called the 'extinction distance' Λ, which can be defined in slightly different ways but is of the order of:

$$\Lambda = \frac{V}{(aC)}\frac{1}{|F_{\mathbf{H}}|\lambda} = \frac{\lambda}{Q\sin 2\theta}^{1/2}. \qquad (1)$$

V is the volume of the unit cell, $F_{\mathbf{H}}$ the structure factor, λ the wavelength. In the X-ray case, a is the classical radius of the electron (e^2/mc^2) and C the polarization factor. In the neutron case, C is equal to 1 and a is equal to 10^{-12} cm. Q is the kinematical integrated reflectivity per unit length,

$$Q = \left|\frac{aC}{V}F_{\mathbf{H}}\right|^2 \frac{\lambda^3}{\sin 2\theta}, \qquad (2)$$

t being the thickness of the perfect part of the crystal;

if $t \ll \Lambda$ the kinematical theory is valid;
if $\gg \Lambda$ the dynamical effects are very important.

Λ represents a coherence length, the necessary distance for dynamical effects to occur. From (1) it is clear that Λ varies with the reciprocal point and is the smallest for strong reflexions and large wavelengths (the cases where extinction effects are the most pronounced).

II. Extinction models: the physical approximations

Most experiments in diffractometry are done on crystals of small size and unknown defect structure. A direct investigation of the defects can only be done in a few cases and leads to an average estimate, as for example the measurement of a dislocation density.

How can the diffraction process be described in such cases? This is the fundamental question to be solved. Correspondingly, if we find a model that suits an experiment, how can we be sure that this model represents reality? Other models might fit the data equally well. In the present section, we shall try to answer the first question.

1. Many developments of the dynamical theory have been proposed to characterize the effects of the various kinds of imperfections on the diffracted intensity (see for example the proceedings of the International Summer School on X-ray Dynamical Theory and Topography, Limoges, France, 1975). Topographic studies allow one to specify and localize the imperfections present in a given crystal. But, in order to be interpretable, they require the crystal to be large enough (at least a few mm) and the imperfections to be in small number. Therefore, at the present time, such experiments are not possible generally for samples that are used in X-ray diffractometry. Topographies may be obtained with neutron samples and they cannot be interpreted, because of the large number of imperfections (see § IV). The theoretical description of scattering by imperfect crystals is extremely complicated and is only feasible in the case of very few defects.

The most promising dynamical approach for our purpose is the theory of Taupin (1964) and Takagi (1962, 1969, 1975). The theory takes into account the local distortion of the lattice, $\mathbf{u}(\mathbf{r})$, the result of which is a spatial modulation of the amplitude of the waves in the crystal. Let $\mathbf{k}$ be the wave vector of the incident wave, $\mathbf{K}_0$ and $\mathbf{K}_{\mathbf{H}}$ the wave vectors of the transmitted and diffracted waves, subject to the condition:

$$\mathbf{K}_{\mathbf{H}} = \mathbf{K}_0 + \mathbf{H}.$$

The displacement vectors $\mathscr{D}_0$ and $\mathscr{D}_{\mathbf{H}}$ of the two waves are:

$$\mathscr{D}_0 = \mathscr{D}_0(\mathbf{r}) \exp\left[-2\pi i(\mathbf{K}_0 \cdot \mathbf{r} - vt)\right]$$
$$\mathscr{D}_{\mathbf{H}} = \mathscr{D}_{\mathbf{H}}(\mathbf{r}) \exp\left[-2\pi i(\mathbf{K}_{\mathbf{H}} \cdot \mathbf{r} - vt)\right]. \qquad (3)$$

Let S_0 and $S_{\mathbf{H}}$ be oblique coordinates of a point inside the crystal, respectively parallel to the incident and diffracted directions). $\chi_{\mathbf{H}}$ is the Fourier component of the electric susceptibility of the ideal perfect crystal:

$$\chi_{\mathbf{H}} = \frac{-a\lambda^2}{\pi V}F_{\mathbf{H}}. \qquad (4)$$

Takagi's equations can be written, for the components of a given polarization:

$$\frac{\partial}{\partial S_0}\mathscr{D}_0 = -i\pi k C\chi_{\mathbf{H}}\mathscr{D}_{\mathbf{H}}$$

$$\frac{\partial}{\partial S_{\mathbf{H}}}\mathscr{D}_{\mathbf{H}} = -i\pi K C\chi_{\mathbf{H}}\mathscr{D}_0 + 2i\pi K\beta'_{\mathbf{H}}\mathscr{D}_{\mathbf{H}} \qquad (5a)$$

with

$$\beta'_{\mathbf{H}} = \frac{K_{\mathbf{H}} - K}{K} - \frac{1}{K}\frac{\partial}{\partial S_{\mathbf{H}}}[\mathbf{H} \cdot \mathbf{u}(\mathbf{r})]. \qquad (5b)$$

Kato (1973) has shown that the approximations made in deriving (5) are the following:

– The Ewald sphere is replaced by its tangential plane near the point of interest.

– The distortions are well behaved enough for the contribution from higher derivatives of $\mathbf{H} \cdot \mathbf{u}(\mathbf{r})$ to be negligible.

Balibar (1975) has shown that Takagi's theory is valid even for large distortions. In the limit of $\mathbf{u}(\mathbf{r}) \equiv 0$, the equations give the description of a perfect crystal. Equations (5) are valid for spherical as well as for plane incident waves.

The practical limitations are the following:

– at each point of the surface of the crystal, boundary conditions are to be applied both for the amplitudes and for the phases of the waves. The phase condition is generally troublesome.

The quantity $\{\partial[\mathbf{H} \cdot \mathbf{u}(\mathbf{r})]/\partial S_{\mathbf{H}}\}$ should be known and a solution can only be found for very simple forms of this factor (like a constant strain gradient).

Nevertheless, one may hope to find a solution of Takagi's equations if the distortions can be described statistically, which implies the introduction of a model.

2. The next step concerns the definition of a reasonable statistical model. The major difficulty comes from the lack of direct experimental information about the distribution of the distortions in a small crystal (some information is now obtained from γ-ray diffraction, but for large crystals; Schneider, 1974, 1975). We shall discuss in § IV some indirect verifications of the statistical assumptions.

For a statistical model to be realistic, many distortions must exist. Each distortion results in a local lack of periodicity. One may think of the crystal in terms of an aggregate of small perfect domains that are slightly misoriented one to the other. The boundary regions generally have a small volume and are highly distorted. They can be assumed to contribute to a diffuse scattering and their contribution is often neglected. The phase relation between the waves diffracted by two adjacent domains is supposed to be random and this results in an incoherent process. Such a model, first introduced by Darwin (1914) and later developed by many authors (see for example: Zachariasen, 1945), is called the 'mosaic model'. The size of the perfect domains, t, may fluctuate around an average value $\bar{t}$ and must verify the con-

dition: $\bar{t} \ll \Lambda$. In that case, the diffraction inside a given domain follows the kinematical theory.

The counters integrate the diffracted intensities around the exact Bragg position, along two directions: perpendicular to the plane of diffraction and perpendicular to the ideal diffracted direction, in the plane of diffraction.

In a plane-wave description, the process is only dependent on the divergence ε of the incident beam (proportional to the departure from Bragg's law) (see for example Becker & Coppens, 1974*a*).

One may therefore define for any perfect region the diffracted power per unit volume and intensity: $\sigma_r(\varepsilon)$, which depends on the position in the crystal. If there are many perfect blocks, one can also define the probability in a given area of the crystal for a block to be misoriented by an angle Δ from the ideal orientation: $W_r(\Delta)$. The effective unit diffracting power will therefore be:

$$\bar{\sigma}_r(\varepsilon) = \sigma_r \times W_r \,. \tag{6}$$

This function will represent the scattering process in the mosaic crystal. Without a direct experimental knowledge of the defect structure, a large arbitrariness is associated with this coupling function $\bar{\sigma}_r(\varepsilon)$. Fortunately, the measured quantities are integrated intensities which are less dependent on the explicit form of the function $\bar{\sigma}_r(\varepsilon)$.

Most theories assume the spatial dependence of $\bar{\sigma}_r(\varepsilon)$ to be negligible: this is equivalent to the assumption of homogeneous mosaic structure. Such an assumption is not obvious (Schneider, 1974, 1975) and the effect of inhomogeneities will be discussed in another paper (Becker, 1977).

If the perfect domains are small enough for absorption to be represented by

$$\exp(-\mu\bar{t}) \sim 1 - \mu\bar{t} \,, \tag{7}$$

the energy exchange process inside the crystal can be formulated as:

$$\frac{\partial I_0}{\partial S_0} = -(\bar{\sigma}+\mu)I_0 + \bar{\sigma} I_{\mathbf{H}}$$

$$\frac{\partial I_{\mathbf{H}}}{\partial S_{\mathbf{H}}} = -(\bar{\sigma}+\mu)I_{\mathbf{H}} + \bar{\sigma} I_0 \,. \tag{8}$$

$I_0(\varepsilon)$ and $I_{\mathbf{H}}(\varepsilon)$ are the incident and diffracted intensities corresponding to a given divergence angle ε. Boundary conditions have to be applied in the following way. Let t_0 and $t_{\mathbf{H}}$ be the depths parallel to the incident and diffracted directions, and $\mathscr{I}_0$ be the intensity of the external incident beam:

$$\begin{aligned} I_0 &= \mathscr{I}_0 \quad \text{for} \quad t_0 = 0 \\ I_{\mathbf{H}} &= 0 \quad \text{for} \quad t_{\mathbf{H}} = 0 \,. \end{aligned} \tag{9}$$

Zachariasen (1945) has shown that if (7) is not satisfied, equations (8) are not valid, the diffraction process being limited to a thin layer below the entrance surface.

If $\mathbf{u}_{\mathbf{H}}$ is the unit vector along the diffracted beam, the integrated power $\mathscr{P}$ is given by the following expression (Becker & Coppens, 1974*a*):

$$\mathscr{P} = \int_{-s}^{+s} \mathrm{d}\varepsilon \int_{\text{exit surface}} I_H(\varepsilon, M)\mathbf{u} \,.\, \mathrm{ds} \,, \tag{10}$$

where ds is the surface element, normal to the exit surface. The extinction correction y is defined as the ratio of the integrated power $\mathscr{P}$ to its kinematical limit $\mathscr{P}_k$.

$$\mathscr{P}_k = \mathscr{I}_0 v Q$$

(v is the volume of the crystal). Therefore:

$$y = \mathscr{I}_0^{-1} v^{-1} Q^{-1} \int \mathrm{d}\varepsilon \int_{\text{exit surface}} I_{\mathbf{H}}(\varepsilon, M)\mathbf{u}\mathrm{ds} \,. \tag{11}$$

The extinction correction that can be obtained by solving equations (8–11) is called secondary extinction and is denoted by y_S.

3. So far we have neglected the dynamical effects inside each perfect region, which is only justified if $\bar{t} \ll \Lambda$. The model can be extended to less strict conditions (namely: $\bar{t} \lesssim \Lambda$) in the following way. One still assumes incoherence of the diffraction by different domains but takes into account the attenuation due to dynamical effects in each domain, by an average factor y_P, called primary extinction. y_P is calculated for the diffraction by a mean block. Equations (8) have therefore to be replaced by

$$\frac{\partial I_0}{\partial S_0} = -(\bar{\sigma} y_P + \mu)I_0 + \bar{\sigma} y_P I_{\mathbf{H}}$$

$$\frac{\partial I_{\mathbf{H}}}{\partial S_{\mathbf{H}}} = -(\bar{\sigma} y_P + \mu)I_{\mathbf{H}} + \bar{\sigma} y_P I_0 \,. \tag{12}$$

In the case of inhomogeneous mosaic structure, y_P should be a function of the position. If absorption is severe and primary extinction to be considered, the approximation (7) may not be satisfied. Therefore the absorption process should be analysed inside each perfect region in a dynamical way, leading to the anomalous absorption effect. Zachariasen (1968) has tried to generalize the equations of the diffraction to include anomalous absorption. Becker & Bonnet (1977) have shown that this approach is physically unrealistic and have proposed another formulation, discussed for the practical case of yttrium iron garnet [a preliminary study has been extensively discussed by Bonnet, Delapalme, Fuess & Thomas (1975)]. It should be kept in mind that no precise description of anomalous absorption and primary extinction can be obtained by the present model. The formulation has to be reconsidered from dynamical equations in the case of severe primary extinction ($\bar{t} \gtrsim \Lambda$).

4. The calculation of y_P should be done from Takagi's equations (5), the solution of which is very difficult, particularly because of the phase boundary conditions. Since only first-order approximations are significant within the present theory, some authors (Zachariasen, 1967; Becker & Coppens, 1974*a*,*b*) have thought that a rough theory of primary extinction should be sufficient. They still use energy transfer equations inside the average block (a sphere for isotropic extinction):

$$\frac{\partial I_0}{\partial S_0} = -\frac{\partial I_{\mathbf{H}}}{\partial S_{\mathbf{H}}} = -\sigma(I_0 - I_{\mathbf{H}}) \,. \tag{13}$$

Becker & Coppens (1974*a*) verified that the solution is resonable to the first order for a sphere. But equations (13) are physically unreasonable and for severe extinction, it is impossible to describe primary extinction (Becker & Coppens, 1975). Becker (1977) shows that solutions from Takagi's equations (in the case of perfect crystals) can be obtained for many shapes of crystals if $\bar{t} \lesssim \Lambda$.

5. The separation between primary and secondary extinction is artificial and a proper theory should not partition the crystal into incoherent domains.

Kato (1975, 1976) has proposed a first dynamical approach to the problem, starting from Takagi's equations (5) for a distorted crystal. He performs the calculation in the

case of a spherical incident wave. It can be shown (Kato, 1974) that there is a Fourier transform relationship between plane-wave and a spherical-wave solutions.

To calculate the wave amplitude, Kato considers all possible routes from the incidence point to the point under study. The displacement vector has the form:

$$\mathscr{D}_{\mathbf{H}}=\sum_{R} A_R \exp(iP_R), \tag{14}$$

where the summation involves all the possible routes. The phase term P_R involves the values of $\mathbf{H}.\mathbf{u}(r_i)$ at the various diffraction centres associated with the chosen route. The intensity $I_{\mathbf{H}}$ is therefore:

$$I_{\mathbf{H}}=\sum_{R}\sum_{R'} A_R A^*_{R'} \exp i(P_R-P_{R'}). \tag{15}$$

It is impossible to go further unless a hypothesis is made concerning the distribution of the distortions. The assumption is that of a homogeneous and isotropic distribution. It is possible to replace $I_{\mathbf{H}}$ by the ensemble average of it over the possible distortions.

$$\langle I_{\mathbf{H}}\rangle=\sum_{R}\sum_{R'} A_R A^*_{R'} \langle\exp[i(P_R-P_{R'})\rangle. \tag{16}$$

The term $\langle\exp[i(P_R-P_{R'})]\rangle$ involves the correlation of the defects. Kato has been able to show that, if τ is the average correlation length, and in the hypothesis where ($\tau \ll \Lambda$), $\langle I_{\mathbf{H}}\rangle$ and the corresponding incident intensity $\langle I_0\rangle$ satisfy the following equations:

$$\frac{\partial\langle I_0\rangle}{\partial S_0}=-(2\tau\mathrm{Re}(\chi_{\mathbf{H}}\chi_{\bar{\mathbf{H}}})+\mu)\langle I_0\rangle+2\tau|\chi_{\bar{\mathbf{H}}}|^2\langle I_{\mathbf{H}}\rangle$$

$$\frac{\partial\langle I_{\mathbf{H}}\rangle}{\partial S_{\mathbf{H}}}=-(2\tau\mathrm{Re}(\chi_{\mathbf{H}}\chi_{\bar{\mathbf{H}}})+\mu)\langle I_{\mathbf{H}}\rangle+2\tau|\chi_{\mathbf{H}}|^2\langle I_0\rangle. \tag{17}$$

Equations (17) are very similar to (8), but the coupling terms are independent of any divergence angle (the spherical waves take all incident directions into account). It can be shown that $\{2\tau|\chi_{\mathbf{H}}|^2\}$ is the diffracting power per unit intensity and unit length, in the kinematical approximation, of a crystal of dimension τ. It is therefore equivalent to $\bar{\sigma}(\varepsilon)$ in plane-wave theory. The small difference that can exist between $\mathrm{Re}(\chi_{\mathbf{H}}\chi_{\bar{\mathbf{H}}})$ and $|\chi_{\mathbf{H}}|^2$ may be related to Borrmann absorption (Becker, 1977). It can be shown also that if $\bar{\sigma}(\varepsilon)$ is replaced by a constant, equations (8) and (17) lead to the same formal expression for the extinction correction. The calculation of τ for some distortion models (block size and angular distortion effects) involves parameters which are similar to those involved in mosaic theory and gives them a more physical meaning. The difference between the two theories may be explained as follows (Becker, 1977). Kato's theory describes the plane-wave intensity as the transform of the ensemble average of the spherical-wave solution. This average is taken over all possible distributions of the distortions. In fact, the ensemble average, for an incident plane wave, is to be taken over the plane-wave intensity, which particularizes the correlations in directions perpendicular to the incident beam. Therefore, the two solutions are different and the correlation length τ has to be modulated by a function of ε. The two theories are equivalent.

Nevertheless, Kato's approach is fundamental for various reasons. First, the intensity coupling is not an *a priori* assumption as in mosaic theory. The method of solution can certainly be extended to the case where ($\tau \gtrsim \Lambda$). It gives a better meaning to the parameters introduced in mosaic theory, which has more validity than could be predicted from its original assumptions. $\bar{\sigma}(\varepsilon)$ becomes a statistical coupling function involving a correlation length without assuming a discontinuous aggregate of small crystallites.

Much progress has still to be made but the agreement of the two theories based on very different hypotheses should give some confidence in the validity of present extinction corrections.

III. The solution of the energy transport equations

The solution of equations (8) [or (17)] has been studied by several authors. Hamilton (1957, 1963) proposed a numerical integration, introducing grid points and replacing the differential equations by difference equations. Werner and coworkers (Werner & Arrott, 1965; Werner, Arrott, King & Kendrick, 1966; Werner, 1974) followed by Zigan (1970, 1976), applied the general method of solution of hyperbolic equations and obtained the intensities for specific geometries. Unfortunately, these authors did not find a practical solution, usable in a least-squares program. Zachariasen (1967) made an important contribution in finding a general approximation that was routinely programmed (Larson, 1969) and extended to anisotropic extinction cases (Coppens & Hamilton, 1970). The success of the method was very satisfactory but in the meantime shortcomings of Zachariasen's theory were pointed out (Cooper & Rouse, 1970), mainly due to an improper angular dependence of the expression for y. Becker & Coppens (1974*a*, *b*, 1975) reconsidered completely the problem and were able to obtain a general approximate solution that is exact for small Bragg angles and only a third-order approximation for large Bragg angles (for which extinction is generally small). It has been shown recently (Bonnet, Delapalme, Becker & Fuess, 1976) that the solution is exact in all Laue geometries and Becker (1977) proposes some ways to obtain a better solution in other cases. The solution has been extended to anisotropic extinction and applied by the authors to various cases; a very significant improvement was observed compared with previous treatments. We shall confine ourselves to the outline of the results.

(1) The solution for secondary extinction is

$$y_S=Q^{-1}\int\bar{\sigma}(\varepsilon)\Phi(\bar{\sigma})\mathrm{d}\varepsilon$$

$$\Phi(\sigma)=v^{-1}A^{-1}\int_v \mathrm{d}v \times\exp\{-(\bar{\sigma}+\mu)(T_0+T'_{\mathbf{H}})\}I_0\{2\bar{\sigma}(T_0T'_{\mathbf{H}})^{1/2}\}$$

$$A=v^{-1}\int_v \mathrm{d}v\exp\{-\mu(T_0+T'_{\mathbf{H}})\}; \tag{18}$$

I_0 is a zero-order modified Bessel function. T_0 and $T'_{\mathbf{H}}$ are the optical path lengths along the incident and diffracted directions. Similar expressions can be obtained for primary extinction, the volume of integration being that of a mean perfect block, $\bar{\sigma}$ being replaced by σ, and μ assumed to be zero. y_S and y_P depend on the orientation matrix, the Bragg angle, the intensity of the reflexion, the absorption coefficient (for y_S only) and the shape of the crystal. Two important parameters are

$$x_S=\tfrac{2}{3}\bar{\sigma}(0)\bar{T}$$
$$x_P=\tfrac{2}{3}\sigma(0)\bar{t}, \tag{19}$$

where $\bar{t}$ is the mean path length associated with a perfect domain, and $\overline{T}$ is given by

$$\overline{T}=\frac{\int_v (T_0+T'_{\mathbf{H}})\exp\{-\mu(T_0+T'_{\mathbf{H}})\}\mathrm{d}v}{\int_v \exp\{-\mu(T_0+T'_{\mathbf{H}})\}\mathrm{d}v}. \quad (20)$$

The extinction correction, solution of equations (12), is

$$y=y_P(x_P)y_S\{x_S y_P(x_P)\}. \quad (21)$$

In the X-ray case, the two polarization states must be considered. The integral (18) was calculated numerically for a spherical crystal, for which y_i is only a function of x_i and θ. An analytical fit was proposed (obviously, a better one might be found), assuming either a Gaussian or a Lorentzian coupling function $\bar{\sigma}$. $\sigma(\varepsilon)$ can be calculated exactly for any block shape.

If $(\mu\overline{T})$ is larger than 0·5, a μ dependence is introduced in the expression for y_S. Becker & Coppens (1975) have shown that if $\overline{T}$ is calculated exactly by (20) for each reflexion, the 'spherical approximation' can be used for many shapes of crystals (unless the ratio of the dimensions of the crystal is too large, >2). Concerning the cases of anisotropic extinction, Thornley & Nelmes (1974) have proposed a formulation slightly different from that of Coppens & Hamilton (1970), which gives better results and is physically more justified.

(2) If a Gaussian distribution $\bar{\sigma}$ is assumed, one gets:

$$\bar{\sigma}_G(0)=\bar{t}\frac{\sin 2\theta}{\lambda}\left\{1+\left(\frac{\bar{t}\sin 2\theta}{\sqrt{2}\lambda g}\right)^2\right\}^{-1/2} \quad (22)$$

where

$$W_G(\varepsilon)=\sqrt{2}g\exp(-2\pi g^2\varepsilon^2)$$

and if $\bar{\sigma}$ is Lorentzian:

$$\bar{\sigma}_L(0)=\bar{t}\frac{\sin 2\theta}{\lambda}\left\{1+\frac{2\bar{t}\sin 2\theta}{3\lambda g}\right\}^{-1} \quad (23)$$

where

$$W_L(\varepsilon)=2g\{1+4\pi^2\varepsilon^2 g^2\}^{-1}.$$

Extreme cases correspond to:

– Type II (extinction dominated by the block-size effect) if the breadth of σ is large compared to the breadth of W:

$$\frac{\bar{t}\sin 2\theta}{\lambda}\ll g \qquad \bar{\sigma}(0)=\bar{t}\frac{\sin 2\theta}{\lambda}. \quad (24)$$

– Type I (extinction dominated by the misorientations)

$$\bar{t}\frac{\sin 2\theta}{\lambda}\ll g \qquad \bar{\sigma}(0)\sim\sqrt{2}g. \quad (25)$$

Becker & Coppens have shown that if extinction is severe, it should be of type I except for very small Bragg angles for which (25) cannot be satisfied and the extinction is of mixed type. Type I extinction is associated with large values of $\bar{t}$ and therefore some primary extinction may be present in such cases.

Type II extinction is mathematically identical to primary extinction alone (type I and g very small). If one assumes type II extinction,

$$X_S=\tfrac{2}{3}Q\bar{t}\frac{\sin 2\theta}{\lambda}\overline{T}. \quad (26a)$$

If one assumes primary extinction,

$$X_P=\tfrac{2}{3}Q\bar{t}^2\frac{\sin 2\theta}{\lambda}. \quad (26b)$$

In quasi-spherical crystals, where $\overline{T}$ is constant, these two possibilities cannot be distinguished. Such a case has been found in the X-ray data collected by Killean, Lawrence & Sharma (1972) on a sphere of LiF. These authors assumed secondary extinction and got $\bar{t}\sim 3\times 10^{-6}$ cm, one hundred times smaller than the expected value obtained from dislocation density measurements (3×10^{-4} cm). The assumption of primary extinction led to $\bar{t}\sim 3\times 10^{-4}$ cm.

At very small Bragg angles, extinction cannot be of pure type I (equations 22 and 23), and particle size effects become important.

At the present time, only Gaussian or Lorentzian shapes have been assumed for $\bar{\sigma}(\varepsilon)$. In fact, $\bar{\sigma}(\varepsilon)$ comes from several experimental effects, which are generally reasonably represented by Gaussian functions, and from intrinsic diffraction effects, which are generally Lorentzian. Therefore a better representation should be a Voigt profile (Armstrong, 1967). The results will be analysed in a subsequent publication.

The distinction between type I and type II is very clear in the present formalism (equations 24 and 25), due to the factor $\sin 2\theta$.

IV. Applicability of the models

The present theory has been programmed (Program *LINEX* 74) and applied to several data sets (Becker & Coppens, 1974*b*, 1975; Bonnet, Delapalme, Fuess & Thomas, 1975; Bonnet, Delapalme, Becker & Fuess, 1976; Jost, Rees & Yelon, 1975; Niimura, Tomiyashi, Takahashi & Harada, 1975; Harvey & Prager, 1975; Kötzler, Scheithe, Knorr & Yelon, 1976). We want here to discuss various possible tests concerning the validity of the application of an extinction correction to a given sample.

In neutron diffraction, where extinction is generally very pronounced, one is only interested in getting unbiased positional and thermal parameters (except when magnetic scattering is present), while in X-ray diffraction it is important to get accurate individual structure factors in order to calculate reliable electron densities.

1. The distinction between type-I and type-II dominated extinction is very clear on the basis of conventional R values. If extinction is severe, it is generally type-I dominated, with a preference for a Lorentzian distribution (for a given width of the reflexion, a Lorentzian allows for more pronounced angular distortions than a Gaussian).

Block size effects may become important for small Bragg angles (equations 22, 23). In the case of type-I predominance, primary extinction may be significant and may even be the major source of extinction (primary extinction correction is mathematically equivalent to secondary type II).

2. The collection of data on different samples is highly recommended. The various data sets should give refined parameters and structure factors that are in good agreement (Bonnet, Delapalme, Becker & Fuess, 1976) and should enable one to select the sample that is the most adequate for the chosen extinction correction.

3. It is of great interest to vary the wavelength. It is obvious from the theory that x_S and x_P vary approximately as λ^2 (for small Bragg angles). Many examples show that the refined thermal parameters are in excellent agreement for the various data sets and a joint refinement on all data may re-

duce the standard deviations. (Positional parameters do not in general depend significantly on the type of extinction correction that is assumed).

However, we do not think that an exact agreement between the refined extinction parameters should be expected. r and g necessarily have some λ dependence, for the following reason. When λ increases, the extinction length decreases. The model is based on the form of the coupling function $\bar{\sigma}(\varepsilon_1)$. This function is an average diffracting power, which is a statistical compromise between the block size and the angular effects and the optimized values of r and g may vary with λ. There is experimental evidence that they slightly increase with λ, which may correspond to some undercorrection for long wavelengths. The significance of r and g is only statistical and the statistical description of the diffraction behaviour of a crystal is expected to depend on the specifications of the radiation that is used. Niimura *et al.* (1975), by a time-of-flight neutron experiment on CuCl, have shown that the proposed correction is adequate in the wavelength range, 0·5–5 Å, the largest discrepancies occurring for short wavelengths. It should be added that if the sample is well suited for an extinction correction, the refined scale factors for the various wavelengths must be in very close agreement, which has been verified on various examples (Becker, 1973).

4. In order to check for the decorrelation of extinction from other experimental effects, several refinements are recommended with thresholds that momentarily exclude the most severely extinction-affected reflexions (Becker & Coppens, 1975). The stability of the thermal parameters is very significant information. It is also instructive to define 'partial R values' that are restricted to reflexions of small y. The conventional R values are not a sufficient test and cases are found where two different corrections lead to very different thermal parameters and the same R values (Becker & Coppens, 1975).

5. The effective block size (t^*), derived from equations (22) and (23) must be compared with Λ. In most neutron experiments, the situation is quite satisfactory: $t^* < \Lambda$ (Bonnet *et al.*, 1976), except for few reflexions for which $t^* \sim \Lambda$. In the X-ray case, structure factors may be higher than in the neutron diffraction experiment, but the perfect domains are often of smaller size and generally few reflexions are affected. As pointed out by Kato (1976), the model may be reasonably applicable in the case where $t^* \sim \Lambda$, and accumulation of results will allow in the future the delimination of the practical domain of applicability of the theory. The major shortcoming seems to come from cases where primary extinction is important.

6. In neutron experiments, the crystal is often large enough for a topographic study to be possible. Such an experiment is informative about the homogeneties of extinction and the validity of a statistical description of the defects. Similarly, dislocation density measurements give an estimate of the order of magnitude of the coherence length in a crystal.

7. γ-ray diffraction (Schneider, 1974, 1975) allows for the investigation of rocking curves. It has been extensively used by Schneider and coworkers on large samples and gives valuable information about the optical image of the defect structure and the inhomogeneity of extinction. In the present form, the resolution of the experiment is limited by the size of the slit: $10 \times 0{\cdot}2$ mm. Therefore only 'long-range' inhomogeneities are revealed.

Recent studies on small samples (suitable for neutron diffraction) have been made (Bonnet *et al.*, 1976; Kötzler *et al.*, 1976). The experimental curve is a convolution of the rocking curve with the resolution function of the instrument (the width of which is of the order of 10″). It has been possible to deconvolute and estimate the width of the rocking curve. In the cases that were studied, a good agreement was observed with the extinction parameters obtained by refinement. The repetition of the experiment for various reflexions and with the orientation of the crystal changed gives valuable information about the anisotropy and 'short-range inhomogeneity' of extinction.

The experimental tests discussed in 6 and 7 are highly recommended for testing the application of any given diffraction theory to a particular sample.

8. Polarized neutron diffraction is a powerful technique for studying extinction in magnetic materials (Bonnet *et al.*, 1976), since it is scale-factor free. When applied to yttrium iron garnet, on various samples and with different wavelengths, it revealed the data to be fairly consistent after the correction had been applied and the Lorentzian distribution to be favoured. The technique is very sensitive to the type of correction that is used and also to the type of statistical distribution that is assumed.

9. A trivial test concerning the accuracy of an experiment is the calculation of the agreement index between symmetry-equivalent reflexions and the averaging of symmetry-equivalent reflexions before any refinement. This procedure may be dangerous. Most of the time, when systematic discrepancies occur among symmetry-equivalent reflexions extinction is assumed to be anisotropic. In fact x_S is proportional to $\overline{T}$, which differs for related reflexions unless the crystal is spherical. Therefore in any case where extinction is present and the crystal is not a sphere, the averaging of reflexions may lead to biased structure factors. This procedure may also give a pessimistic experimental agreement (we call this agreement index α). One generally assumes the variance of the observation to be given by:

$$\sigma^2(I) = \sigma_c^2 + \alpha^2 I^2,$$

where I is the measured intensity and σ_c^2 accounts for the counting statistics. For strong reflexions, σ_c^2 is proportional to I and often

$$\sigma^2(I) \sim \alpha^2 I^2 .$$

Therefore the standard deviation is artificially increased by the averaging procedure, as is the noise in an electron density calculation.

On the other hand, the comparison of the structure factors of equivalent reflexions, after individual corrections, may be very informative about the applicability of the correction.

10. In powder diffraction experiments, extinction may be present and owing to the small value of $\overline{T}$ for individual particles, primary extinction is to be expected. Price (1975) has shown that extinction in diamond is of primary type. The use of the Becker & Coppens formulation (x_P being proportional to $\bar{t} \sin 2\theta/\lambda$ instead of $\bar{t}$ in Zachariasen's treatment) changes the Debye–Waller factor significantly and leads to a value in close agreement with the lattice-dynamical value.

V. Conclusion

Until now the application of extinction theories has been quite successful and its range of applicability, concerning secondary extinction, seems to be quite wide.

The preceding discussion shows that many checks exist, some of them being experimental. Because of the size of the crystals, experimental checks can only be applied to the

neutron case and X-ray data should be analysed with special care.

The recent theory of Kato puts the conventional extinction theories developed by Becker & Coppens on a physical basis and specifies the conditions of application.

Because of the statistical nature of the problem, it is difficult to get close agreement between a 'refined parameter' and its estimate from some experiment.

Some people claim that extinction can be accounted for only if $y<0{\cdot}90$. This is certainly not true. The suitability of a given sample for an extinction theory depends essentially on the local description of its defect structure and not at all on the size of the crystal. If extinction is mainly primary, the correction may be unreliable for $y\sim 0{\cdot}8-0{\cdot}9$. But if $t^*\ll\Lambda$, the range of applicability can be very large. We think that the tests discussed in § IV are very important for understanding the nature of the sample but they do not prevent one from using a correction.

Much effort should be made in the near future to extend the theory to cases where $t^*>\Lambda$ and to get accurate solutions to the diffraction equations associated with a model.

Even with the present limitations we believe that it is possible to obtain experimental electron densities accurate to within 0·01 e Å^{-3}. Only very sophisticated quantum-mechanical calculations are able to reproduce equivalent features (Becker, 1975).

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