HENDRICKSON, W. A. & KONNERT, J. H. (1980). In *Computing in Crystallography*, edited by R. DIAMOND, S. RAMASESHAN & K. VENKATESAN, pp. 13.01-13.23. Bangalore: Indian Academy of Sciences.
JONES, T. A. (1982). In *Computational Crystallography*, edited by D. SAYRE, pp. 303-317. Oxford: Clarendon Press.
KIMBALL, M. R., SATO, A., RICHARDSON, J. S., ROSEN, L. S. & LOW, B. W. (1979). *Biochem. Biophys. Res. Commun.* **88**, 950-959.
KONNERT, J. H. (1976). *Acta Cryst.* A**32**, 614-617.
LOW, B. W. & CORFIELD, P. W. R. (1986). *Eur. J. Biochem.* **161**, 579-587.
LOW, B. W., PRESTON, H. S., SATO, A., ROSEN, L. S., SEARL, J. E., RUDKO, A. D. & RICHARDSON, J. S. (1976). *Proc. Natl Acad. Sci. USA*, **73**, 2991-2994.
NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* A**24**, 351-359.
SHERIFF, S. & HENDRICKSON, W. A. (1987). *Acta Cryst.* A**43**, 118-121.
SMITH, J. L., HENDRICKSON, W. A., HONZATKO, R. B. & SHERIFF, S. (1986). *Biochemistry*, **25**, 5018-5027.
TSERNOGLOU, D. & PETSKO, G. A. (1976). *FEBS Lett.* **68**, 1-4.

Acta Cryst. (1988). A**44**, 368-373

A Reconciliation of Extinction Theories

BY T. M. SABINE

NSW Institute of Technology, Sydney, NSW 2007, *Australia*

(*Received* 20 *December* 1986; *accepted* 15 *January* 1988)

Abstract

The differences between previous theoretical treatments of extinction based on the Darwin intensity equations arise because of the different functional form chosen for the coupling constant σ. When the same function is used these theories make closely similar predictions. It is shown that a limiting condition on integrated intensity as the crystal size increases puts restrictions on the functions which may be used. A Lorentzian or Fresnellian function can be used for primary extinction while secondary extinction requires a Gaussian, rectangular or triangular function. An analytical expression is given for the variation in the value of the extinction factor with scattering angle.

1. Introduction

The kinematic theory of the diffraction of X-rays or neutrons predicts that the intensity of the diffracted beam is proportional to the volume of the crystal. If this were the case the intensity of the diffracted beam would exceed the intensity of the incident beam for sufficiently large crystals. The drawback of the kinematic theory is that it ignores the possibility of rescattering of the diffracted beam as it passes through the crystal. When the incident beam satisfies the Bragg condition in a perfect crystal so must the diffracted beam, and an interchange of energy between the diffracted beam and the incident beam will occur as both beams flow through the crystal. The rescattering probability increases as the size of the crystal increases.

For the imperfect crystal (Darwin, 1922), which is composed of blocks of perfect crystal (called mosaic blocks) tilted at small angles to each other, the beam diffracted by one block has a probability of being scattered again by a block of identical orientation during the passage of the diffracted beam through the crystal. The rescattering probability is proportional to the distribution of mosaic block orientations and the size of the crystal. For the perfect crystal spatial coherence between scattering centres is preserved across the entire specimen. In the imperfect crystal each block is a perfect crystal but there is no coherence between scattering centres located in different blocks.

In crystal structure analysis the phenomenon of increasing reduction of the intensity of the diffracted beam from the prediction of the kinematic theory as the crystal volume increases is termed extinction. The extinction factor, y, is defined by $I^{obs} = yI^{kin}$. I^{obs} is the integrated intensity measured in an experiment. I^{kin} is the integrated intensity a Bragg reflection would have if the kinematic theory applied exactly to the system being examined.

Extinction within a perfect crystal is termed primary extinction. In an ideally imperfect crystal, which is one in which extinction within mosaic blocks can be ignored, it is termed secondary extinction. Both types can occur in the same specimen.

The randomly oriented powder is a special case of the imperfect crystal. For this specimen the mosaic block distribution is known explicitly.

The object of the theories of extinction is to obtain an expression for y in terms of the dimensions and microstructure of the crystal so that I^{obs} can be correc-

0108-7673/88/030368-06$03.00

ted to I^{kin}. I^{kin} is then used as a starting point for the determination of atomic positions, thermal vibration parameters and electron density distributions. These are the interests of crystallographers. A very different interest in extinction was shown by Fermi, Sturm & Sachs (1947), who were concerned with the effect of reinforcement of the transmitted beam on measurements of the removal cross section for neutrons passing through matter.

To be of use in crystal structure refinement y should be expressed analytically in terms of the scattering angle, the size of the perfect crystal block, the size of the crystal (for primary extinction these are the same) and the angular distribution of mosaic blocks.

The projection into the diffraction plane of the normals to each block is assumed to have a Gaussian distribution, which is usually given as

$$W(\Delta) = [\eta(2\pi)^{1/2}]^{-1} \exp[-(\Delta^2/2\eta^2)], \quad (1)$$

where Δ is the angular deviation of the projected normal to a mosaic block from the mean orientation of projected normals to mosaic blocks. It is measured on the glancing-angle (θ) scale. The standard deviation of the distribution is η. Normalization is such that $\int W(\Delta)\, d\Delta = 1$.

Theories which lead to expressions for y which can be used in computer programs are those of Hamilton (1957, 1963), Zachariasen (1967), Werner (1974) and Becker & Coppens (1974). Kato has discussed primary and secondary extinction and a combination of both in a series of papers (Kato, 1976, 1979, 1980); however, no usable expressions are given. Olekhnovich & Olekhnovich (1978, 1980) have discussed primary extinction for the square-section parallelepiped and for the cylinder, while Wilkins (1981) has given computer solutions for certain types of distorted crystals. Borie (1982) has pointed out the implication of Werner's (1974) work for finding a usable solution, but does not give one. Sabine (1985) has given a theory of primary extinction, without absorption, and has experimentally verified the theory by neutron diffraction experiments on polycrystalline specimens of magnesium oxide. In this paper that theory is extended and compared with previous results. It is concluded that Hamilton (1957, 1963), Zachariasen (1967), Werner (1974), Becker & Coppens (1974) and the present work lead to results which are essentially identical.

2. A general observation on extinction

The model used for the present analysis is shown in Fig. 1. As in the discussion of Hamilton (1957) the finite crystal can have any shape, but its surface is everywhere convex, so that an emergent beam cannot re-enter the crystal. It is bathed in a beam which can be represented as a plane wave of infinite lateral extent. A consequence of this representation is perfect collimation, that is the incident beam has no angular divergence. Since this discussion deals with integrated intensity no error is introduced by using this approximation.

The incident beam enters the crystal along the boundary AB from the left and emerges along the boundary CD to the right. To determine the integrated intensity it is necessary to integrate the current in the diffracted beam over the exit surface. The extinction factor is then the ratio of this quantity to the kinematic integrated intensity.

From this diagram some general observations concerning the asymptotic behaviour of the extinction factor can be made.

When there is no true absorption of the incident radiation the kinematic integrated intensity will increase linearly with the volume of the crystal. Under extinction conditions, no matter how severe, the integrated intensity must increase linearly with the increase in fresh crystal surface exposed to the incident beam.

Hence the extinction factor, which is defined as the ratio of I^{obs} to I^{kin}, must become proportional to the rate of increase in area of the entrance surface divided by the rate of increase in volume.

This argument puts limiting conditions on the behaviour of the extinction factor as the crystal size increases. For commonly used crystal shapes the limiting values are:

(a) The parallelepiped with sides parallel to the incident- and diffracted-beam directions, and height h normal to the diffraction plane.

This shape is called the AB crystal by Werner (1974). For the special case of sides of equal length t_0 (called the AA crystal in this paper) the volume is proportional to $t_0^2 \sin 2\theta$, and the area of the entrance surface is proportional to t_0. Hence $y_{t_0 \to \infty}$ tends towards proportionality to $1/(t_0 \sin 2\theta)$.

The variable, $t_\perp$, used by Zachariasen (1967) is $t_0 \sin 2\theta$, and the above argument may be the reason why he made that choice.

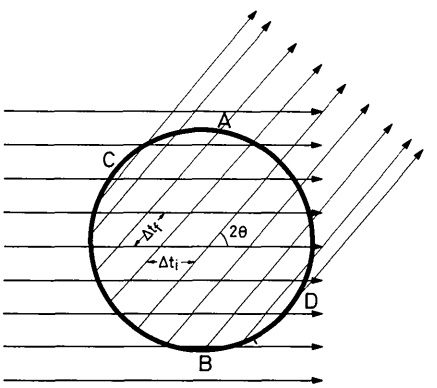


Fig. 1. The beam enters the crystal through the surface ACB and exits through the surface CAD.

(*b*) For the mosaic block of edge a

$$y_{a\to\infty} \to \text{proportionality to } 1/a.$$

(*c*) For the sphere of radius r

$$y_{r\to\infty} \to \text{proportionality to } 1/r.$$

(*d*) For the right cylinder of radius r and axis of length h normal to the diffraction plane

$$y_{r\to\infty} \to \text{proportionality to } 1/r.$$

3. The Darwin intensity equations

The starting point for theories of extinction proposed by Hamilton (1957), Zachariasen (1967), Werner (1974), and by Becker & Coppens (1974), is the generalization of the Darwin energy transfer equations by Hamilton (1957).

These equations are

$$\partial P_i/\partial t_i = \tau P_i + \sigma P_f \qquad (2)$$

$$\partial P_f/\partial t_f = \tau P_f + \sigma P_i. \qquad (3)$$

P_i and P_f are the current densities (neutrons $\text{cm}^{-2}\,\text{s}^{-1}$) at the position in the crystal whose coordinates are t_i, t_f. The distance t_i is measured along the incident-beam direction while t_f is measured along the diffracted-beam direction. The coefficient τ is the removal cross section per unit volume. It includes all processes which remove energy from a beam bathing a crystal. The sign of τ is always negative. The coefficient σ is the cross section per unit volume for Bragg scattering. The angle between t_i and t_f is 2θ.

Exact solutions of these equations for $2\theta = 0$ and for $2\theta = \pi$ in a semi-infinite flat plate of thickness D_0 are given by Hamilton (1957).

In this paper it is assumed that Bragg scattering is the only removal process. For this case ($\tau = -\sigma$) the solutions for the current at the exit surface of the crystal are given by Zachariasen (1945).

(*a*) *Symmetric Laue case*

$$P_f = \tfrac{1}{2}P_1^0[1 - \exp(-2\sigma D)], \quad D = D_0/\cos\theta. \qquad (4)$$

(*b*) *Symmetric Bragg case*

$$P_f = P_i^0 \sigma D/(1+\sigma D), \quad D = D_0/\sin\theta. \qquad (5)$$

P_i^0 is the current at the entrance surface. D_0 is again the plate thickness.

Zachariasen (1967) and Sabine (1985) chose the solution to the symmetrical Bragg case as an approximation to the general solution. Hamilton (1957, 1963) used a finite difference method to provide a general solution by computer. Becker & Coppens (1974) express (2) and (3) in integral form and use numerical methods. Werner (1974) found an exact solution in terms of tabulated functions.

4. The functional form for σ

The coupling coefficient σ in the transfer equations is the cross section per unit volume for scattering into a single Bragg reflection. As shown in many texts on diffraction theory (*e.g.* Marshall & Lovesey, 1971), $\sigma = Q_k\delta(\Delta k)$ on the scattering-vector scale [$k = 2(\sin\theta)/\lambda$] where $Q_k = N_c^2\lambda^2F^2/\sin\theta$, and $\sigma = Q_\theta W(\Delta\theta)$ on the glancing-angle scale, where $Q_\theta = N_c^2\lambda^3F^2/\sin 2\theta$.

In these expressions N_c is the number of unit cells per unit volume, λ is the neutron wavelength, 2θ is the scattering angle. F is the structure factor per unit cell for the reflection under consideration. The Debye–Waller factor is *included* in F. The arguments of the delta functions are small deviations from the Bragg position.

For primary extinction the delta function is replaced by a function of Δk normalized to unity. For secondary extinction, where the controlling quantity is the angle between mosaic blocks, $\sigma(\Delta\theta) = Q_\theta\delta(\Delta\theta)$, and the delta function is replaced by a mosaic block orientation distribution normalized so that $\int W(\Delta\theta)\,\mathrm{d}(\Delta\theta) = 1$.

Possible functional forms (also given by Sabine, 1985) are

$$\sigma(\Delta k) = Q_kT/[1+(\pi T\Delta k)^2], \qquad \text{Lorentzian } (L)$$

$$\sigma(\Delta k) = Q_kT\sin^2(\pi T\Delta k)/(\pi T\Delta k)^2, \qquad \text{Fresnellian } (F)$$

$$\sigma(\Delta k) = Q_kT\exp[-\pi(T\Delta k)^2], \qquad \text{Gaussian } (G)$$

$$\sigma(\Delta k) = Q_kT, \quad |\Delta k| \le 1/2T,$$
$$= 0 \text{ otherwise}, \qquad \text{Rectangular } (R)$$

$$\sigma(\Delta k) = Q_kT(1-|\Delta k|T), \quad |\Delta k| \le 1/T,$$
$$= 0 \text{ otherwise}. \qquad \text{Triangular } (T)$$

For each profile conversion to the 2θ scale and calculation of the integral breadth leads to the Scherrer equation for particle-size broadening with T the volume average of the thickness of the crystal normal to the diffracting plane (Wilson, 1949, p. 35).

For secondary extinction identical functions to the primary-extinction case can be used by substituting Q_θ for Q_k and G for T where G is the value of $W(\Delta\theta)$ at $\Delta\theta = 0$. For the Gaussian distribution of (1) $G^{-1} = \eta(2\pi)^{1/2}$, Zachariasen (1967) and Becker & Coppens (1974) used Fresnellian, Lorentzian and Gaussian functions; Hamilton (1957) and Werner (1974) used a rectangular function.

5. Calculation of the extinction factor

The notation used in this section is L, F, G, R, T as a superscript to identify the functional form of σ, and L, B as a subscript to identify the cases $2\theta = 0$ and $2\theta = \pi$, respectively.

The extinction factor, y, is defined in § 2 as the ratio of the integrated intensity of the reflection to the integrated intensity it would have under kinematic conditions. Then

$$y_L = \frac{\frac{1}{2}\int \{1-\exp[-2\sigma(\Delta k)D]\}\,\mathrm{d}(\Delta k)}{\int \sigma(\Delta k)D\,\mathrm{d}(\Delta k)},$$

Laue case from (4)

$$y_B = \int \frac{\sigma(\Delta k)\,\mathrm{d}(\Delta k)}{1+\sigma(\Delta k)D} \Big/ \int \sigma(\Delta k)\,\mathrm{d}(\Delta k).$$

Bragg case from (5)

The limits of integration depend on the specific form of $\sigma(\Delta k)$.

Substitution of each expression for $\sigma(\Delta k)$ into the above equations and integration over Δk lead to the following expressions for y. In all cases $x = Q_k TD$ for primary extinction and $x = Q_\theta GD$ for secondary extinction. D is the path-length parameter.

(*a*) *Laue case*

$$y^L = 1 - x/2 + x^2/4 - 5x^3/48 + \ldots, \quad (6)$$

$$y^F = 1 - 2x/3 + 11x^2/30 - 151x^3/945 + \ldots, \quad (7)$$

$$y^G = 1 - 2x/(2!\,2^{1/2}) + 4x^2/(3!\,3^{1/2}) - 8x^3/(4!\,4^{1/2}) + \ldots, \quad (8)$$

$$y^R = (1/2x)[1-\exp(-2x)], \quad (9)$$

$$y^T = (1/x)\{1-(1/2x)[1-\exp(-2x)]\}. \quad (10)$$

(*b*) *Bragg case*

$$y^L = 1/(1+x)^{1/2}, \quad (11)$$

$$y^F = 1 - 2x/3 + 11x^2/20 - 151x^3/315 + \ldots, \quad (12)$$

$$y^G = 1 - x/2^{1/2} + x^2/3^{1/2} - x^3/4^{1/2} + \ldots, \quad (13)$$

$$y^R = 1/(1+x), \quad (14)$$

$$y^T = (2/x^2)(x - \ln|1+x|). \quad (15)$$

6. Comparison with dynamical theory

In § 2 it was shown that the extinction factor should approach a limiting value as the crystal size increases. For primary extinction only the Lorentzian or Fresnellian form satisfies this condition. A choice between these forms can be made through a comparison with the results of the dynamical theory.

For the semi-infinite flat plate of thickness D_0 the dynamical theory (Zachariasen, 1945, pp. 133–134) gives for the Bragg case

$$y_B = (\tanh A)/A, \quad A = N_c\lambda FD/\sin\theta$$

and for the Laue case

$$y_L = \sum_0^\infty J_{2n+1}(2A)/A, \quad A = N_c\lambda FD/\cos\theta.$$

In these equations D is the average path length for the beam. The limiting values of the extinction factor are

$$y_B(x\to\infty) = A^{-1}, \quad y_L(x\to\infty) = (2A)^{-1}.$$

The series for y_L^L [(6)] is divergent for large x; however, it approaches the asymptotic series

$$y_L^L = (2/\pi x)^{1/2}[1 - 1/(8x) - 3/(128x^2) - 15/(1024x^3) + \ldots]. \quad (16)$$

The limiting values of the solutions (11) and (16) are

$$y_B^L(x\to\infty) = (1/x)^{1/2}, \quad y_L^L(x\to\infty) = (2/\pi x)^{1/2}.$$

The quantity A of the dynamical-theory solutions can be readily identified with the square root of x. Following Zachariasen (1945, p. 130), in the Bragg case, $T = D_0$, $D = D_0/\sin\theta$, and hence $x = A^2$; while, in the Laue case, the substitutions $T = D_0\tan\theta$, $D = D_0/\cos\theta$ again lead to $x = A^2$.

Asymptotic solutions for the extinction factors of this paper are then

$$y_B^L \to A^{-1}, \quad y_L^L \to (1{\cdot}25A)^{-1}.$$

Becker & Coppens (1974) note that their value of their primary-extinction factor approaches $c/(x^{1/2})$. They do not comment on the numerical value of c. For a Fresnellian function, which they use in discussing primary extinction, $y_B \to 2/(\pi x^{1/2})$ as x increases.

7. Primary extinction in finite crystals

(*a*) *The AA crystal*

This crystal is defined in § 2. It has edges of equal length t_0 along the directions of the incident beam and the diffracted beam. The thickness of the crystal normal to the diffracting plane (T) is then $t_0\sin\theta$ and the average path length through the crystal (D) is t_0; hence $x = Q_k DT = (N_c\lambda F t_0)^2$.

(*b*) *The sphere*

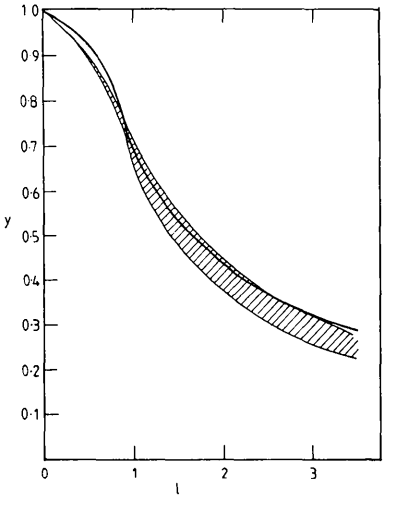
Straightforward application of the formulae of this paper with $T = D = \frac{3}{2}r$ would give $x = 9(N_c\lambda Fr)^2/4\sin\theta$. Zachariasen (1967) gives $x(\mathrm{Zach}) = 3(N_c\lambda Fr)^2/2\sin 2\theta$. He has taken $T = t_\perp/\cos\theta$, $t_\perp = \frac{3}{2}r$ where $t_\perp$ is the thickness of the crystal perpendicular to the incident beam. When this is done the quantity x of this paper contains the factor $1/\sin 2\theta$.

(*c*) *The mosaic block*

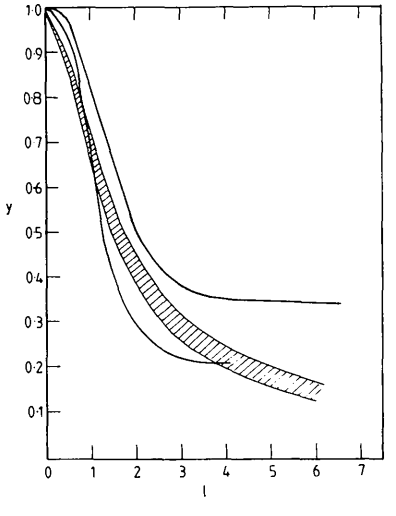
The mosaic block, in the form of a square-section parallelepiped, has been examined by Olekhnovich

& Olekhnovich, (1978) and by Wilkins (1981). The variable used by both authors is, in neutron units, $N_c\lambda F l_0$ where l_0 is the block side. This variable will be denoted by l. The starting points for both sets of authors are the equations of the dynamical theory.

Olekhnovich & Olekhnovich (1978) give a solution for the primary-extinction factor when the Bragg angle is 45° [their Fig. 4, curve (6)]. Their result is the full curve in Fig. 2(*a*).



(*a*)



(*b*)

Fig. 2. (*a*) The single curve is the result for the square-section parallelepiped at a Bragg angle of 45° obtained by Olekhnovich & Olekhnovich (1978). The hatched region spans the Bragg (upper) and Laue (lower) solutions for the *AA* crystal given in this paper. (*b*) The lower curve is the result for the square-section parallelepiped with a Bragg angle of 20° obtained by Olekhnovich & Olekhnovich (1978). The hatched region spans the Bragg (upper) and Laue (lower) solutions for the *AA* crystal given in this paper. The upper curve is the result given by Wilkins (1981) for a mosaic block.

At $\theta = 45°$ the *AA* crystal is a square-section parallelepiped. The hatched region in Fig. 2(*a*) corresponds to the range of values given by (6), (11), (16) of this paper. The upper boundary is the Bragg case; the lower boundary is the Laue case. The variable l is the square root of the x for the *AA* crystal used in this work.

Wilkins (1981) gives a result only for a Bragg angle of 20°. In Fig. 2(*b*) his extinction factor [his Fig. 14(*b*)] is compared with the value obtained by Olekhnovich & Olekhnovich (1978) [their Fig. 4, curve (3)].

Again the hatched region is bounded by the Laue and Bragg solutions of this paper. Wilkins (1981) finds empirically that the substitution $T = t_0 \sin\theta$, which is exact for the *AA* crystal, is a good approximation for the mosaic block.

Werner (1974) suggested that the solution to the *AA* crystal may be a good approximation for real crystals. The results of the present investigation indicates that this is the case.

8. Secondary extinction in finite crystals

According to § 2 the secondary-extinction factor must also approach proportionality to the reciprocal of a quantity with the dimensions of length. It can be seen from the list of extinction factors [(6)-(15)] that when G, which is dimensionless, is substituted for T only the Gaussian, rectangular and triangular functional representations of σ satisfy this criterion.

It is not clear if the variable x for secondary extinction in finite crystals should include the factor $\sin 2\theta$ which is the basic difference between the formulae of Becker & Coppens (1974) and Zachariasen (1967). For primary extinction it occurs naturally in the treatment of the *AA* crystal, and appears to be necessary for the general mosaic block.

Hamilton (1957), Werner (1974), and this paper use $x = Q_\theta GD$ while Becker & Coppens (1974) use $x = Q_\theta GD \sin 2\theta$.

9. The angular dependence of extinction

It is essential that any expression for the extinction factor which is to be incorporated in a crystal structure refinement code must allow for the dependence of extinction on scattering angle.

Hamilton (1957) and Becker & Coppens (1974) give tables of computer solutions to this problem. Zachariasen (1967) and Sabine (1985) used the Bragg-case solution for all values of 2θ. Werner (1974) suggested that the appropriate solution should be the arithmetic mean of the two cases.

In this work the angular variation is given by the average

$$y(2\theta) = y_L \cos^2\theta + y_B \sin^2\theta. \qquad (17)$$

10. The theories of Hamilton and Becker & Coppens

While the theories of Hamilton (1957, 1963) and of Becker & Coppens (1974) appear to give very different values of the extinction factor it is not difficult to show, using the results of this paper, that their solutions to the transfer equations are closely similar.

(*a*) *Hamilton*

Hamilton has used a rectangular functional form for σ and has calculated the extinction factor for a cylinder. His variable σD is the same as $Q_\theta GD$ of this paper. To convert x for the *AA* crystal to a value appropriate to a cylinder x is multiplied by $3\pi/8$ since the average path length through a cylinder of diameter D is $8D/3\pi$. Application of (17) to the values of y_L^R and y_B^R given by (9) and (14) for the converted x gives the full line of Fig. 3(*a*).

(*b*) *Becker & Coppens*

Inspection of the formulae given by Becker & Coppens (1974) shows that x of their Table 1 is identical to x for the *AA* crystal; however, their extinction factor extrapolates as $(2x)^{-1/2}$. To compare with the present work the x of Becker & Coppens must be taken as one-half the x of this paper. When this is done the application of (17) to y_L^L and y_B^L found from (6), (16) and (11) gives the full line of Fig. 3(*b*).

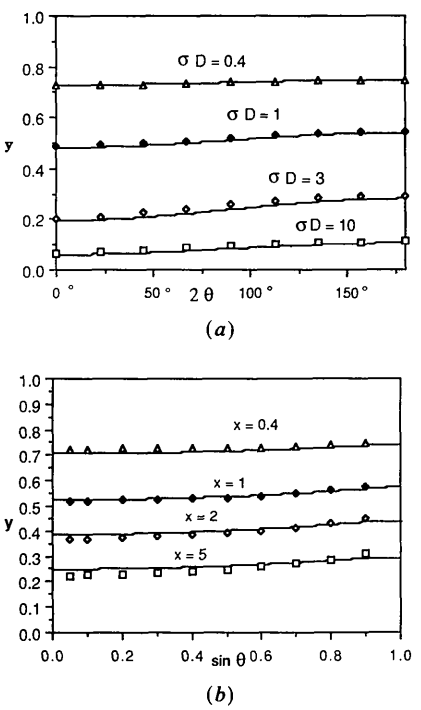


Fig. 3. (*a*) The points are taken from Table 1 of Hamilton (1963) for secondary extinction in a cylinder. The full lines are the predictions of the present work. (*b*) The points are taken from Table 1 of Becker & Coppens (1974) for primary extinction in a sphere. The full lines are the predictions of the present work.

11. Experimental verification

The conclusions of this work concerning primary extinction have been verified to a level of $y = 0{\cdot}6$ by Sabine (1985) using neutron powder data from specimens of MgO of controlled grain size. A conventional diffractometer was used at a single wavelength.

Sabine, Von Dreele & Jørgensen (1988) have used time-of-flight methods on similar specimens of MgO to compare experimental and calculated primary-extinction factors to a level $y = 0{\cdot}3$.

12. Concluding remarks

For very general reasons the extinction factor, whether primary or secondary, must allow the integrated intensity to increase at a rate not less than the rate at which the area of the entrance surface increases with crystal size.

The primary-extinction factor may be calculated using as a starting point the Darwin energy-transfer equations. With the choice of a Lorentzian functional representation for the coupling coefficient these equations provide numerical values which are satisfactory for use in crystal structure refinement.

A suitable analytical form of the extinction factor at an arbitrary scattering angle 2θ is given by

$$y(2\theta) = y_L \cos^2\theta + y_B \sin^2\theta.$$

The extinction factors at $2\theta = 0$ and $2\theta = \pi$ are y_L and y_B respectively.

I am indebted to Dr D. G. Blair for providing limiting solutions to the series representations of extinction factors.

References

BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* A**30**, 129-147.

BORIE, B. (1982). *Acta Cryst.* A**38**, 248-252.

DARWIN, C. G. (1922). *Philos. Mag.* **43**, 800-829.

FERMI, E., STURM, W. J. & SACHS, R. G. (1947). *Phys. Rev.* **71**, 589-594.

HAMILTON, W. C. (1957). *Acta Cryst.* **10**, 629-634.

HAMILTON, W. C. (1963). *Acta Cryst.* **16**, 609-611.

KATO, N. (1976). *Acta Cryst.* A**32**, 453-457, 458-466.

KATO, N. (1979). *Acta Cryst.* A**35**, 9-16.

KATO, N. (1980). *Acta Cryst.* A**36**, 171-177.

MARSHALL, W. & LOVESEY, S. W. (1971). *Theory of Thermal Neutron Scattering.* Oxford: Clarendon Press.

OLEKHNOVICH, N. M. & OLEKHNOVICH, A. I. (1978). *Acta Cryst.* A**34**, 321-326.

OLEKHNOVICH, N. M. & OLEKHNOVICH, A. I. (1980). *Acta Cryst.* A**36**, 22-27.

SABINE, T. M. (1985). *Aust. J. Phys.* **38**, 507-518.

SABINE, T. M., VON DREELE, R. B. & JØRGENSEN, J.-E. (1988). *Acta Cryst.* A**44**, 374-379.

WERNER, S. A. (1974). *J. Appl. Phys.* **45**, 3246-3254.

WILKINS, S. W. (1981). *Philos. Trans. R. Soc. London*, **299**, 275-317.

WILSON, A. J. C. (1949). *X-ray Optics.* London: Methuen.

ZACHARIASEN, W. H. (1945). *Theory of X-ray Diffraction in Crystals.* New York: Wiley.

ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558-564.

Acta Cryst. (1988). A44, 374-379

Extinction in Time-of-Flight Neutron Powder Diffractometry

BY T. M. SABINE

NSW Institute of Technology, Sydney, NSW 2007, *Australia*

R. B. VON DREELE

*LANSCE, MS H*805, *Los Alamos National Laboratory, Los Alamos, NM* 27545, *USA*

AND J.-E. JØRGENSEN

The Studsvik Neutron Research Laboratory, S-611 *Nyköping, Sweden*

(*Received* 14 *September* 1987; *accepted* 15 *January* 1988)

Abstract

Time-of-flight data have been collected from polycrystalline specimens of magnesium oxide in which the grain size distribution is known. These data were obtained at scattering angles of 150, 90 and 60°. A primary extinction factor given in an analytical form by Sabine [*Acta Cryst.* (1988), A44, 368-373] is included in a Rietveld program. The experimental data from the two high-angle histograms are refined to give an effective mosaic block size and overall temperature factors. The effective mosaic block size is used in the calculation of an extinction factor for each reflection. This factor is then compared with the ratio of measured integrated intensities. The theoretical form of the extinction factor is verified to a level of 0·30. The temperature factors measured from each specimen are identical and in agreement with the best literature value.

1. Introduction

A well known problem in the analysis of time-of-flight (TOF) data by the Rietveld method (Rietveld, 1969) has been an inability to extract consistent temperature factors, when analyses are made of data on the same specimen taken over different ranges in TOF. In most cases the temperature factors from the complete data set are low and in some cases negative. As the upper TOF bound of the data is made shorter the values of the apparent temperature factor rise.

This problem is caused by primary extinction within each perfect crystal block in the powder. In a brittle material the block size may be equal to the grain size; in a ductile material the block size may be orders of magnitude smaller than the grain size and may coincide with the sub-grain size.

Extinction is dependent on both wavelength and scattering angle. However, the large range of wavelengths used in TOF experiments makes the problem more obvious. In both techniques the measured temperature factors have lower values than the true temperature factors.

A factor which can be used to correct integrated intensities for the effect of primary extinction has been derived by Sabine (1985, 1988). The first experimental tests of the validity of that factor were carried out by neutron measurements on polycrystalline specimens of magnesium oxide using a constant wavelength.

An attempt was made to arrange the experiment so that there were no disposable parameters. The only crystallographic parameters for MgO are the Debye-Waller factors for each atom. Values found for these have been reviewed in detail by Barron (1977).

The shape of the grains and the grain size distribution in each specimen were determined by scanning electron microscopy. An untested assumption was that each grain was a perfect crystal.

In the present experiment time-of-flight methods are used on the same specimens to provide a more stringent test of the theory. TOF measurements have the advantage of a larger range of $(\sin\theta)/\lambda$, and a direct method of scaling data collected from specimens of different mass.

Four sets of TOF data are analysed by the Rietveld computer program of Larson & Von Dreele (1986) to give an overall temperature factor and an average mosaic block size. The block size is compared with direct measurements of the extinction factors and the temperature factor is compared with literature values.

2. Magnesium oxide

Magnesium oxide has the rock salt structure. The space group is O_h^5-$Fm\bar{3}m$ (No. 225); a = 4·21145 (3) Å (Howard & Sabine, 1974). The Mg and O atoms are located at 0, 0, 0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$, respectively. The only crystallographic parameters are the temperature factors for each atom. Since the material is cubic these are isotropic.

0108-7673/88/030374-06$03.00