

## Absorption and Secondary Extinction

BY F. R. THORNLEY

Department of Applied Physics, University of Strathclyde, 107 Rottenrow, Glasgow G4 0NG, Scotland

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### Abstract

A comparison is made of the treatments of absorption in the theories of secondary extinction by Werner [*J. Appl. Phys.* (1974), **45**, 3246–3254] and by Becker & Coppens [*Acta Cryst.* (1974), **A30**, 129–147]. The Werner approach treats absorption and extinction together, whereas Becker & Coppens assume a prior correction for absorption, and make an approximate allowance for the effect of absorption on the extinction by modifying the parameter representing the effective crystal dimension. By consideration of the form of the corrections for a specially simple crystal shape, it is shown that the Becker & Coppens method predicts slightly greater extinction than does the unified treatment of Werner. However, the difference is small, and likely to be unimportant in practice. The Werner solution of the Hamilton–Zachariasen transfer equations is exact, but not easy to use. The Becker & Coppens results are approximate, but they are presented in a form convenient for computation.

### Introduction

A recent paper by Borie (1982) compares two approaches to the solution of the equations describing energy interchange between incident and diffracted beams – those of Becker & Coppens (1974) and of Werner (1974). The general form of solution derived was the same. Becker & Coppens (1974) provided practical expressions for general use in crystallographic investigations. Numerical approximations to the solutions for spherical non-absorbing crystals were given. Separate corrections for absorption and extinction were assumed, with a modified form of extinction correction for absorbing crystals. Werner (1974) gave the general solution, treating absorption and extinction together, in the form of an infinite series, with numerical coefficients dependent upon the boundary conditions at the crystal surface. Attention was drawn by Borie (1982) to certain consequences of the different treatments of absorption by these authors. The purpose of the present paper is to argue that these two approaches are closer in practice than was suggested by Borie (1982), who was critical of the approximations made by Becker & Coppens.

It is assumed to be appropriate to use the energy-transfer equations

$$\begin{aligned}\frac{\partial I_0}{\partial x} &= -(\sigma + \mu)I_0 + \sigma I \\ \frac{\partial I}{\partial y} &= -(\sigma + \mu)I + \sigma I_0,\end{aligned}\tag{1}$$

where  $I_0$ ,  $I$  are the intensities of the incident and scattered beams within the crystal,  $\sigma$ ,  $\mu$  are scattering and absorption coefficients and  $x$ ,  $y$  indicate coordinates along the incident and scattered beam directions. These are the traditional energy-transfer equations of extinction theory, developed by Hamilton (1957) from the original treatment of Darwin (1922). Very similar equations are used in the well-known and much criticized paper by Zachariasen (1967), with the variables  $x$  and  $y$  replaced by path lengths within the crystal along the incident and scattered beam directions. Following Kato (1980), equations (1) will be referred to as the DHZ equations.

The scattering coefficient  $\sigma$  is the cross section per unit volume of crystal for unit incident intensity. In the normal plane-wave treatment,  $\sigma = \sigma(\varepsilon)$  is a function of  $\varepsilon$ , the angle of misorientation of the incident wave from the exact Bragg position. It is assumed that the effective value of  $\sigma(\varepsilon)$  is the same throughout the crystal. The physical interpretation of the effective value of the parameter  $\sigma$  in an imperfect crystal has been discussed by Becker (1977*a*) and by Kato (1980, and references therein).

Borie (1982) also uses a dimensionless coordinate system with length scale  $(1/\mu)$  and  $u = \mu x$ ,  $v = \mu y$  and  $g = \sigma/\mu$ . Equations (1) then become

$$\begin{aligned}\frac{\partial I_0}{\partial u} &= -(1 + g)I_0 + gI \\ \frac{\partial I}{\partial v} &= -(1 + g)I + gI_0.\end{aligned}\tag{2}$$

The power of the diffracted beam  $P(\varepsilon)$  was written by Zachariasen (1967) and by Becker & Coppens (1974) as

$$P(\varepsilon) = JV\sigma\phi(\sigma),\tag{3}$$

where a convex sample crystal of volume  $V$  is bathed in a beam of uniform intensity  $J$ . The kinematical diffracted power  $P_k(\varepsilon) = JV\sigma$ : this is the definition of the cross section  $\sigma$ . The deviation from kinematical behaviour is expressed by the extinction correction function  $\varphi(\sigma)$ . The expression for this correction function follows from a transformation of the DHZ equations (1) to integral form. [The similarity of treatment up to this point may be seen by comparing § II.B of Werner (1974) with Appendix A of Becker & Coppens (1974).]

The extinction factor  $\gamma$  deduced from the DHZ equations (1), in the absence of absorption,  $\mu = 0$ , was given by Zachariassen (1967) and by Becker & Coppens (1974) in the form

$$\begin{aligned} \gamma &= \int P(\varepsilon) d\varepsilon / \int P_k(\varepsilon) d\varepsilon \\ &= \int \sigma\varphi(\sigma) d\varepsilon / \int \sigma d\varepsilon \\ &= \frac{1}{Q} \int \sigma\varphi(\sigma) d\varepsilon, \end{aligned} \quad (4)$$

where  $Q$  is the average cross section per unit volume of crystal. The corresponding correction function  $\varphi(\sigma, \mu)$  for extinction and absorption may be written, from equations (49), (B5), (B6) of Becker & Coppens (1974), as

$$\begin{aligned} \varphi(\sigma, \mu) &= \frac{1}{V} \int_V dV \exp[-(\sigma + \mu)(t_1 + t'_2)] \sum_{n=0}^{\infty} \frac{(\sigma^2 t_1 t'_2)^n}{(n!)^2} \\ &= \sum_{n=0}^{\infty} \varphi_n(\sigma, \mu). \end{aligned} \quad (5)$$

The  $n$ th term in the series corresponds to the contribution of the  $(2n + 1)$ -times Bragg-reflected radiation to the diffracted beam. The diffracted power is equal to  $J\sigma V\varphi(\sigma, \mu)$ .  $t_1$  and  $t'_2$  are path lengths within the crystal,  $t_1$  from the surface to the volume element  $dV$  along the incident-beam direction ( $x$  or  $u$ ), and  $t'_2$  from the volume element  $dV$  to the surface along the diffracted-beam direction ( $y$  or  $v$ ).

This paper will consider the solution represented by (4) and (5) for a specially simple crystal shape. It will be shown that the approximate treatment of absorption by Becker & Coppens (1974) predicts slightly greater extinction than does the unified treatment of Werner (1974). However, the difference is small.

### Parallelepiped crystal

The simple case that was considered by Borie (1982), following Zachariassen (1967) and Werner (1974), was a crystal whose cross section has edges parallel to the directions of incidence and diffraction, as shown in Fig. 1. The crystal has sides  $A, B, C$  along the  $u, v, w$  axes ( $a, b, c$  along  $x, y, z$  axes with  $A = \mu a$  and so on), and a volume  $V = ABC \sin 2\theta$ . The boundary conditions are

uniform incident intensity  $I_0(0, v) = J$  and zero diffracted intensity at  $v = 0$ ,  $I(u, 0) = 0$ . (It should be borne in mind that this rather artificial shape conceals the important angle dependence of secondary extinction.)

For this special shape of crystal, the volume integration in (5) separates; the result is

$$\varphi_n(g) = \left( \frac{g}{1+g} \right)^{2n} \frac{H_n[(1+g)A]}{(1+g)A} \frac{H_n[(1+g)B]}{(1+g)B} \quad (6)$$

in the notation of Borie (1982). The  $H_n$  function was introduced by Werner (1974) as notation for a normalized incomplete  $\gamma$  function  $\gamma(n, x)$ :

$$\begin{aligned} H_n(x) &= \frac{\gamma(n+1, x)}{\Gamma(n+1)} = \frac{1}{n!} \int_0^x Z^n \exp(-Z) dZ \\ &= 1 - \exp(-x) \left( 1 + x + \frac{x^2}{2!} + \dots + \frac{x^n}{n!} \right) \\ &= \sum_{r=n+1}^{\infty} P_r(x), \end{aligned} \quad (7)$$

where

$$P_r(x) = \frac{x^r \exp(-x)}{r!} \quad (8)$$

is the Poisson distribution with parameter  $x$ .

Comparison of (6) with equation (33) of Werner (1974) confirms the identity of his treatment and that of Becker & Coppens (1974) for this special case, where the DHZ equations can be solved exactly. This particular example provides an opportunity for a direct comparison of the approaches to absorption, since

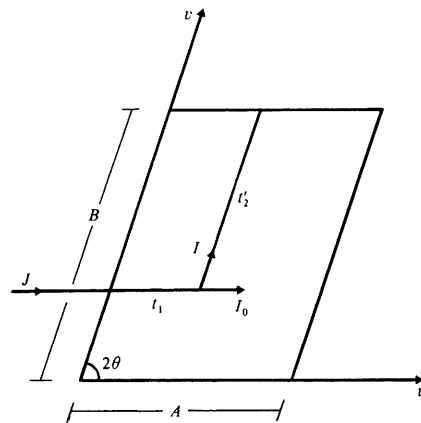


Fig. 1. A crystal cut in the form of a rectangular parallelepiped, with edges of lengths  $A, B$  parallel to the incident and diffracted beams. The third edge, of length  $C$ , is normal to the plane of the figure. Dimensions are in units of  $1/\mu$ , where  $\mu$  is the absorption coefficient. Energy transfer between the incident beam  $I_0$  and the diffracted beam  $I$  at the point  $(u, v)$  within the crystal is described by the DHZ equations (2).

there is no additional complication of different methods of approximate solution of the DHZ equations.

Two simplifications will be made in the comparison of the approaches to absorption. Firstly, it will be assumed that  $\sigma = \sigma(\epsilon)$  has a constant value across the diffracting range, with angular width  $W$ , rather than the common empirical forms of a Gaussian or a Lorentzian: thus  $Q = \int \sigma d\epsilon = \sigma W$ . The value of  $W$  is determined either by domain size (type II extinction) or misorientation (type I extinction). The effect of this assumption is that the integral (4), for an absorbing crystal, takes the form

$$y = \sum_{n=0}^{\infty} \varphi_n(g). \quad (9a)$$

Secondly, the crystal will be assumed to be a rhombus in cross section,  $A = B$ . Then (6) becomes

$$\varphi_n(g) = \left( \frac{g}{1+g} \right)^{2n} \left( \frac{H_n(x)}{x} \right)^2 \quad (9b)$$

with  $x = (1+g)A$ . In the absence of absorption,  $g/(1+g) = \sigma/(\mu + \sigma) = 1$ , so the first term in (9b) is equal to unity, and  $x = gA$ .

The two restrictions are made to simplify the analysis. If they are relaxed, the general conclusions are unaltered. To introduce the comparison of the method of Werner with that of Becker & Coppens, the behaviour of the solution represented by (9) will be discussed, initially for a non-absorbing crystal.

#### Properties of extinction expression (9)

The series (9a) is a sum of diminishing terms since, from (7),

$$H_{n+1}(x) = H_n(x) - P_{n+1}(x).$$

The series is convergent for all finite  $x$ ; from the integral definition of  $H_n(x)$  in (7) it may be seen that

$$\sum_{n=0}^{\infty} H_n(x) = x$$

or

$$\sum_{n=0}^{\infty} \left( \frac{H_n(x)}{x} \right) = 1. \quad (10)$$

All of these  $H_n(x)$  are positive [again from (7) – for example, the definition as an integral contains an integrand which is always positive], thus all of the terms in (10) must be less than unity. Hence the sum of the squares of these terms

$$y = \sum_{n=0}^{\infty} \left( \frac{H_n(x)}{x} \right)^2 \quad (11)$$

must be less than unity, as is required for an extinction function. The kinematical result  $y(0) = 1$  is obtained since

$$\lim_{x \rightarrow 0} \left( \frac{H_n(x)}{x} \right) = \delta_{0n}.$$

The rate of convergence of the series (11) with  $n$  follows from the definition (7). As  $r$  increases, the Poissonian distribution  $P_r(x)$  tends to a Gaussian with mean and variance equal to  $x$ . Thus for  $n > x$ , the terms in the series (7) for  $H_n(x)$  are falling off rapidly with  $n$ . This is indicated in Fig. 2, which shows the variation of the partial sum

$$\sum_{n=0}^{n_{\max}} \left( \frac{H_n(x)}{x} \right)^2,$$

with  $n_{\max}$  for  $x = 4, 8, 12$ . It is clear from Fig. 2 that the terms in (11) with  $n > x + 1$ , say, contribute little to the final answer.

Differentiating (11) with respect to  $x$  gives the result

$$\frac{dy}{dx} = \sum_{n=0}^{\infty} \frac{2H_n(x)[xP_n(x) - H_n(x)]}{x^3},$$

which may be rearranged to give

$$\frac{dy}{dx} = - \sum_{n=0}^{\infty} \frac{2P_n(x)H_{n+1}(x)}{x^2}. \quad (12)$$

This expression is a sum of negative terms, hence  $dy/dx$  is always negative, and  $y(x)$  is a monotone

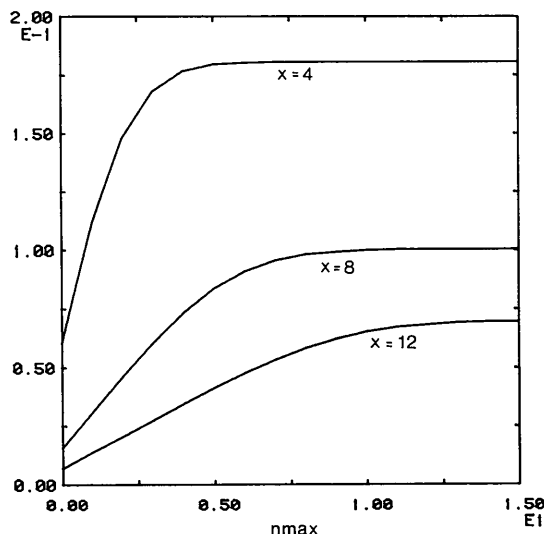


Fig. 2. Variation of the partial sum  $\sum_{n=0}^{n_{\max}} [H_n(x)/x]^2$  with  $n_{\max}$ , where  $H_n(x)$  is defined by (7) and calculations have been made for  $x = 4, 8, 12$ . The sum has been evaluated for  $n_{\max}$  from 0 to 15: the individual values are joined by straight-line segments.

decreasing function of  $x$ ; this is again what would be expected of an extinction function.

If the restriction to absorption-free crystals is relaxed, then the convergence of (9) will be more rapid, since the weighting factor  $[g/(1+g)]^{2n}$  applied to the  $n$ th term in the series is less than (equal to) unity for  $n > 0$  ( $n = 0$ ). The restriction to a crystal with  $A = B$  is for simplicity in the expressions given in this section. The general conclusions would be unaltered for a parallelogram, with convergence at a rate intermediate between that for a rhombus of side  $A$  and one of side  $B$ .

For small values of  $x$ , the ( $n = 0$ ) term dominates in (9) for the extinction correction. For example, the contribution made by the ( $n = 1$ ) terms is less than 1% for  $x < 0.2$  and less than 5% for  $x < 0.49$ . In the following comparison of the different treatments of absorption, it will be assumed that the  $n = 0$  term (single Bragg reflection) is the only significant one. This is done to simplify the analysis. At the end of this section of the paper it will be argued that the conclusions are valid for the full series (9).

The  $n = 0$  expression has, from (7) and (9), the simple form

$$\varphi_0(g) = L[(1+g)A] L[(1+g)B], \quad (13)$$

where the  $L$  function is defined to be

$$L(x) = \frac{H_0(x)}{x} = \frac{1 - \exp(-x)}{x}. \quad (14)$$

#### Method of Werner (1974)

Using the notation  $y(g)$  for (4) with  $\varphi(\sigma)$  replaced by  $\varphi(\sigma, \mu)$ , with the above approximations, we have

$$\begin{aligned} y(g) &= L[(1+g)A] L[(1+g)B] \\ &= \frac{\{1 - \exp[-(1+g)A]\} \{1 - \exp[-(1+g)B]\}}{(1+g)^2 AB}. \end{aligned} \quad (15)$$

This expression includes attenuation due both to absorption and to extinction: it is the first term in the series called the 'AB-extinction' formulation by Werner (1974).

The attenuation produced by absorption alone is the transmission factor, denoted here by  $M$  since  $A$  is being used for a crystal dimension. In the notation of (5),

$$M = \varphi_0(0, \mu) = \frac{1}{V} \int_V \exp[-\mu(t_1 + t_2')] dV = L(A) L(B). \quad (16)$$

In order to make a comparison with the method of Becker & Coppens (1974), it is helpful to consider the

attenuation produced by extinction alone; from (15) and (16) this is

$$y_w = \frac{y(g)}{M} = \left\{ \frac{L[(1+g)A]}{L(A)} \right\} \left\{ \frac{L[(1+g)B]}{L(B)} \right\} = y_w^A y_w^B. \quad (17)$$

It is sufficient, here and below, to consider the extinction functions dependent upon the dimension  $A$  along the incident beam direction. The series expansion of the function in (17), for extinction only, is

$$\begin{aligned} y_w^A &= \frac{L[(1+g)A]}{L(A)} \\ &= 1 - \frac{gA}{2} + \frac{(g+2g^2)A^2}{12} - \frac{(g^2+g^3)A^3}{24} + \dots \end{aligned} \quad (18)$$

#### Method of Becker & Coppens (1974)

The integral (4) for extinction alone is evaluated. It is assumed that corrections for absorption have already been applied. The extinction correction will be dependent upon the mean path lengths through the crystal for the incident and diffracted beams. Allowance for absorption, which from (5) is actually entirely correlated with extinction effects, is made by replacing the path lengths by absorption-weighted path lengths.

For the crystal being considered, the expression for extinction in the absence of absorption is, from (4) and (6),

$$\begin{aligned} y_{BC} &= \frac{[1 - \exp(-gA)][1 - \exp(-gB)]}{ABg^2} \\ &= L(gA) L(gB) \end{aligned} \quad (19)$$

and the function  $L(gA)$  has the series expansion

$$L(gA) = 1 - \frac{gA}{2} + \frac{g^2 A^2}{6} - \frac{g^3 A^3}{24} + \dots \quad (20)$$

Expression (19) may be obtained directly from (17) by taking the limit of (17) as the absorption coefficient  $\mu$  goes to zero. This follows because the arguments of the  $L$  functions in (18) are  $(1+g)A = (\mu + \sigma)a$  and  $A = \mu a$ , which become  $\sigma a$  and 1 as  $\mu$  goes to zero. It is convenient to write  $\sigma a$  as  $gA$  even for the limit of negligible absorption. The results (18) and (20) look more like normal secondary-extinction expressions on recalling  $gA = \sigma a = Qa/W$ ; the extinction depends upon  $Q$  for the reflection, the crystal dimension and the reflection width.

An improved approximation to (18) may be obtained with an expression in which the parameter representing the effective crystal dimension is modified to make

allowance for absorption. The simplest absorption-weighted mean path length is

$$\bar{i} = \int_V (t_1 + t_2) \exp[-\mu(t_1 + t_2)] dV \times \left\{ \int_V \exp[-\mu(t_1 + t_2)] dV \right\}^{-1}. \quad (21)$$

From (16),

$$\bar{i} = -\frac{1}{M} \frac{dM}{d\mu} = -\frac{1}{L(A)} \frac{dL(A)}{d\mu} - \frac{1}{L(B)} \frac{dL(B)}{d\mu},$$

which gives, in dimensionless units,

$$\bar{T} = \mu \bar{i} = T(A) + T(B),$$

where

$$T(A) = 1 - A/[\exp(A) - 1] = \frac{A}{2} - \frac{A^2}{12} + \frac{A^4}{720} + \dots \quad (22)$$

The function  $T(A)$  is the absorption-weighted mean path length for the incident beam [and similarly  $T(B)$  for the diffracted beam]. For small absorption,  $A \ll 1$ , and  $T(A) \simeq A/2$ : it is to be expected that the mean path length should be half the crystal dimension in the direction of the incident beam. Expression (19) describes extinction when absorption is negligible. We may allow for absorption in (19) by replacing  $A$  by  $2T(A)$  and  $B$  by  $2T(B)$ . The series expansion for the function

$$L[2gT(A)] = \{1 - \exp[-2gT(A)]\}/2gT(A)$$

is, from (19) and (22),

$$L[2gT(A)] = 1 - \frac{gA}{2} + \frac{(g + 2g^2)A^2}{12} - \frac{g^2 A^3}{18} - \frac{g^3 A^3}{24} + \dots \quad (23)$$

#### Argument of Borie (1982)

It will be shown that the expressions given by Borie (1982) for the intensities within the crystal may be developed to give (17) and (19). For the unified treatment of extinction and absorption, the intensity  $I(u, v)$  of the diffracted beam in the kinematical limit is

$$I(u, v) = Jg[1 - \exp(-v)] \exp(-u), \quad (24)$$

where  $[1 - \exp(-v)]$  represents the build up of a diffracted beam in the  $v$  direction, and  $\exp(-u)$  represents the effect on the diffracted beam of the attenuation of the incident beam by absorption.

The kinematical diffracted power  $P_k$  for an absorbing

crystal is obtained by integrating  $I(u, B)$  across the surface of the crystal  $v = B$ , giving

$$P_k = C \sin 2\theta \int_0^A I(u, B) du = JVgL(A)L(B). \quad (25)$$

The angular factor appears because the diffracted beam is not emerging normal to the crystal face. Borie (1982) also gives the exact solution of Werner (1974), which involves an infinite sum over modified Bessel functions of the first kind  $\mathcal{Y}_p(z)$  of integer order  $p$  with argument  $z = 2\sigma(xy)^{1/2} = 2g(uv)^{1/2}$ . For small  $z$ , these Bessel functions may be replaced by  $(z/2)^p/p!$ , which is the first term in their series expansion

$$\mathcal{Y}_p(z) = (z/2)^p {}_0F_1[p + 1; (z/2)^2]/p! \quad (26)$$

(Sneddon, 1961). This approximation assumes that only the singly Bragg-reflected radiation contributes to the diffracted beam – it is equivalent to taking just the  $n = 0$  term in (5). And successive terms in the expansion of the hypergeometric series in (26) represent the  $(2n + 1)$ -times-Bragg-reflected beams. However, there is no simple physical interpretation of the order  $p$  of the Bessel function. The coefficients multiplying these Bessel functions are determined by the boundary conditions for the incident and diffracted beams at the surface of the crystal (see Werner, 1974; Becker, 1977b, 1983).

The resulting approximate form given by Borie (1982) is

$$I(u, v) = J \frac{g}{1 + g} \{1 - \exp[-(1 + g)v]\} \times \exp[-(1 + g)u]. \quad (27)$$

The corresponding diffracted power is

$$P = JVgL[(1 + g)A]L[(1 + g)B]. \quad (28)$$

The ratio of (28) and (25) gives an expression for extinction alone which is in agreement with (17). Expression (19) for extinction in the absence of absorption may be obtained from (28) and (25) as previously, in the limit as  $\mu$  goes to zero.

#### Comparison of methods

The result (18) from the Werner (1974) method will be compared with the Becker & Coppens (1974) expressions (20) and (23). From the series expansions we have

$$Y_w^A - L(gA) = \frac{gA^2}{12} - \frac{g^2 A^3}{24} + \dots \quad (29)$$

$$Y_w^A - L[2gT(A)] = \frac{g^2 A^3}{72} + \dots \quad (30)$$

These expressions suggest that use of the absorption-weighted path length  $T(A)$  does indeed give an improved approximation to the unified result of Werner (1974), and that the Becker & Coppens (1974) treatment predicts greater extinction for a given value of  $g$ . This behaviour is confirmed by the calculations of Fig. 3, which shows the variation of (18), (20) and (23) with scaled cross section  $g$  for selected values of the crystal dimension  $A$ . All three expressions give the kinematical value of unity for  $g = 0$ . The limiting gradients at  $g = 0$  of the curves shown in Fig. 3 have the same value of  $-T(A)$  for the Werner expression (18) and for the improved Becker & Coppens expression (23), and a value of  $-A/2$  for the original Becker & Coppens expression (20). Since  $T(A) < A/2$  for all  $A > 0$ , the uncorrected expression (20) will have a steeper initial gradient, as shown in Fig. 3. As  $g$  increases, both of the Becker & Coppens curves lie below the corresponding Werner curve, but the absorption-weighted expression (23) is much closer, especially for smaller values of  $A$ ; equation (30) shows that this difference depends upon  $A^3$ .

These comparisons have included only the  $n = 0$  term in (9). Similar conclusions, on the accuracy of the Becker & Coppens approach, may be obtained by inspection of the higher terms. For example, the expression corresponding, for  $n = 1$ , to the  $n = 0$  Werner extinction function  $y_w^A$ , equation (18), is, from (6) and (17),

$$\left(\frac{g}{1+g}\right)\left(\frac{H_1(x)}{x}\right)/L(A), \quad (31)$$

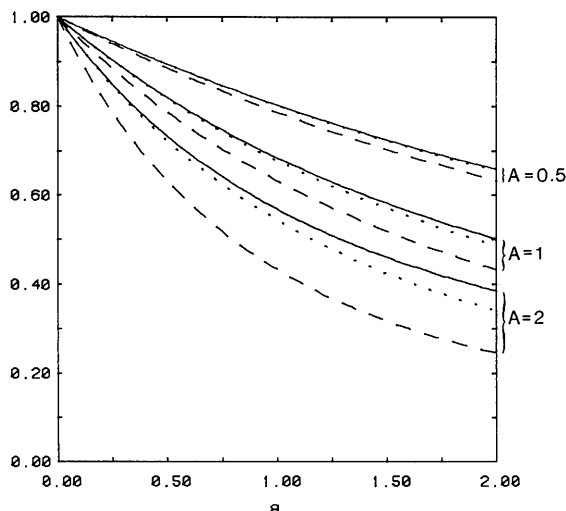


Fig. 3. Variation of the extinction functions with scaled cross section  $g = \sigma/\mu$  for crystal dimensions  $A = 0.5, 1.0, 2.0$ . The curves shown are the Werner function  $y_w^A$ , equation (18) (solid lines), the Becker & Coppens function  $L(gA)$ , equation (20) (dashed lines), and the Becker & Coppens function with absorption-weighted path lengths  $L[2gT(A)]$ , equation (23) (dotted lines). For small  $g$ , the solid and dotted lines almost coincide.

where  $x = (1 + g)A$ . The series expansion of (31) is

$$\frac{gA}{2} \left[ 1 - \frac{(1 + 4g)A}{6} + \frac{(2 + 3g)gA^2}{12} + \dots \right]. \quad (32)$$

The uncorrected Becker & Coppens expression corresponding to (31) is  $H_1(x)/x$  with  $x = gA$ ; this has series expansion

$$\frac{gA}{2} \left[ 1 - \frac{2gA}{3} + \frac{g^2 A^2}{4} + \dots \right]. \quad (33)$$

Allowance for an absorption-weighted path length  $T(A)$ , given by (22), may be made as before by taking  $x = 2gT(A)$ . The resulting corrected form of (33) is

$$\frac{gA}{2} \left[ 1 - \frac{(1 + 4g)A}{6} + \frac{(8 + 9g)gA^2}{36} + \dots \right]. \quad (34)$$

So equations (32), (33), (34) for  $n = 1$  correspond to (18), (20), (23) respectively for  $n = 0$ . Just as for the  $n = 0$  case, the Becker & Coppens result (34) with an absorption-weighted path length is a close approximation to the Werner expression (32).

The accuracy of the Becker & Coppens approximation to the overall extinction factor  $y$ , (9), is indicated by the calculations, shown in Fig. 4, of the variation of  $y$  with scaled cross section  $g$  for a crystal with  $A = B = 2.0$ . Terms in (9) with  $n$  up to 5 were included, *i.e.* contributions from 1-, 3-, ..., 11-times

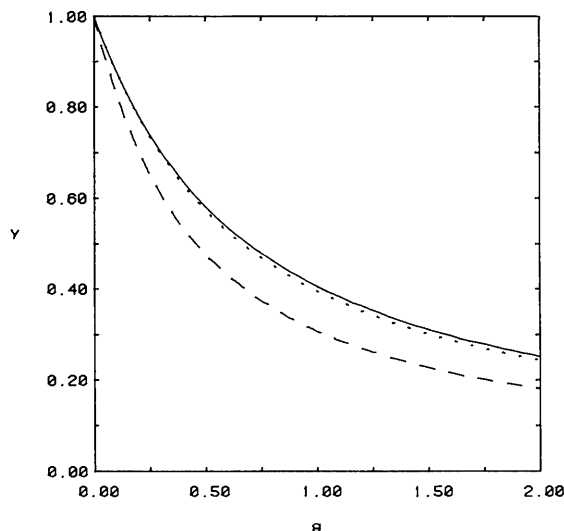


Fig. 4. Variation of the extinction factor  $y$  with scaled cross section  $g = \sigma/\mu$  for a crystal with dimensions  $A = B = 2.0$ . The curves shown are the Werner expression (9) for extinction and absorption, with  $x = (1 + g)A$ , divided by the absorption expression (16) (solid line), the Becker & Coppens expression (9) for extinction, with  $x = gA$  (dashed line), and the Becker & Coppens expression (9) for extinction with absorption-weighted path lengths,  $x = 2gT(A)$  (dotted line). For small  $g$ , the solid and dotted lines almost coincide. Terms in the sum (9) were included up to  $n = 5$ ; contributions for  $n > 5$  were negligible (less than 0.001).

Bragg-reflected radiation. As in Fig. 3, the solid line indicates the Werner solution and the dashed (dotted) lines indicate the uncorrected (absorption-weighted) Becker & Coppens results.

### Discussion

It has been argued that, for the simple crystal shape considered in the previous section, the approximate treatment of absorption by Becker & Coppens (1974) predicts greater extinction than does the exact solution of Werner (1974), but only slightly greater. This result is likely to be true for other crystal shapes also, since absorption will always act to reduce the effective crystal dimension for secondary extinction.

A number of criticisms of the Zachariasen (1967) and Becker & Coppens (1974) approaches have been made by Borie (1982). How may these be reconciled with the present conclusions?

(i) In describing the Zachariasen treatment, Borie (1982) quotes the equation

$$I = I' \exp[-(u + v)] \quad (35)$$

relating the diffracted intensities  $I$  and  $I'$  for absorbing and for non-absorbing crystals respectively, with a similar equation for the incident beam. It is then pointed out that these equations fail in general, as is clear on comparing (27) for  $I(u, v)$  with its limit

$$I'(u, v) = J \exp(-gu) [1 - \exp(-gv)] \quad (36)$$

as  $\mu$  goes to zero. However, the result (36) is nowhere used by Becker & Coppens (1974), who develop their treatment of absorbing crystals from a general result, given in the present paper as (5), which for the special parallelepiped crystal of the previous section leads to the same exact expression as that given by Werner (1974).

(ii) Approximations are made by Becker & Coppens (1974) in their solution of the DHZ equations for a spherical crystal. But the Werner (1974) solution, though exact, is not easy to use. This is not so much due to the presence of an infinite series of modified Bessel functions (26) as to the difficulty of determining the coefficients multiplying these Bessel functions for each reflection. The successive approximations of Becker & Coppens (1974) are directed towards obtaining expressions for extinction-containing parameters which may be estimated in a least-squares refinement, with path-length information provided by a prior absorption correction.

(iii) Both Werner (1974) and Borie (1982) criticize the factoring out of a separate absorption correction, and state that it is only valid when  $\mu \gg \sigma$ , i.e. when  $g \ll 1$ . From (29) and (30) this is correct, but the limit is the kinematic value, which is unhelpful. The cal-

culations of Figs. 3 and 4 are intended to show that in practice this approximate factoring out works well.

A numerical example may be given. The crystal will be assumed to be a rhombus in cross section, with the same dimensions as for Fig. 4. Thus  $A = B = 2.0$ ; extinction is most severe when  $g = 2.0$ , the largest value used. The values obtained for the sum (9) are 0.251, 0.180 and 0.243, for the Werner, uncorrected Becker & Coppens and absorption-weighted Becker & Coppens expressions respectively. For somewhat less severe extinction,  $g = 1.0$ , the corresponding values are 0.405, 0.307, 0.395. It is clear that the Becker & Coppens approach is working well here. The small difference between the solid and dotted curves of Fig. 4 is likely to be accommodated in practice by slight adjustment of the extinction parameter determined by a least-squares fitting procedure.

For investigations of crystal structures, where the objective is to make a reliable correction for extinction, Becker & Coppens (1974) provide convenient empirical expressions. That their correction works well has been shown by a number of experimental investigations, for example that of Hutton, Nelmes & Scheel (1981) on  $\text{SrTiO}_3$ , where it was possible to correct for severe extinction (more than half the reflections had  $y < 0.7$ ; about 10% of the reflections had  $y < 0.2$ ), and then obtain thermal parameters in good agreement with values obtained independently by lattice-dynamical calculations. The circumstances in which it is appropriate to use the Becker & Coppens (1974) or similar corrections have been reviewed by Becker (1977a). The other conditions which should be satisfied – for example that the domain dimension is not larger than the extinction distance, that the effective cross section is uniform throughout the crystal, and that the extinction is correctly characterized as type I or type II – are likely to be a more severe limitation on the accuracy of an extinction correction than is the treatment of absorption.

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