

Toward a Secondary-Extinction Correction*

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Abstract

The treatment of secondary extinction currently in general use by crystallographers is due to Becker & Coppens [*Acta Cryst.* (1974), A30, 129–147]. It is derived from approximate solutions to the Darwin transfer equations developed by Zachariasen [*Acta Cryst.* (1967), 23, 558–564]. Among the approximations invoked by Zachariasen is that the effects of scattering and absorption are to be treated separately. A scheme is here proposed which makes that unnecessary. It is further suggested that progress in the correction of experimental data for secondary-extinction effects is more likely if one begins with the exact solution to the transfer equations due to Werner [*J. Appl. Phys.* (1974), 45, 3246–3254]. That solution has so far not penetrated the diffraction literature, probably because it is in the form of a difficult infinite series of Bessel functions. In one special case, which nevertheless has attracted the general attention of those interested in this subject, it is shown that the Werner series may be summed, yielding an integral equation involving only the zero-order Bessel function. Excellent closed-form approximations to this integral, accurate to about 1% or less, are displayed.

Introduction

The treatment proposed by Becker & Coppens (1974) for secondary-extinction corrections to diffraction data sets is now in general use by crystallographers. It is derived from an approximate theory due to Zachariasen (1967). This theory presumes that the phenomenon of secondary extinction is governed by the Darwin transfer equations:

$$\left. \begin{aligned} \frac{\partial I_0}{\partial x} &= -(\sigma + \mu) I_0 + \sigma I \\ \frac{\partial I}{\partial y} &= -(\sigma + \mu) I + \sigma I_0. \end{aligned} \right\} \quad (1)$$

The incident and diffracted intensities, I_0 and I , are functions of position within the crystal which is specified by the variables x and y in the directions of the incident and diffracted beams. The coupling parameter σ is the diffracted power per unit volume per unit incident intensity and μ is the linear absorption coefficient.

An aspect of the Zachariasen treatment is that only solutions I'_0 and I' to the transfer equations for which μ is zero are considered. The resultant simplified intensity distributions, dependent only on σ , are modified by an absorption correction dependent only on μ to arrive at a secondary-extinction correction:

$$\left. \begin{aligned} I_0 &= I'_0 \exp[-\mu(x + y)] \\ I &= I' \exp[-\mu(x + y)]. \end{aligned} \right\} \quad (2)$$

This procedure, of correcting separately for extinction and absorption, is preserved in the Becker & Coppens treatment. Though equations (2) appear formally to satisfy (1), in general upon application of boundary conditions appropriate for a specific crystal shape, they fail. That is, I and I' differ by more than the exponential factor of equations (2). In addition to this simplification, only an approximate solution to the absorption-free transfer equations is used in the treatment of Becker & Coppens.

To emphasize and clarify the interrelation of absorption and extinction, it is useful to scale the linear dimensions of the crystal by μ . The intensity distributions within the crystal may now be considered functions of the dimensionless variables $u = \mu x$ and $v = \mu y$. In terms of a single secondary-extinction parameter $\gamma = \sigma/\mu$ (also dimensionless) equations (1) become

$$\left. \begin{aligned} \frac{\partial I_0}{\partial u} &= -(1 + \gamma) I_0 + \gamma I \\ \frac{\partial I}{\partial v} &= -(1 + \gamma) I + \gamma I_0. \end{aligned} \right\} \quad (3)$$

A rigorous general solution to equations (1) or (3) due to Werner (1974) exists:

$$\begin{aligned} I_0(u, v) &= \exp[-(1 + \gamma)(u + v)] \sum_{p=-\infty}^{+\infty} a_p \left(\frac{u}{v}\right)^{p/2} \\ &\quad \times \mathcal{F}_p(2\gamma\sqrt{uv}) \end{aligned} \quad (4a)$$

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$$I(u,v) = \exp[-(1 + \gamma)(u + v)] \sum_{p=-\infty}^{+\infty} a_{p+1} \left(\frac{u}{v}\right)^{p/2} \times \mathcal{J}_p(2\gamma\sqrt{uv}). \quad (4b)$$

Here \mathcal{J}_p is a modified Bessel function of the first kind of order p . Note that its argument, $2\gamma\sqrt{uv} = 2\sigma\sqrt{xy}$, is independent of μ . In order that the Zachariassen assumption, equations (2), hold, it would be necessary that the integration constants a_p , to be found from boundary conditions, also be independent of μ . In general they are not.

A boundary condition to find the a_p 's is that along some crystal face, say $u = k^2 v$, that is bathed by an incident beam of unit intensity, $I_0(k^2 v, v) = 1$. Then from (4a)

$$\exp[(1 + \gamma)(k^2 + 1)v] = \sum_{p=-\infty}^{+\infty} a_p k^p \mathcal{J}_p(2\gamma kv)$$

or

$$\exp[(\sigma + \mu)(k^2 + 1)y] = \sum_{p=-\infty}^{+\infty} a_p k^p \mathcal{J}_p(2\sigma ky). \quad (5)$$

Relations among the a_p are found by expanding the transcendental functions of (5) as power series and equating the coefficients of like powers of y . Clearly such relations must contain the linear absorption coefficient.

To the writer's knowledge, the Werner solution remains excluded from the crystallographer's array of tools for the reduction of integrated intensity measurements to structure factors, perhaps because it is in the form of a cumbersome infinite series of Bessel functions. It is the purpose of this contribution to consider ways to redress that deficiency. It will be shown that in certain simple cases the series of equations (4) may be summed, providing simple expressions in closed form for I_0 and I .

A crystal whose boundaries are parallel to the directions of incidence and diffraction

A special simple case that has interested Zachariassen, Werner, and Becker & Coppens is illustrated in Fig. 1. The crystal cross section is a parallelogram whose edges are parallel to the directions of incidence and diffraction. Then the appropriate boundary conditions to find the integration constants of (4) are that

$$\left. \begin{aligned} I_0(0,v) &= 1 \\ I(u,0) &= 0. \end{aligned} \right\} \quad (6)$$

Werner has shown them to be $a_p = 0$ for $p > 0$; $a_{-p} = [(1 + \gamma)/\gamma]^p$ for $p \geq 0$, so that equation (4b) becomes

$$I(u,v) = \exp[-(1 + \gamma)(u + v)] \sum_{p=1}^{\infty} \left(\frac{1 + \gamma}{\gamma}\right)^{p-1} \left(\frac{v}{u}\right)^{p/2} \times \mathcal{J}_p(2\gamma\sqrt{uv}). \quad (7)$$

If μ were set to zero in equations (1), their solution found, the boundary conditions of equations (6) applied, and then modified as in equation (2), there results

$$I(u,v) = \exp[-(1 + \gamma)(u + v)] \sum_{p=1}^{\infty} \left(\frac{v}{u}\right)^{p/2} \mathcal{J}_p(2\gamma\sqrt{uv}). \quad (8)$$

Equation (7) is the exact solution to the transfer equations for our simple crystal, equation (8) the Zachariassen result.

In the kinematic limit all coupling between the incident and diffracted beams is ignored. In that case the intensity distribution within the crystal is readily found. It is

$$I(u,v) = \gamma(1 - \exp[-v]) \exp[-u].$$

If $\mathcal{J}_p(z)$ in (7) is replaced by $(\frac{1}{2}z)^p/p!$, its limit for z small, the series is readily summed giving

$$I(u,v) = \frac{\gamma}{1 + \gamma} \{1 - \exp[-(1 + \gamma)v]\} \exp[-(1 + \gamma)u]$$

which reduces to the kinematic result for γ small. The Zachariassen result fails this test. Equation (8) approximates (7) only for γ large, that is, only if $\sigma \gg \mu$. The quality of the approximation is questionable.

Note that the series of both (7) and (8) are of the form $\sum_{p=1}^{\infty} \beta^p \mathcal{J}_p(z)$. Following a treatment quoted by Watson (1922) we show that this series may be summed.

Let

$$S(z) = \mathcal{J}_0(z) + 2 \sum_{p=1}^{\infty} \beta^p \mathcal{J}_p(z).$$

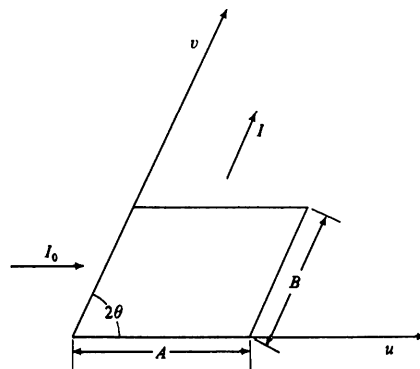


Fig. 1. A crystal whose cross section has edges parallel to the directions of incidence and diffraction.

Then

$$\frac{dS}{dz} = \mathcal{J}_1(z) + \sum_{p=1}^{\infty} \beta^p [\mathcal{J}_{p-1}(z) + \mathcal{J}_{p+1}(z)],$$

or

$$\frac{dS}{dz} = (\beta + 1/\beta) \sum_{p=1}^{\infty} \beta^p \mathcal{J}_p(z) + \beta \mathcal{J}_0(z),$$

or

$$\frac{dS}{dz} = \frac{1}{2}(\beta + 1/\beta) S + \frac{1}{2}(\beta - 1/\beta) \mathcal{J}_0(z).$$

With $S(0) = 1$, the solution to this differential equation is

$$S = \exp\left[\frac{1}{2}z(\beta + 1/\beta)\right] + \frac{1}{2}(\beta - 1/\beta) \exp\left[\frac{1}{2}z(\beta + 1/\beta)\right] \times \int_0^z \exp\left[-\frac{1}{2}z(\beta + 1/\beta)\right] \mathcal{J}_0(z) dz.$$

So

$$\begin{aligned} \sum_{p=1}^{\infty} \beta^p \mathcal{J}_p(z) &= \frac{1}{2} \{ \exp\left[\frac{1}{2}z(\beta + 1/\beta)\right] + \frac{1}{2}(\beta - 1/\beta) \\ &\quad \times \exp\left[\frac{1}{2}z(\beta + 1/\beta)\right] \\ &\quad \times \int_0^z \exp\left[-\frac{1}{2}z(\beta + 1/\beta)\right] \mathcal{J}_0(z) dz \\ &\quad - \mathcal{J}_0(z) \}. \end{aligned} \quad (9)$$

To evaluate the integral of (9) and clear it of the zero-order Bessel function, we make use of two approximate representations:

$$\text{For } z < 2, \mathcal{J}_0(z) \simeq 1 + \left(\frac{1}{2}z\right)^2 + \frac{1}{4}\left(\frac{1}{2}z\right)^4. \quad (10)$$

$$\text{For } z > 2, \mathcal{J}_0(z) \simeq \left\{ 1 + \frac{1}{8z} + \frac{9}{128z^2} \right\} \frac{\exp[z]}{\sqrt{2\pi z}}. \quad (11)$$

Each of these approximations improves the more z differs from two. Each is worst for its range of use at $z = 2$. We have from the tables $\mathcal{J}_0(2) = 2.2796$, while expression (10) gives 2.2500 and from (11), 2.2513. At $z = 2$ each of the approximations yields an error of about 1%. Hence their use in equation (9) should result in errors significantly less than 1%.

Insertion of (10) into (9) gives, for $z < 2$,

$$\begin{aligned} \sum_{p=1}^{\infty} \beta^p \mathcal{J}_p(z) &= \left\{ \frac{\beta^5 + 5\beta^3 + 10\beta}{(\beta + 1/\beta)^5} \right\} \\ &\quad \times \{ \exp\left[\frac{1}{2}z(\beta + 1/\beta)\right] - 1 \} \\ &\quad - \left\{ \frac{\beta^3 + 4\beta - 4/\beta - 1/\beta^3}{(\beta + 1/\beta)^4} \right\} \left(\frac{z}{2} \right) \end{aligned}$$

$$\begin{aligned} & - \frac{1}{2} \left\{ \frac{2\beta^3 + 7\beta - 1/\beta}{(\beta + 1/\beta)^3} \right\} \left(\frac{z}{2} \right)^2 \\ & - \frac{1}{2} \left\{ \frac{\beta - 1/\beta}{(\beta + 1/\beta)^2} \right\} \left(\frac{z}{2} \right)^3 \\ & - \frac{1}{4} \left\{ \frac{\beta}{\beta + 1/\beta} \right\} \left(\frac{z}{2} \right)^4. \end{aligned} \quad (12)$$

From (12) we may readily find $\sum_{p=1}^{\infty} (-\beta)^p \mathcal{J}_p(z)$; it may be combined with (12) to find expressions for sums over even- and odd-order Bessel functions:

$$\begin{aligned} \sum_{p=1}^{\infty} \beta^{2p} \mathcal{J}_{2p}(z) &= \left\{ \frac{\beta^5 + 5\beta^3 + 10\beta}{(\beta + 1/\beta)^5} \right\} \\ &\quad \times \{ \cosh\left[\frac{1}{2}z(\beta + 1/\beta)\right] - 1 \} \\ &\quad - \frac{1}{2} \left\{ \frac{2\beta^3 + 7\beta - 1/\beta}{(\beta + 1/\beta)^3} \right\} \left(\frac{z}{2} \right)^2 \\ &\quad - \frac{1}{4} \left\{ \frac{\beta}{\beta + 1/\beta} \right\} \left(\frac{z}{2} \right)^4, \end{aligned} \quad (13)$$

and

$$\begin{aligned} \sum_{p=1}^{\infty} \beta^{2p-1} \mathcal{J}_{2p-1}(z) &= \left\{ \frac{\beta^5 + 5\beta^3 + 10\beta}{(\beta + 1/\beta)^5} \right\} \\ &\quad \times \sinh\left[\frac{1}{2}z(\beta + 1/\beta)\right] \\ &\quad - \left\{ \frac{\beta^3 + 4\beta - 4/\beta - 1/\beta^3}{(\beta + 1/\beta)^4} \right\} \left(\frac{z}{2} \right) \\ &\quad - \frac{1}{2} \left\{ \frac{\beta - 1/\beta}{(\beta + 1/\beta)^2} \right\} \left(\frac{z}{2} \right)^3. \end{aligned} \quad (14)$$

For $z > 2$, it is convenient to rewrite equation (9). Since

$$\begin{aligned} \int_0^z \exp[-kz] \mathcal{J}_0(z) dz &= \int_0^{\infty} \exp[-kz] \mathcal{J}_0(z) dz \\ &\quad - \int_z^{\infty} \exp[-kz] \mathcal{J}_0(z) dz \end{aligned}$$

and

$$\int_0^{\infty} \exp\left[-\frac{1}{2}z(\beta + 1/\beta)\right] \mathcal{J}_0(z) dz = \left| \frac{2}{\beta - 1/\beta} \right|$$

for $\beta > 1$, equation (9) becomes

$$\begin{aligned} \sum_{p=1}^{\infty} \beta^p \mathcal{J}_p(z) &= \frac{1}{2} \{ 2 \exp\left[\frac{1}{2}z(\beta + 1/\beta)\right] - \frac{1}{2}(\beta - 1/\beta) \\ &\quad \times \exp\left[\frac{1}{2}z(\beta + 1/\beta)\right] \\ &\quad \times \int_z^{\infty} \exp\left[-\frac{1}{2}z(\beta + 1/\beta)\right] \mathcal{J}_0(z) dz \\ &\quad - \mathcal{J}_0(z) \} \end{aligned} \quad (15)$$

and for $0 < \beta < 1$,

$$\sum_{p=1}^{\infty} \beta^p \mathcal{F}_p(z) = \frac{1}{2} \left\{ \frac{1}{2} (1/\beta - \beta) \exp[\frac{1}{2}z(\beta + 1/\beta)] \times \int_z^{\infty} \exp[-\frac{1}{2}z(\beta + 1/\beta)] \mathcal{F}_0(z) dz - \mathcal{F}_0(z) \right\}. \quad (16)$$

Insertion of approximation (11) into equation (15) gives, for $z > 2$ and $\beta > 1$,

$$\sum_{p=1}^{\infty} \beta^p \mathcal{F}_p(z) = \left\{ 1 - \frac{1}{4} \frac{(\beta + 1)}{\sqrt{\beta}} \left[1 - \frac{(\beta - 1)^2}{8\beta} + \frac{3(\beta - 1)^4}{128\beta^2} \right] \operatorname{erfc} \left[(\beta - 1) \sqrt{\frac{z}{2\beta}} \right] \right\} \times \exp[\frac{1}{2}z(\beta + 1/\beta)] - \left\{ \left[\frac{1}{2} + \frac{(\beta^2 - 1)}{16\beta} - \frac{3(\beta^2 - 1)(\beta - 1)^2}{256\beta^2} \right] + \left[\frac{1}{16} + \frac{3(\beta^2 - 1)}{256\beta} \right] \frac{1}{z} + \frac{9}{256z^2} \right\} \frac{\exp[z]}{\sqrt{2\pi z}}; \quad (17)$$

and with equations (11) and (16), one finds for $z > 2$ and $0 < \beta < 1$,

$$\sum_{p=1}^{\infty} \beta^p \mathcal{F}_p(z) = \left\{ \frac{1}{4} \frac{(\beta + 1)}{\sqrt{\beta}} \left[1 - \frac{(\beta - 1)^2}{8\beta} + \frac{3(\beta - 1)^2}{128\beta^2} \right] \operatorname{erfc} \left[(1 - \beta) \sqrt{\frac{z}{2\beta}} \right] \right\} \times \exp[\frac{1}{2}z(\beta + 1/\beta)] - \left\{ \left[\frac{1}{2} - \frac{(1 - \beta^2)}{16\beta} + \frac{3(1 - \beta^2)(1 - \beta)^2}{256\beta^2} \right] + \left[\frac{1}{16} - \frac{3(1 - \beta^2)}{256\beta} \right] \frac{1}{z} + \frac{9}{256z^2} \right\} \frac{\exp[z]}{\sqrt{2\pi z}}. \quad (18)$$

In equations (17) and (18), erfc is the complementary error function. Note that (17) and (18) reduce to a common result for $\beta = 1$.

To test the utility of the treatment described above for evaluating the Bessel-function sums of equations (7) and (8) for a crystal with the configuration of Fig. 1, we

have taken $A = B = 1$, $\gamma = \frac{1}{2}$, and we have found $I(u, 1)$ across the exit face of the crystal for the kinematic approximation, the exact solution to the transfer equations [equation (7)], and the Zachariasen result [equation (8)]. The result is shown in Fig. 2. It is evident that none of these curves is a good approximation to either of the other two. Curves B and C were both found from the sums of equations (7) and (8) and by their approximate representations from equation (12). The differences are imperceptible. The curves of Fig. 2 represent either calculation equally well.

Discussion

There are several approximations in the Zachariasen (1967) treatment of secondary extinction, some of which are propagated into the Becker & Coppens (1974) theory of that phenomenon. It is useful to quote them and comment on them. At the root of the Zachariasen theory is the assumption that absorption and extinction may be treated separately [equations (2)]. We have argued here that that is a poor approximation and not necessary. Further, both Zachariasen and Becker & Coppens use only approximate solutions to the absorption-free transfer equations. As we have pointed out, an exact solution to the general transfer equations with absorption is available. In its earliest form, it is given by Werner, Arrott, King & Kendrick (1966). A possible argument against its use is that it consists of a difficult infinite sum of Bessel functions. We have attempted to show here that at least in some cases an excellent closed-form approximation to that sum exists. Perhaps in other cases analogous closed-form representations of the Bessel-function sum can be found. Neither Zachariasen nor Becker & Coppens refer to the exact solution found by Werner *et al.*

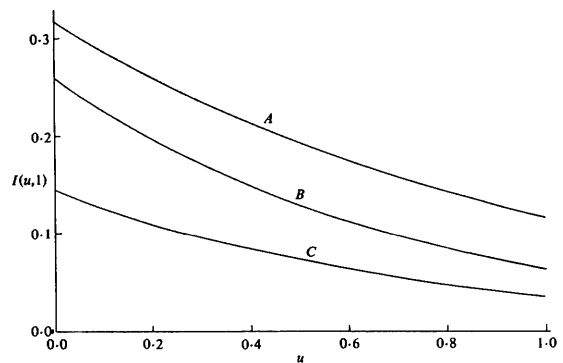


Fig. 2. The intensity across the exit face of the crystal of Fig. 1 for $A = B = 1$, $\gamma = \frac{1}{2}$. Curve A : kinematic. Curve B : the exact Werner solution. Curve C : the Zachariasen solution.

Subsequent to the approximation given by equations (2) Zachariassen appends a further approximation. It is that (2) may be written

$$I = I' \exp[-\mu(x + y)] = I' A(\mu) \quad (19)$$

[Zachariassen's (1967) equation (41)]. Here $A(\mu)$ is simply the absorption correction appropriate for the kinematic result. This approximation modifies the Zachariassen solution displayed in Fig. 2 in that the solution is normalized so that it agrees with the kinematic solution in the limit that σ is small. However, its justification is obscure. Zachariassen claims that it is appropriate unless absorption effects are large. In actuality equation (19) holds in the limit that $\mu \gg \sigma$, in which case absorption effects and scattering may be treated separately and there results the kinematic theory. Becker & Coppens develop a rather more involved treatment of the effect of absorption. However, it is evolved still within the context of their approximate solution to the transfer equations, and it appears to contain the conclusion that often the diffraction effects related to σ and μ may essentially be treated separately.

It is probably still useful to retain clearly the distinction between primary and secondary extinction. That the coupling of the incident and diffracted

amplitudes, with specific phase relations, is a phenomenon describable by solutions to the transfer equations, appropriate only for the incoherent phenomenon of secondary extinction, seems unlikely.

Experimental tests that allow the identification of observed extinction as of either the primary or secondary variety should also be useful. A description of such a test will be the subject of a subsequent contribution.

It seems to this writer that the present state of the theory of secondary extinction is primitive. The calculations described here are intended to suggest that the appropriate point of departure for further quantitative insights into this phenomenon is the exact solution to the transfer equations given by Werner.

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On the Co-existence of Structurally Different Regions in the Low-High-Quartz and Other Displacive Phase Transformations

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Dedicated to Professor Dr Heinz Jagodzinski on the occasion of his 65th birthday

Abstract

The mechanism of the low \rightleftharpoons high quartz phase transformation is discussed in terms of tilting of $[\text{SiO}_4]$ tetrahedra and formation of Dauphiné twin domains below the transformation temperature. The low-quartz domain boundaries have a finite thickness. Within the domain wall the tilt angle changes gradually from $+\varphi$ to $-\varphi$. Depending on temperature, the gradual change may be static or there may be a change of the average

value of φ due to a dynamical process. Around the center of the wall between the low-quartz domains the structure resembles that of high quartz. The co-existence of low- and high-quartz-type regions in a temperature range below the transformation temperature is a necessary consequence of the formation of coherent domains. It is concluded that analogous ranges of coexistence of low- and high-symmetry regions exist in many, if not all, displacive phase transformations in which the phases involved have