Acta Cryst. (1976). A**32**, 631

The Influence of the Primary Beam Shape on the Extinction Correction

BY J. P. URBAN*

University of the Witwatersrand, Physics Department, Johannesburg, South Africa

(*Received* 1 *September* 1975; *accepted* 3 *December* 1975)

On the basis of the solutions of Darwin's energy-transfer equations the influence of the line profile of the primary beam on the extinction of X-ray and neutron intensities has been studied. Numerical calculations for the plane parallel plate, a wedge and a spherical sample were performed. The plane parallel plate is not affected by the primary beam. For the wedge only small influences were found (up to 12%). Spherically shaped crystals were investigated with a constant, a sawtooth-shaped and a δ-function-shaped primary beam. The influence of the primary beam increases with the variable σr_0. General formulae for arbitrary shapes of crystals and primary beams are given which may be used for specific experiments.

Introduction

In order to correct X-ray and neutron intensities for extinction effects a theory based on the solutions of Darwin's energy-transfer equations was accomplished by Zachariasen (1967) and generalized by Becker & Coppens (1974, 1975). However, in both treatments the line shape of the primary beam was not taken into consideration. In their solutions of Darwin's equations the primary intensity appears only as a constant factor. As this is only true for crystals which are very small compared to the width of the primary beam and for which the intensity is constant over this range the present treatment investigates how far the line profile of the primary beam influences the results obtained with the theories by Zachariasen (1967) and Becker & Coppens (1974, 1975).

Solutions of the transfer equations

In order to solve Darwin's transfer equations, the following coordinate system $l,\tilde{l}$ is introduced (Fig. 1): Axis $\tilde{l}$ points in the direction of the primary beam while axis l points in the direction of the scattered intensity. l and $\tilde{l}$ make an angle of 2θ. The origin of the system is chosen in such a way that the maximum of the primary beam meets the crystal in the origin. The intensity field in the $\tilde{l}$ direction is called $I(l,\tilde{l})$ and the one in the l direction is called $R(l,\tilde{l})$. In order to simplify the calculations the absorption in the crystal was neglected. An intıoduction of absorption can be easily done.

* Present address: Fritz-Haber-Institut, Abt. Prof. R. Hosemann, 1 Berlin 33, Faradayweg 4–6, Germany.

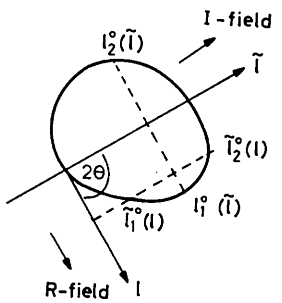

Fig. 1. Definition of the coordinate system $l,\tilde{l}$.

In this approximation the transfer equations become:

$$\frac{\partial R}{\partial l} = -\sigma(R-I) \qquad (1a)$$

$$\frac{\partial I}{\partial \tilde{l}} = -\sigma(I-R)\,. \qquad (1b)$$

σ is the diffracting cross section per unit volume and unit intensity defined by Zachariasen (1967) and Becker & Coppens (1974).

R and I can be written as a sum of multiple scattering terms:

$$R=\sum_{n=1} R_n \quad \text{and} \quad I=\sum_{n=0} I_n\,.$$

For the R field the numbers n have the following meaning: $n=1$: onefold scattering, $n=2$: threefold scattering, *etc.* For the I field the following definitions were used: $n=0$: zerofold scattering, $n=1$: twofold scattering, *etc.* Equations (1*a*) and (1*b*) can be solved by using R_n and I_n rather than the functions R and I. The following results weıe obtained:

$$R_{n+1}(l,\tilde{l})=\begin{cases}\sigma\int_{l'=l_2^\circ(\tilde{l})}^{l} I_n(l',\tilde{l})\exp[-\sigma(l-l')]\mathrm{d}l' & \text{for } l_2^\circ(\tilde{l})\le l\le l_1^\circ(\tilde{l})\\ \sigma\int_{l'=l_2^\circ(\tilde{l})}^{l_1^\circ(\tilde{l})} I_n(l',\tilde{l})\exp\{-\sigma[l_1^\circ(\tilde{l})-l']\}\mathrm{d}l' & \text{for } l_1^\circ(\tilde{l})\le l\\ 0 & \text{otherwise;}\end{cases} \qquad (2a)$$

$$I_n(l,\tilde{l})=\begin{cases}\sigma\displaystyle\int_{\tilde{l}'=\tilde{l}_1^0(l)}^{\tilde{l}} R_n(l,\tilde{l}')\exp\left[-\sigma(\tilde{l}-\tilde{l}')\right]\mathrm{d}\tilde{l}' & \\ \qquad\text{for } \tilde{l}_1^0(l)\leq\tilde{l}\leq\tilde{l}_2^0(l) & \\ \sigma\displaystyle\int_{\tilde{l}'=\tilde{l}_1^0(l)}^{\tilde{l}_2^0(l)} R_n(l,\tilde{l}')\exp\left\{-\sigma[\tilde{l}_2^0(l)-\tilde{l}']\right\}\mathrm{d}\tilde{l}' & \\ \qquad\text{for } \tilde{l}_2^0(l)\leq\tilde{l} & \\ 0 & \text{otherwise;}\end{cases} \tag{2b}$$

$$I_0(l,\tilde{l})=\begin{cases}P(l) & \text{for } \tilde{l}\leq\tilde{l}_1^0(l)\\ P(l)\exp\left\{-\sigma[\tilde{l}-\tilde{l}_1^0(l)]\right\} & \\ & \text{for } \tilde{l}_1^0(l)\leq\tilde{l}\leq\tilde{l}_2^0(l)\\ P(l)\exp\left\{-\sigma[\tilde{l}_2^0(l)-\tilde{l}_1^0(l)]\right\} & \\ & \text{for } \tilde{l}\geq\tilde{l}_2^0(l)\,.\end{cases} \tag{2c}$$

The quantities $l_1^0(\tilde{l})$, $l_2^0(\tilde{l})$, $\tilde{l}_1^0(l)$ and $\tilde{l}_2^0(l)$ are the coordinates of points on the surface of the sample as illustrated in Fig. 1. $P(l)$ is the intensity profile of the primary beam before it enters the crystal. A generalization for crystals with absorption is obvious and need not be considered here.

Obviously, equation (2) can be solved simultaneously once the shape of the crystal, *i.e.* the coordinates $\tilde{l}_1^0$, $\tilde{l}_2^0$, l_1^0 and l_2^0, is known. It can be seen that the function R must depend on the shape of the crystal and on the shape of the primary beam. In order to investigate their influence on the extinction coefficient, the function $\varphi(\sigma)$ which was introduced by Zachariasen (1967) is investigated with regard to the various shapes of crystals and the primary beam.

In order to account for the dimension of the primary beam perpendicular to $l,\tilde{l}$, a new axis z was introduced which is perpendicular to $l,\tilde{l}$.

Through the scattering power of the diffracted beam for multiple scattering

$$Q(\varepsilon_1)=\iint R[l_1^0(\tilde{l}),\tilde{l}]\mathrm{d}\tilde{l}\mathrm{d}z\sin 2\theta \tag{3a}$$

and for kinematical scattering

$$Q_k(\varepsilon_1)=\sigma\iint\int_{l=l_2^0(\tilde{l})}^{l_1^0(\tilde{l})} P(l)\mathrm{d}l\mathrm{d}\tilde{l}\mathrm{d}z\sin 2\theta$$
$$=\sigma\iint P(l)\,[\tilde{l}_2^0(l)-\tilde{l}_1^0(l)]\mathrm{d}l\mathrm{d}z\sin 2\theta, \tag{3b}$$

the function $\varphi(\sigma)$ is defined as:

$$\varphi(\sigma)=Q(\varepsilon_1)/Q_k(\varepsilon_1)\,. \tag{3c}$$

The integrations with respect to l, $\tilde{l}$ and z must be performed over the maximal dimension of the crystal. Although equations (2*a*–*c*) are general, it is not possible to give general solutions for arbitrary shapes of crystals and primary beams. The purpose of the present representation is to show how far the primary beam can affect the results obtained with a constant primary beam. Therefore only two examples will be discussed in the following: wedge-shaped crystals (including plane parallel plate), and spherically shaped crystals.

Wedge-shaped crystals (symmetrical Bragg case)

For the symmetrical Bragg case the following condition between the angles θ and α must hold: $\theta\geq\alpha$ (Fig. 2). The surface functions $\tilde{l}^0$ and l^0 become:

$$\begin{aligned}&\tilde{l}_1^0(l)=l && l_1^0(\tilde{l})=A\tilde{l}+B\\ &\tilde{l}_2^0(l)=A'l+B && l_2^0(\tilde{l})=\tilde{l}\end{aligned} \tag{4}$$

with

$$A'=1/A\quad B'=l^0\quad B=-Al_0$$

$$A=(\sin\theta+\tan\alpha\cos\theta)/(\sin\theta-\tan\alpha\cos\theta)$$
$$l\leq A\leq\infty\,.$$

For $A=1$ the case of the plane parallel plate of thickness l_0 is obtained while for $A=\infty$ the scattered beam is parallel to the far side of the wedge, *i.e.* $\theta=\alpha$. Up to second-order effects, *i.e.* threefold scattering, equations (2) have been solved:

With

$$Q_n=\iint R_n[l_1^0(\tilde{l}),\tilde{l}]\mathrm{d}\tilde{l}\sin 2\theta\mathrm{d}z$$

$$Q_1=\iint_{l=-\infty}^{B/1-A} P(l)\left\{\tfrac{1}{2}-\tfrac{1}{2}\exp\left[-2\sigma\left(\frac{1-A}{A}l-\frac{B}{A}\right)\right]\right\}\mathrm{d}l\sin 2\theta\mathrm{d}z \tag{5a}$$

and

$$Q_2=\iint_{l=-\infty}^{B/1-A} P(l)\left\{\tfrac{1}{8}+\left[\frac{\sigma}{4}l\frac{A^2-1}{A}+\frac{\sigma}{4}B\frac{A+1}{A}+\frac{A^2-1}{8}\right]\right.$$
$$\times\exp\left[-2\sigma\left(\frac{1-A}{A}l-\frac{B}{A}\right)\right]$$
$$\left.-\frac{A^2}{8}\exp\left[-2\sigma\left(\frac{1-A^2}{A^2}l-B\frac{A+1}{A^2}\right)\right]\right\}\mathrm{d}l\sin 2\theta\mathrm{d}z \tag{5b}$$

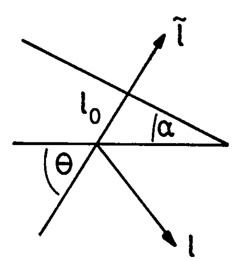

Fig. 2. Geometry of the wedge-shaped crystal.

and

$$Q_k = \iint P(l)\,[(A'-1)l+B']\mathrm{d}l \sin 2\theta \mathrm{d}z\,. \qquad (5c)$$

With $\varphi_n = Q_n/Q_k$ the following expressions for φ are obtained:

1. $P(l,z) = \begin{cases} P_0 & |l| \le c \\ 0 & \text{otherwise} \end{cases} \qquad c = l_0/(1-1/A)$

$$\varphi_1 = \frac{1}{2\sigma l_0} - \frac{1}{2\sigma l_0}\exp(-2\sigma l_0) \times \sinh\left(2\sigma\frac{1-A}{A}c\right)\Big/2\sigma\frac{1-A}{A}c$$

$$\varphi_2 = \frac{1}{8\sigma l_0} - \frac{A^2-1}{4l_0A}c\exp(-2\sigma l_0) \times \cosh\left(2\sigma\frac{1-A}{A}c\right)\Big/2\sigma\frac{1-A}{A}c + \left(-\frac{A+1}{8\sigma l_0} - \frac{A+1}{4} + \frac{A^2-1}{8\sigma l_0}\right) \times \exp\left[-2\sigma l_0\right]\sinh\left(2\sigma\frac{1-A}{A}c\right) - \frac{A^2}{8\sigma l^0}\exp\left[-2\sigma l_0(A+1)/A\right] \times \sinh\left(2\sigma\frac{1-A^2}{A^2}c\right)2\sigma\frac{1-A^2}{A^2}c\,.$$

2. $P(l,z) = P_0\delta(l)\delta(z)$

$$\varphi_1 = \frac{1-\exp(-2\sigma l_0)}{2\sigma l_0}$$

$$\varphi_2 = \frac{1}{8\sigma l_0} + \left(\frac{A^2-1}{8\sigma l_0} - \frac{A+1}{4}\right)\exp(-2\sigma l_0) - \frac{A^2}{8\sigma l_0}\exp\left[-2\sigma l_0(A+1)/A\right].$$

In order to compare the different cases, the limits $A=1$ (plane parallel plate) and $A=\infty$ were investigated.

$A=1$: plane parallel plate

The influence of the primary beam cancels, *i.e.* for all different shapes the known result of Zachariasen (1967) is obtained:

$$\varphi_1 = \frac{1-\exp(-2\sigma l_0)}{2\sigma l_0}$$

$$\varphi_2 = \frac{1}{8\sigma l_0} - \tfrac{1}{2}\exp(-2\sigma l_0) - \frac{1}{8\sigma l_0}\exp(-4\sigma l_0)$$

$$\varphi = \frac{1}{1+\sigma l_0}$$

$A=\infty$.

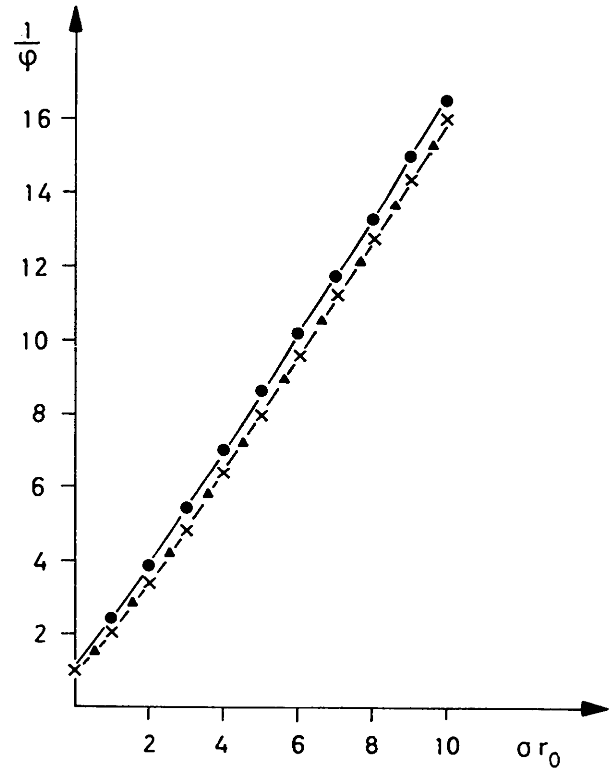

Fig. 3. $1/\varphi$ plotted as a function of σl_o for a wedge-shaped crystal. ● $A=\infty$, primary beam constant. × $A=\infty$, primary beam δ-function. ▲ $A=1$, plane parallel plate, arbitrary primary beam.

The shape of the primary beam becomes important:

(*a*) $P = \begin{cases} P_0 & |l| \le l_0 \\ 0 & \text{otherwise} \end{cases}$

$$\varphi_1 = \frac{1}{2\sigma l_0} - \frac{1}{8(\sigma l_0)^2} + \frac{1}{8(\sigma l_0)^2}\exp(-4\sigma l_0)$$

$$\varphi_2 = \frac{1}{8\sigma l_0} - \frac{3}{32(\sigma l_0)^2} + \left[\frac{1}{4\sigma l_0} + \tfrac{1}{4} + \frac{3}{32(\sigma l_0)^2}\right]\exp(-4\sigma l_0)\,.$$

(*b*) $P = P_0\delta(l)\delta(z)$

$$\varphi_1 = \frac{1}{2\sigma l_0} - \frac{1}{2\sigma l_0}\exp(-2\sigma l_0)$$

$$\varphi_2 = \frac{1}{8\sigma l_0} - \left(\tfrac{1}{4} + \frac{\sigma l_0}{4} + \frac{1}{8\sigma l_0}\right)\exp(-2\sigma l_0)\,.$$

In Fig. 3 the function $1/\varphi$ is plotted as a function of $l_0\sigma$. The deviations are not serious. They are of the order of 12% for $l_0\sigma=1$ and 2% for $l_0\sigma=10$ in the case $A=\infty$. The plane parallel plate is unaffected by the primary beam and is therefore the most simple case with respect to extinction.

Spherical crystals

The calculations for spherical crystals become rather involved. Therefore only two limiting cases have been investigated, *i.e.* $2\theta=0$ and $2\theta=\pi$. These two cases can be solved analytically and were therefore used to demonstrate the influence of the primary beam. For the two cases the coordinate system $(l,\bar{l})$ introduced above is ill-defined. Therefore, a Cartesian system has been introduced, *i.e.* (x,y,z).

x points in the direction of the primary beam and passes through the centre of the sphere. The origin of the system lies on the surface of the sphere. The following expressions for the scattered intensities are obtained:

$$R=\begin{cases} P(y,z)\,\dfrac{2\sigma(r_0^2-y^2-z^2)^{1/2}}{1+2\sigma(r_0^2-y^2-z^2)^{1/2}} \text{ for } 2\theta=\pi \\ P(y,z)\exp\left[-2\sigma(r_0^2-y^2-z^2)^{1/2}\right] \\ \times\sinh\left[2\sigma(r_0^2-y^2-z^2)^{1/2}\right] \text{ for } 2\theta=0; \end{cases}$$

r_0 is the radius of the sphere.

The shape of the primary beam has been assumed to be a sawtooth in the y direction and to be constant in the z direction in the first case, and a δ-function in the y and z directions in the second case:

$$(1) \qquad P(y,z)=P_1\left(\frac{P_0}{P_1}+1-\frac{1}{r_0}|y|\right)=P_s$$

$$(2) \qquad P(y,z)=P_0\delta(y)\delta(z)=P_\delta\,.$$

The case (1) contains the case of a constant beam if $P_1=0$. The following results for the functions φ were obtained:

$2\theta=0$

$$\varphi^0=\frac{1}{64(\sigma r_0)^3(P_0/P_1+\frac{5}{8})}\Big\{3(P_0/P_1+1)\,[8(\sigma r_0)^2 +4\sigma r_0\exp(-4\sigma r_0)-1+\exp(-4\sigma r_0)] -\frac{32}{\pi}(\sigma r_0)^2+\frac{96}{\pi}(\sigma r_0)^2\int_0^1 z(1-z^2)^{1/2} \times\exp(-4\sigma r_0 z)\mathrm{d}z\Big\} \quad \text{for } P=P_s$$

and

$$\varphi^0=\exp(-2\sigma r_0)\frac{\sinh(2\sigma r_0)}{2\sigma r_0} \quad \text{for } P=P_\delta;$$

$2\theta=\pi$

$$\varphi^\pi=\frac{1}{4(\sigma r_0)^3(P_0/P_1\times\frac{5}{8})}\Big\{3[P_0/P_1+1]\,[(\sigma r_0)^2 -\sigma r_0+\tfrac{1}{2}\ln(1+2\sigma r_0)]-\frac{24}{\pi}(\sigma r_0)^3 \times\int_0^1\frac{z^2\sqrt{1-z^2}}{1+2\sigma r_0 z}\mathrm{d}z\Big\} \quad \text{for } P=P_s$$

and

$$\varphi^\pi=\frac{1}{1+2\sigma r_0} \quad \text{for } P=P_\delta\,.$$

The results are plotted in Fig. 4.

Conclusion

It has been shown that the solutions of Darwin's energy-transfer equations must contain the shape function of the primary beam. Consequently, in an extinction theory which takes these solutions as basis this effect must be taken into account. The theory of Zachariasen (1967) and of Becker & Coppens (1974) considers only a special case, *i.e.* a constant primary beam over the whole entrance surface of the crystal, which may be sufficient for very small samples, *i.e.* very small compared to the width of the primary beam and for crystals shaped as plane parallel plates. The presentation given above accounts for this additional effect in a general form. The solutions of the transfer equations given as integral equations contain the shape of the primary beam. Obviously, the special case of Zachariasen's and Becker & Coppens's treatment is included in the present representation. In the

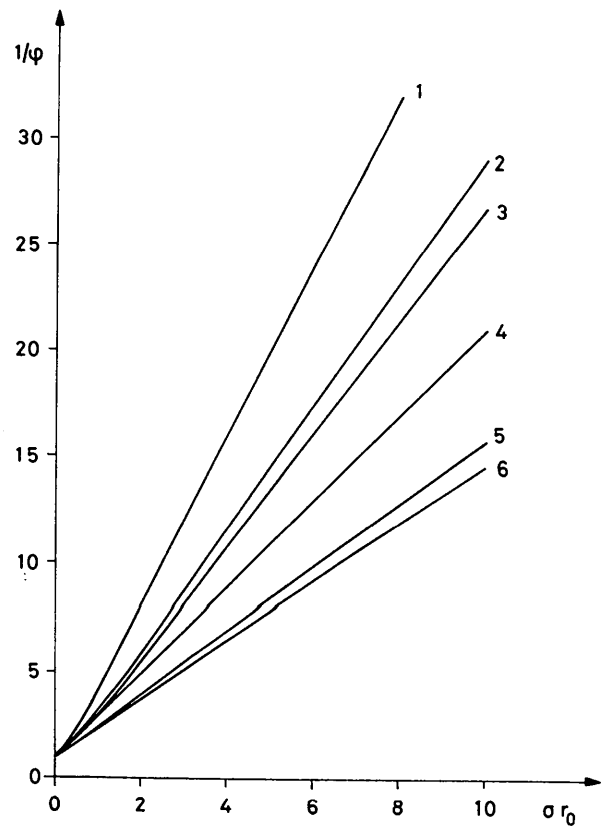

Fig. 4. Spherical crystal ($1/\varphi$ plotted against σr_0). 1: $2\theta=0$, $P=P_\delta$. 2: $2\theta=0$, $P=P_s$, $P_0/P_1=0$. 3: $2\theta=0$, $P=P_s$, $P_0/P_1=\infty$. 4: $2\theta=\pi$, $P=P_\delta$, 5: $2\theta=\pi$, $P=P_s$, $P_0/P_1=0$. 6: $2\theta=\pi$, $P=P_s$, $P_0/P_1=\infty$.

case of a wedge-shaped crystal the new correction is very small [up to 12% for the function $\varphi(\sigma)$] and is zero for the plane parallel plate. For spherical crystals the influence of the primary beam is more serious. If σr_0 becomes large compared to 1 the deviation from a crystal bathed in a constant beam increases. This case becomes important for small scattering angles and large crystals, *i.e.* when extinction effects become large. Under these circumstances, corrections for primary beam shapes might not be negligible.

In any case, before applying the uncorrected theory it is recommended that each specific experiment should be carefully in vestigated in order to establish whether a treatment for the primary beam is necessary. With the use of high-speed computers this can be done for arbitrarily shaped crystals and primary beams by using equations (2*a*–*c*).

References

BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* **A30**, 129–147.

BECKER, P. J. & COPPENS, P. (1974). *Acta Cryst.* **A30**, 148–153.

BECKER, P. J. & COPPENS, P. (1975). *Acta Cryst.* **A31**, 417–425.

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

Acta Cryst. (1976). A**32**, 635

Extinction in Neutron Diffraction

BY N. C. POPA

Institute for Atomic Physics, P.O. Box 5206, *Bucharest, Romania*

(*Received* 26 *August* 1975; *accepted* 13 *January* 1976)

This article re-analyses the extinction problem in diffraction. It has been proved that Hamilton's equations are valid only for mosaic crystals, type I. The solution of these equations has been found for any shape of crystal using general initial conditions.

Introduction

The extinction problem received considerable attention once it was found necessary to make corrections for extinction, when determining crystallographic structures. Later, the necessity of using monochromatic crystals more efficiently led to the same problem.

For an ideal crystal, the extinction factor is determined from the dynamic theory, but in practice its formula has been computed only for an infinite, plane parallel crystal plate (see Zachariasen, 1945). For a real crystal, however, Darwin's equations formulated for an infinite plane parallel plate, were generalized by Hamilton (1957) for a crystal of arbitrary shape and these were solved numerically by him. Werner & Arrott (1965) arranged Hamilton's equations into an integral form and solved them by successive approximations. This, in practice, is a tedious method which requires much calculation. But, as will be indicated below, there are regions in the crystal where it is possible to obtain a direct solution of Hamilton's equations by solving two initial-value problems. It should be mentioned that Werner, Arrott, King & Kendrick (1966) have proposed another method for solving Hamilton's equations for both finite and infinite plane parallel crystal plates. This method involves the expansion of the incident and diffracted intensities, in terms of modified Bessel functions. This method is not general because, when another crystal shape is considered, another set of functions must be found from which the expansion may be performed.

Zachariasen (1967) has suggested a general extinction theory. Several authors have carried out a number of experimental tests and no experimental agreement has been found for Zachariasen's theory for strong extinction. It has been concluded that some approximations used by Zachariasen are not valid (see Cooper & Rouse, 1970). Werner (1969) also found fault with this theory. One criticism is that Hamilton's equations do not hold good for a perfect crystal. Zachariasen wrote Hamilton's equations using variables t_1 and t_2 to represent the depths below the surface measured along the two propagation directions. But for these variables the form of the equations is not always preserved. A new term appears, which contains the derivative of the function describing the boundary. This term disappears only if the crystal takes the form of a parallelepiped whose edges are oriented in the two propagation directions. Therefore, Zachariasen's theory is valid in this case only.

Consequently, it is necessary to reconsider the extinction problem. §1 of this article is devoted to a general discussion of the transport equations for Bragg diffraction. It will be demonstrated that the Hamilton equations are valid for type I mosaic crystals only. In the §2, these equations are solved for a crystal of any shape. An application of the formulae derived in §2 is given in §3.