Theory of Neutron Diffraction in Mosaic Crystals

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It is shown that the Darwin equations, which describe the effect of multiple Bragg reflexion in mosaic crystals and have previously been obtained by heuristic arguments, arise naturally in a systematic solution of the neutron transport equation. With a method similar to that developed for calculating multiple-scattering corrections for neutron inelastic scattering in liquids, an approximate expression for the secondary extinction factor is obtained, which is applicable to a crystal of arbitrary size and shape. The results are compared with exact results for a plane slab, with Hamilton's [*Acta Cryst.* (1963), **16**, 609–611] results for a cylinder and with Becker & Coppens's [*Acta Cryst.* (1974), A**30**, 129–147] results for a sphere.

1. Introduction

The conventional theory of neutron diffraction in mosaic crystals (Bacon, 1962) is based on equations which were originally constructed by Darwin (1922) by heuristic arguments for the analogous X-ray problem. For many years only the plane-slab solutions of these equations were discussed (Darwin, 1922; Zachariasen, 1945; Lonsdale, 1947; Bacon & Lowde, 1948; Chandrasekhar, 1960; Bacon, 1962; James, 1965). However, in more recent years there has been increasing interest in finding approximate numerical and analytical solutions for other crystal shapes in order to obtain accurate secondary extinction factors for use in crystal-structure refinements (Hamilton, 1957, 1963; Zachariasen, 1963, 1965, 1967a,b; Coppens & Hamilton, 1970; Cooper & Rouse, 1970; Becker & Coppens, 1974a,b, 1975; Thornley & Nelmes, 1974; Werner, 1974).

In the present article the theory of neutron diffraction in mosaic crystals is discussed within the framework of neutron transport theory. This has two advantages over the conventional approach. Firstly, it provides a more rigorous derivation of the Darwin equations by demonstrating how these equations arise in a systematic solution of the neutron transport equation. Secondly, it shows that the transmission factors which govern the multiple Bragg reflexion in mosaic crystals are special cases of more general transmission factors which also govern multiple diffuse scattering processes in macroscopic bodies. Thus, for example, we show that the approximate theory of multiple inelastic scattering in liquids, which we have recently developed (Sears, 1975a), can also be applied to the calculation of secondary extinction corrections for Bragg reflexion in mosaic crystals.

We begin in §2 by constructing the neutron transport equation with a collision integral appropriate to a mosaic crystal. We then show how this equation can be decoupled to yield a system of homogeneous equations for the transmitted and Bragg-reflected beams, which we call the generalized Darwin equations, plus an inhomogeneous equation for the diffusely scattered neutrons. The solution of the former equations determines the transmissivity and Bragg reflectivity while the solution of the latter equation determines the double differential cross-section for diffuse scattering. In §3 we obtain general multiple scattering expansions of the transmissivity and reflectivity for the two-beam case where the generalized Darwin equations, mentioned above, reduce to the ordinary Darwin equations. The corresponding multiple-scattering expansion of the secondary extinction factor is obtained in §4. Finally, in §5, an approximate expression for the terms in the latter expansion is developed which leads to a simple, closed expression for the secondary extinction factor and is applicable to a crystal of arbitrary size and shape. The results are compared with exact results for a plane slab, with the results of Hamilton (1963) for a cylinder and with the results of Becker & Coppens (1974a) for a sphere.

2. Neutron scattering in a mosaic crystal

In this section we present a general discussion of neutron scattering in a mosaic crystal of arbitrary size and shape. We assume for simplicity that the mosaic structure is macroscopically homogeneous, though not necessarily isotropic, and that the linear dimensions of the mosaic blocks are sufficiently small that primary extinction can be neglected. In this case, the neutron distribution inside the crystal is governed by the neutron transport equation which, for steady-state conditions, assumes the form (see, for example, Sears, 1975a)

$$[\hat{\mathbf{k}}.\nabla + \Sigma(\mathbf{k})]f(\mathbf{r},\mathbf{k}) = \int d\mathbf{k}' \Gamma(\mathbf{k}',\mathbf{k}) f(\mathbf{r},\mathbf{k}'). \quad (2.1)$$

Here $f(\mathbf{r},\mathbf{k})$ is the phase-space distribution function which is defined such that $f(\mathbf{r},\mathbf{k})d\mathbf{r}d\mathbf{k}$ is the average number of neutrons in the volume element $d\mathbf{r}$ with wave vector in $d\mathbf{k}$. Also, $\hat{\mathbf{k}}$ denotes a unit vector in the direction of $\mathbf{k}$ and ∇ is the gradient operator. $\Sigma(\mathbf{k})$ is

the total collision cross-section per unit volume for a neutron with wave vector $\mathbf{k}$. Finally, $\Gamma(\mathbf{k}',\mathbf{k})$ is the transference function which governs the scattering of a neutron from $\mathbf{k}'$ to $\mathbf{k}$.

In the present context

$$\Sigma(\mathbf{k}) = \sum_{h \neq 0} \Sigma_h(\mathbf{k}) + \Sigma'(\mathbf{k}), \qquad (2.2)$$

in which the sum runs over all reciprocal-lattice points h except the origin and $\Sigma_h(\mathbf{k})$ is the cross-section per unit volume for Bragg reflexion via the reciprocal lattice vector $\mathbf{K}_h$. The residual term $\Sigma'(\mathbf{k})$ is the cross-section per unit volume for all collisions other than Bragg reflexion, i.e. absorption and diffuse scattering. The most important property of $\Sigma_h(\mathbf{k})$ is that it is appreciably different from zero only if $\mathbf{k}$ satisfies Bragg's law, i.e.

$$\Sigma_h(\mathbf{k}) \simeq 0 \quad \text{unless} \quad \mathbf{k}.\mathbf{K}_h \simeq \tfrac{1}{2}K_h^2. \qquad (2.3)$$

The transference function can likewise be expressed as

$$\Gamma(\mathbf{k}',\mathbf{k}) = \sum_{h \neq 0} \Sigma_h(\mathbf{k}')\delta(\mathbf{k}' - \mathbf{k} - \mathbf{K}_h) + \Gamma'(\mathbf{k}',\mathbf{k}), \quad (2.4)$$

in which $\Gamma'(\mathbf{k}',\mathbf{k})$ denotes the contribution from diffuse scattering.

We assume the crystal is completely bathed in a collimated, monoenergetic beam of incident neutrons each with wave vector $\mathbf{k}_0$. We want to find the corresponding solution of equation (2.1) at all points $\mathbf{r}$ inside the crystal and for all wave vectors $\mathbf{k}$. We consider a trial solution of the form

$$f(\mathbf{r},\mathbf{k}) = \sum_h n_h(\mathbf{r})\delta(\mathbf{k} - \mathbf{k}_h) + f'(\mathbf{r},\mathbf{k}), \qquad (2.5)$$

in which $n_0(\mathbf{r})$ is the neutron number density in the transmitted beam with wave vector $\mathbf{k}_0$ and, for $h \neq 0$, $n_h(\mathbf{r})$ is the neutron number density in the beam which is Bragg reflected via the reciprocal-lattice vector $\mathbf{K}_h$ and has wave vector $\mathbf{k}_h = \mathbf{k}_0 - \mathbf{K}_h$. Finally, $f'(\mathbf{r},\mathbf{k})$ is the phase-space distribution function for the diffusely scattered neutrons. The number of Bragg-reflected beams with non-vanishing number density $n_h(\mathbf{r})$ will, of course, depend on the value of the incident-neutron wave vector $\mathbf{k}_0$ as discussed below.

Substituting the trial solution (2.5) into (2.1) we find that

$$\sum_h \{[\hat{\mathbf{k}}_h.\nabla + \Sigma(\mathbf{k}_h)]n_h(\mathbf{r}) - \sum_{h'(\neq h)} \Sigma_{h-h'}(\mathbf{k}_{h'})n_{h'}(\mathbf{r})\}\delta(\mathbf{k} - \mathbf{k}_h)$$

$$+ \{[\hat{\mathbf{k}}.\nabla + \Sigma'(\mathbf{k})]f'(\mathbf{r},\mathbf{k})$$

$$- \sum_h \Gamma'(\mathbf{k}_h,\mathbf{k})n_h(\mathbf{r}) - \int d\mathbf{k}'\Gamma'(\mathbf{k}',\mathbf{k})f'(\mathbf{r},\mathbf{k}')\}$$

$$+ \sum_{h \neq 0} [\Sigma_h(\mathbf{k})f'(\mathbf{r},\mathbf{k}) - \Sigma_{-h}(\mathbf{k} - \mathbf{K}_h)f'(\mathbf{r},\mathbf{k} - \mathbf{K}_h)] = 0,$$

$$(2.6)$$

in which $h-h'$ refers to the reciprocal-lattice vector $\mathbf{K}_{h-h'} \equiv \mathbf{K}_h - \mathbf{K}_{h'}$. The third group of terms in (2.6) describes the effect of the Bragg reflexion of neutrons which have already been diffusely scattered. This group of terms is different from zero only if $\mathbf{k}$ is in the

neighbourhood of a Brillouin zone boundary and, except in special experimental arrangements, is of negligible importance in comparison with the second group of terms. In other words, there is a negligible probability that a diffusely scattered neutron has a wave vector $\mathbf{k}$ which satisfies the condition for Bragg reflexion. By neglecting the third group of terms we therefore assume that once a neutron has been diffusely scattered then any subsequent scattering collisions are also diffuse scatterings and not Bragg reflexions. In this case, diffuse scattering is equivalent to absorption as far as its effect on the attenuation of the transmitted and Bragg-reflected beams is concerned. It is for this reason that the quantity $\Sigma'(\mathbf{k})$, which is usually denoted by μ, is called the absorption coefficient even though it contains contributions from both true absorption and diffuse scattering.

Thus, after omitting the third group of terms in (2.6), it follows that this equation can hold for an arbitrary value of $\mathbf{k}$ only if

$$[\hat{\mathbf{k}}_h.\nabla + \Sigma(\mathbf{k}_h)]n_h(\mathbf{r}) = \sum_{h'(\neq h)} \Sigma_{h-h'}(\mathbf{k}_{h'})n_{h'}(\mathbf{r}), \quad (2.7)$$

and

$$[\hat{\mathbf{k}}.\nabla + \Sigma'(\mathbf{k})]f'(\mathbf{r},\mathbf{k})$$

$$= \sum_h \Gamma'(\mathbf{k}_h,\mathbf{k})n_h(\mathbf{r}) + \int d\mathbf{k}'\Gamma'(\mathbf{k}',\mathbf{k})f'(\mathbf{r},\mathbf{k}'). \quad (2.8)$$

The equations (2.7) will be called the generalized Darwin equations. These are a system of homogeneous linear equations which can be solved, subject to the boundary conditions given below, to determine the neutron number densities, $n_h(\mathbf{r})$, in the transmitted and Bragg-reflected beams. (2.8) is an inhomogeneous linear equation for the phase-space distribution function of the diffusely scattered neutrons. The inhomogeneous term in (2.8) is determined by the solution of (2.7) and its presence indicates that the transmitted and Bragg-reflected beams are each a source of diffuse scattering.

In what follows, we shall assume that the shape of the crystal is such that its surface is nowhere concave. This restriction is convenient to avoid the possibility that a neutron re-enter the crystal after passing out through the surface. Let $L(\mathbf{r},\hat{\mathbf{k}})$ denote the distance from an arbitrary point $\mathbf{r}$ inside the crystal to the surface in the direction $-\hat{\mathbf{k}}$ as illustrated in Fig. 1. Since the surface
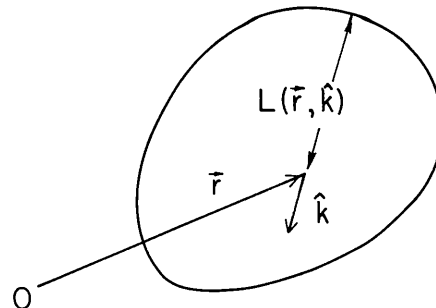

Fig. 1. The quantity $L(\mathbf{r},\hat{\mathbf{k}})$.

is nowhere concave, the only neutrons which can enter the crystal from outside are the incident neutrons. Thus (2.7) must be solved subject to the boundary conditions

$$n_h[\mathbf{r} - L(\mathbf{r}, \hat{\mathbf{k}}_h)\hat{\mathbf{k}}_h] = \delta_{h0} n, \qquad (2.9)$$

in which δ_{h0} denotes the Kronecker delta and n the incident-neutron number density. The boundary condition for (2.8) is

$$f'[\mathbf{r} - L(\mathbf{r}, \hat{\mathbf{k}})\hat{\mathbf{k}}, \mathbf{k}] = 0. \qquad (2.10)$$

Let $\Lambda_\mathbf{k}$ denote the following linear integral operator:

$$\Lambda_\mathbf{k}[g(\mathbf{r})] \equiv \int_0^{L(\mathbf{r}, \hat{\mathbf{k}})} \mathrm{d}\xi \exp[-\Sigma(\mathbf{k})\xi] g(\mathbf{r} - \xi\hat{\mathbf{k}}), \quad (2.11)$$

in which $g(\mathbf{r})$ is an arbitrary function of $\mathbf{r}$, and let $\Lambda'_\mathbf{k}$ denote the corresponding operator when $\Sigma(\mathbf{k})$ is replaced by $\Sigma'(\mathbf{k})$. Then one can easily verify that the system of differential equations (2.7) and the boundary conditions (2.9) are together equivalent to the following system of integral equations:

$$n_h(\mathbf{r}) = \delta_{h0} n \exp[-\Sigma(\mathbf{k}_h) L(\mathbf{r}, \hat{\mathbf{k}}_h)]$$
$$+ \sum_{h'(\neq h)} \Sigma_{h-h'}(\mathbf{k}_{h'}) \Lambda_{\mathbf{k}_h}[n_{h'}(\mathbf{r})]. \quad (2.12)$$

Similarly, the inhomogeneous integro-differential equation (2.8) and the boundary condition (2.10) are together equivalent to the following inhomogeneous Fredholm equation (cf. Sears 1975a):

$$f'(\mathbf{r}, \mathbf{k}) = \sum_h \Gamma'(\mathbf{k}_h, \mathbf{k}) \Lambda'_\mathbf{k}[n_h(\mathbf{r})]$$
$$+ \int \mathrm{d}\mathbf{k}' \Gamma'(\mathbf{k}', \mathbf{k}) \Lambda'_\mathbf{k}[f'(\mathbf{r}, \mathbf{k}')]. \quad (2.13)$$

The quantities in which we are primarily interested are the transmissivity, $T(\mathbf{k}_0)$, which is defined as the fraction of incident neutrons which are transmitted by the crystal when the incident-neutron wave vector is $\mathbf{k}_0$, and the reflectivity, $R_h(\mathbf{k}_0)$, which is defined as the fraction of incident neutrons which are Bragg reflected via $\mathbf{K}_h$ when the incident-neutron wave vector is $\mathbf{k}_0$. Equivalently, $T(\mathbf{k}_0)$ is the ratio of the transmitted current to the incident current and $R_h(\mathbf{k}_0)$ the ratio of the reflected current to the incident current. The transmissivity is given by

$$T(\mathbf{k}_0) = \frac{1}{nA(\hat{\mathbf{k}}_0)} \int_{S(\hat{\mathbf{k}}_0)} \mathrm{d}S \hat{\mathbf{e}} \cdot \hat{\mathbf{k}}_0 n_0(\mathbf{r}), \qquad (2.14)$$

in which $\mathrm{d}S$ denotes an element of area at a point $\mathbf{r}$ on the surface of the crystal, $\hat{\mathbf{e}}$ is a unit vector in the direction of the outward normal to the surface at that point and $S(\hat{\mathbf{k}}_0)$ is that part of the surface of the crystal which is visible from the direction $\hat{\mathbf{k}}_0$. Since the surface is nowhere concave $S(\hat{\mathbf{k}}_0)$ is, more precisely, the subset of surface points $\mathbf{r}$ for which $\hat{\mathbf{e}} \cdot \hat{\mathbf{k}}_0 > 0$. Finally, $A(\hat{\mathbf{k}}_0)$ is the cross-sectional area of the crystal perpendicular to the direction $\hat{\mathbf{k}}_0$,

$$A(\hat{\mathbf{k}}_0) = \int_{S(\hat{\mathbf{k}}_0)} \mathrm{d}S \hat{\mathbf{e}} \cdot \hat{\mathbf{k}}_0. \qquad (2.15)$$

Similarly, the reflectivity is given for $h \neq 0$ by

$$R_h(\mathbf{k}_0) = \frac{1}{nA(\hat{\mathbf{k}}_0)} \int_{S(\hat{\mathbf{k}}_h)} \mathrm{d}S \hat{\mathbf{e}} \cdot \hat{\mathbf{k}}_h n_h(\mathbf{r}). \qquad (2.16)$$

The basic problem is to solve the generalized Darwin equations (2.7) or the equivalent integral equations (2.12) to determine $n_h(\mathbf{r})$ and, hence, to compute the transmissivity (2.14) and the reflectivity (2.16). The solution of the generalized Darwin equations can also be used in (2.8) to determine $f'(\mathbf{r}, \mathbf{k})$ and, hence, the double differential cross section for diffuse scattering (Sears, 1975a).

As in the dynamical theory of neutron diffraction in a perfect crystal, the solution of the generalized Darwin equations for a mosaic crystal depends on the number of reciprocal-lattice points which lie on or near the surface of the Ewald sphere corresponding to $\mathbf{k}_0$. For the m-beam case, in which there are m such points, it follows with the help of (2.3) that (2.7) and (2.12) each reduce to a system of m coupled equations for the transmitted beam and the $m-1$ Bragg-reflected beams. Thus, in the one-beam case, in which there are no Bragg-reflected beams, $n_0(\mathbf{r})$ is simply attenuated exponentially by absorption and diffuse scattering inside the crystal. In the two-beam case (2.7) reduces to the familiar Darwin equations (Darwin, 1922) for the transmitted beam and the single Bragg-reflected beam. For $m \geq 3$ the generalized Darwin equations provide a basis for the discussion of parasitic reflexions and the Renninger effect in mosaic crystals. The three-beam case has been discussed by Moon & Shull (1964) for the special case of a plane slab. In the remainder of the present article we shall confine our attention to the two-beam case.

3. The two-beam case

Suppose the incident-neutron wave vector $\mathbf{k}_0$ satisfies the condition for Bragg reflexion via one particular reciprocal-lattice vector $\mathbf{K}_h$. In this case (2.7) reduces to the ordinary Darwin equations (Darwin, 1922),

$$[\hat{\mathbf{k}}_0 \cdot \nabla + \Sigma(\mathbf{k}_0)] n_0(\mathbf{r}) = \Sigma_{-h}(\mathbf{k}_h) n_h(\mathbf{r}),$$
$$[\hat{\mathbf{k}}_h \cdot \nabla + \Sigma(\mathbf{k}_h)] n_h(\mathbf{r}) = \Sigma_h(\mathbf{k}_0) n_0(\mathbf{r}), \qquad (3.1)$$

in which

$$\Sigma(\mathbf{k}_0) = \Sigma_h(\mathbf{k}_0) + \Sigma'(\mathbf{k}_0),$$
$$\Sigma(\mathbf{k}_h) = \Sigma_{-h}(\mathbf{k}_h) + \Sigma'(\mathbf{k}_h), \qquad (3.2)$$

and $n_{h'}(\mathbf{r}) = 0$ if $h' \neq 0, h$. The corresponding integral equations (2.12) become

$$n_0(\mathbf{r}) = n \exp[-\Sigma(\mathbf{k}_0) L(\mathbf{r}, \hat{\mathbf{k}}_0)] + \Sigma_{-h}(\mathbf{k}_h) \Lambda_{\mathbf{k}_0}[n_h(\mathbf{r})],$$
$$n_h(\mathbf{r}) = \Sigma_h(\mathbf{k}_0) \Lambda_{\mathbf{k}_h}[n_0(\mathbf{r})]. \qquad (3.3)$$

In what follows we shall adopt the abbreviated notation

$$T = T(\mathbf{k}_0), \qquad R = R_h(\mathbf{k}_0),$$
$$\Sigma_h = \Sigma_h(\mathbf{k}_0), \qquad \Sigma_{-h} = \Sigma_{-h}(\mathbf{k}_h), \qquad (3.4)$$
$$\Lambda_0 = \Lambda_{\mathbf{k}_0}, \qquad \Lambda_h = \Lambda_{\mathbf{k}_h}.$$

The coupled equations (3.3) can then be combined to give

$$n_0(\mathbf{r}) = n \exp\left[-\Sigma(\mathbf{k}_0)L(\mathbf{r}, \hat{\mathbf{k}}_0)\right] + \Sigma_{-h}\Sigma_h\Lambda_0\Lambda_h[n_0(\mathbf{r})]. \tag{3.5}$$

Similar integral equations have been obtained by other authors (Werner & Arrott, 1965; Werner, 1974; Becker & Coppens, 1974a). Apart from differences in notation, the main difference between the present work and that of the above authors is in the approximations used to evaluate the terms in the iterated solution of (3.5). The iterated solution of this equation gives the multiple-scattering expansion

$$n_0(\mathbf{r}) = \sum_{j=0}^{\infty} n_0^{(2j)}(\mathbf{r}), \tag{3.6}$$

in which $n_0^{(2j)}(\mathbf{r})$ is the contribution to the transmitted beam from neutrons which have been Bragg reflected $2j$ times and is given by the recursion relation

$$n_0^{(2j)}(\mathbf{r}) = \begin{cases} n \exp\left[-\Sigma(\mathbf{k}_0)L(\mathbf{r}, \hat{\mathbf{k}}_0)\right], & j=0, \\ \Sigma_{-h}\Sigma_h\Lambda_0\Lambda_h[n_0^{(2j-2)}(\mathbf{r})], & j\geq 1. \end{cases} \tag{3.7}$$

Also,

$$n_h(\mathbf{r}) = \sum_{j=0}^{\infty} n_h^{(2j+1)}(\mathbf{r}), \tag{3.8}$$

in which $n_h^{(2j+1)}(\mathbf{r})$ is the contribution to the Bragg-reflected beam from neutrons which have been Bragg reflected $2j+1$ times and is given by

$$n_h^{(2j+1)}(\mathbf{r}) = \Sigma_h\Lambda_h[n_0^{(2j)}(\mathbf{r})]. \tag{3.9}$$

The transmissivity (2.14) can therefore be expressed as

$$T = \sum_{j=0}^{\infty} T^{(2j)}, \tag{3.10}$$

in which

$$T^{(2j)} = \frac{V}{A(\hat{\mathbf{k}}_0)}(\Sigma_{-h}\Sigma_h)^j H_{2j}, \tag{3.11}$$

where V is the volume of the crystal and

$$H_{2j} = \frac{1}{V}\int_{S(\hat{\mathbf{k}}_0)} \mathrm{d}S\hat{\mathbf{e}}\cdot\hat{\mathbf{k}}_0(\Lambda_0\Lambda_h)^j\{\exp\left[-\Sigma(\mathbf{k}_0)L(\mathbf{r}, \hat{\mathbf{k}}_0)\right]\}. \tag{3.12}$$

The reflectivity (2.16) can likewise be expressed as

$$R = \sum_{j=0}^{\infty} R^{(2j+1)}, \tag{3.13}$$

in which

$$R^{(2j+1)} = \frac{V}{A(\hat{\mathbf{k}}_0)}\Sigma_{-h}^j\Sigma_h^{j+1}H_{2j+1}, \tag{3.14}$$

and

$$H_{2j+1} = \frac{1}{V}\int_{S(\hat{\mathbf{k}}_h)} \mathrm{d}S\hat{\mathbf{e}}\cdot\hat{\mathbf{k}}_h$$
$$\times \Lambda_h(\Lambda_0\Lambda_h)^j\{\exp\left[-\Sigma(\mathbf{k}_0)L(\mathbf{r}, \hat{\mathbf{k}}_0)\right]\}. \tag{3.15}$$

The evaluation of these quantities is facilitated by the general theorem

$$\int_{S(\hat{\mathbf{k}})} \mathrm{d}S\hat{\mathbf{e}}\cdot\hat{\mathbf{k}}\Lambda_{\mathbf{k}}[g(\mathbf{r})] = \int_V \mathrm{d}\mathbf{r}\exp\left[-\Sigma(\mathbf{k})L(\mathbf{r}, -\hat{\mathbf{k}})\right]g(\mathbf{r}), \tag{3.16}$$

from which it follows, for example, that

$$H_1 = \frac{1}{V}\int_V \mathrm{d}\mathbf{r}\exp\left[-\Sigma(\mathbf{k}_0)L(\mathbf{r}, \hat{\mathbf{k}}_0) - \Sigma(\mathbf{k}_h)L(\mathbf{r}, -\hat{\mathbf{k}}_h)\right]. \tag{3.17}$$

To the extent that $\mu \equiv \Sigma'(\mathbf{k})$ is independent of $\mathbf{k}$ and Friedel's law is satisfied, so that $\Sigma_{-h} = \Sigma_h$, it follows from (3.2) that

$$\Sigma(\mathbf{k}_0) = \Sigma(\mathbf{k}_h) = \mu + \Sigma_h, \tag{3.18}$$

and, hence, that

$$H_1 = A(\mu + \Sigma_h), \tag{3.19}$$

where $A(\mu)$ is the absorption factor,

$$A(\mu) = \frac{1}{V}\int_V \mathrm{d}\mathbf{r}\exp\{-\mu[L(\mathbf{r}, \hat{\mathbf{k}}_0) + L(\mathbf{r}, -\hat{\mathbf{k}}_h)]\}. \tag{3.20}$$

In the kinematical theory of neutron diffraction, the reflectivity is given by

$$R_k = \Sigma_h t, \tag{3.21}$$

in which $t \equiv V/A(\hat{\mathbf{k}}_0)$ is the average crystal thickness in the direction of the incident beam (Table 1). Hence,

$$R^{(2j+1)} = R_k\Sigma_h^{2j}H_{2j+1}. \tag{3.22}$$

In particular, the contribution from single reflexions is

$$R^{(1)} = R_kA(\mu + \Sigma_h). \tag{3.23}$$

The problem of calculating the transmissivity and reflectivity in the two-beam case is therefore reduced to evaluating the multi-dimensional integrals (3.12) and (3.15) for the transmission factors H. These quan-

Table 1. *The average crystal thickness in the direction of the incident beam, t, and the average path length of a singly-reflected neutron through the crystal, D, for crystals of various shapes*

The angles φ and φ' are defined in the Appendix. The values for the cylinder apply only to equatorial reflexions where the plane of scattering is perpendicular to the axis.

Crystal shape	Dimensions	t	D
plane slab	thickness d	$d\operatorname{cosec}\varphi$	$\frac{d}{2}(\operatorname{cosec}\varphi + \operatorname{cosec}\varphi')$
cylinder	radius r	$\frac{\pi}{2}r$	$\frac{16}{3\pi}r$ [a,b]
sphere	radius r	$\frac{4}{3}r$	$\frac{3}{2}r$ [b]

References: [a] Hamilton (1957). [b] Zachariasen (1965).

tities are special cases of more general transmission factors which also govern multiple diffuse scattering processes in macroscopic bodies (Sears, 1975a). They can be evaluated analytically for an infinite plane slab as discussed in the Appendix. An approximate model, which is applicable to a crystal of arbitrary shape, is presented in §5.

4. The extinction factor

In general, $\Sigma_h = QW(\theta')$ where Q denotes the neutron Q-value and $W(\theta')$ the normalized mosaic function. Here $\theta' = \theta - \theta_B$ where θ is the angle of incidence on the Bragg planes and θ_B the nominal Bragg angle. The kinematical reflectivity (3.21) can therefore be expressed in the form

$$R_k = \varrho_k W(\theta'),\qquad(4.1)$$

in which ϱ_k is the integrated reflectivity in the kinematical theory,

$$\varrho_k \equiv \int R_k \mathrm{d}\theta' = Qt.\qquad(4.2)$$

Hence, it follows from (3.22) that

$$R^{(2j+1)} = \varrho_k Q^{2j} H_{2j+1} W(\theta')^{2j+1},\qquad(4.3)$$

in which, according to (3.18), H_{2j+1} is to be evaluated with

$$\Sigma(\mathbf{k}_0) = \Sigma(\mathbf{k}_h) = \mu + QW(\theta').\qquad(4.4)$$

It then follows from (3.13) that the integrated reflectivity,

$$\varrho \equiv \int R \mathrm{d}\theta',\qquad(4.5)$$

can be expressed in the form

$$\varrho = \varrho_k E,\qquad(4.6)$$

in which the factor E has a multiple-scattering expansion of the form

$$E = \sum_{j=0}^{\infty} E^{(2j+1)},\qquad(4.7)$$

where $E^{(2j+1)}$ is the contribution from neutrons which have been Bragg reflected $2j+1$ times and is given by

$$E^{(2j+1)} = Q^{2j} \int H_{2j+1} W(\theta')^{2j+1} \mathrm{d}\theta'.\qquad(4.8)$$

In particular, the single scattering ($j=0$) contribution is given, according to (3.19), by

$$E^{(1)} = \int A[\mu + QW(\theta')] W(\theta') \mathrm{d}\theta'.\qquad(4.9)$$

The factor E describes the reduction in the integrated reflectivity due to the attenuation of the transmitted and Bragg-reflected beams inside the crystal which is neglected in the kinematical theory. The attenuation contains contributions, not only from absorption (*i.e.*

true absorption and diffuse scattering), but also a self-consistent contribution from multiple Bragg reflexion (*i.e.* secondary extinction). If the latter contribution is neglected by putting $Q = 0$ then $E^{(1)} = A(\mu)$ and $E^{(2j+1)} = 0$ for $j \geq 1$ with the result that $E = A(\mu)$. In general, for $Q \neq 0$, we can therefore write

$$E \equiv A(\mu) E_s,\qquad(4.10)$$

in which the quantity E_s, so defined, is called the secondary extinction factor. While the above distinction between the absorption factor and the secondary extinction factor is clear and unambiguous and while there are good practical reasons for making such a distinction, particularly in X-ray diffraction, the distinction is nonetheless quite artificial since E_s depends on μ. From a physical point of view, the effects of absorption and secondary extinction on E are inextricable and the fundamental quantity is simply E. For lack of a better name, we shall sometimes call E the 'extinction factor' even though this name is really appropriate only in the case of zero absorption ($\mu = 0$) where $A(\mu) = 1$ and $E = E_s$.

For a small crystal the absorption factor (3.20) can be evaluated by expanding the exponential with the result that (4.9) becomes

$$E^{(1)} = 1 - (\mu + gQ)D + O(L^2),\qquad(4.11)$$

in which L characterizes the linear dimensions of the crystal, D is the average path length of a singly reflected neutron through the crystal and g is the Darwin g-value,

$$g = \int W(\theta')^2 \mathrm{d}\theta'.\qquad(4.12)$$

The values of D for some simple crystal shapes are given in Table 1. Since $E^{(2j+1)} = O(L^{2j})$ for $j \geq 1$, it follows that likewise

$$E = 1 - (\mu + gQ)D + O(L^2).\qquad(4.13)$$

This result is of limited usefulness since the higher-order terms are often not negligible in practice. An approximate expression for E, which is valid beyond the linear region, is developed in the next section.

5. Approximate theory of secondary extinction

Since the detailed shape of $W(\theta')$ is usually not known in practice, it is necessary to introduce a suitable model for this quantity. One such model is the Gaussian (Darwin, 1922),

$$W(\theta') = \frac{1}{\sqrt{(2\pi)}\eta} \exp\left(-\theta'^2/2\eta^2\right),\qquad(5.1)$$

for which

$$g = \frac{1}{2\sqrt{\pi}\eta} = \frac{0\cdot282}{\eta}.\qquad(5.2)$$

Alternatively, one might employ the step-function model (Hamilton, 1957),

$$W(\theta') = \frac{1}{2\sqrt{3}\eta}, \quad |\theta'| < \sqrt{3}\eta,$$
$$= 0, \qquad |\theta'| > \sqrt{3}\eta, \qquad (5.3)$$

in which η is again the standard deviation,

$$\eta^2 = \int \theta'^2 W(\theta') d\theta', \qquad (5.4)$$

for which

$$g = \frac{1}{2\sqrt{3}\eta} = \frac{0.289}{\eta}, \qquad (5.5)$$

and differs from the previous value by only 2%. Thus, it is evident from (4.13) that, at least to a first approximation, E is not sensitive to the precise shape of $W(\theta')$. Fig. 2 suggests that this is true quite generally. In what follows we shall employ the step-function model. The advantage of this model is that the integral (4.8) can then be performed analytically to give

$$E^{(2j+1)} = (gQ)^{2j} H_{2j+1}, \qquad (5.6)$$

for $j \geq 0$ in which the transmission factor H_{2j+1} is to be evaluated with $\Sigma(\mathbf{k}) = \mu + gQ$ and is given for a crystal of arbitrary size and shape by the $(2j+3)$-dimensional integral (3.15).

In §6 of a recent article (Sears, 1975a) we have introduced an approximate, analytical method for calculating the corresponding transmission factors which govern multiple diffuse scattering in liquids. The method has been applied in the calculation of multiple scattering corrections for slow-neutron inelastic scattering experiments on liquid neon (Sears, 1975a; Buyers, Sears, Lonngi & Lonngi, 1975) and liquid helium (Sears, 1975b; Martel, Svensson, Woods, Sears & Cowley, 1976; Svensson, Martel, Sears & Woods, 1976). In the present context it gives an expression of the following form, which we shall refer to as the 'factor model',

$$H_{2j+1} = \frac{2^{2j}}{(2j+1)!} H_1 [B(\mathbf{k}_0)B(\mathbf{k}_h)]^j, \qquad (5.7)$$
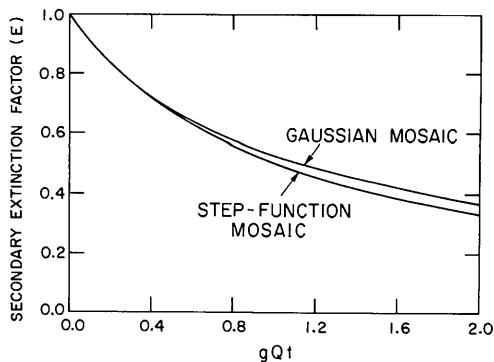

Fig. 2. Secondary extinction factor for an infinite plane slab in the case of zero absorption. The results are for the symmetric Bragg case and show a comparison of the Gaussian and step-function models for $W(\theta')$.

in which

$$B(\mathbf{k}) = \frac{p}{\mu + gQ} \{1 - \exp[-q(\mu + gQ)L(\hat{\mathbf{k}})]\}, \quad (5.8)$$

where $L(\hat{\mathbf{k}})$ is the maximum crystal thickness in the direction $\pm \hat{\mathbf{k}}$. It has been shown (Sears, 1975a) that the factor model (5.7) satisfies exact upper and lower bounds if $0 \leq p \leq 1$ and $0 \leq pq \leq 1$. The optimum values of p and q were determined in the above reference by fitting the factor model for H_2 to analytical results for the small-sample limit. The resulting numerical values for p and q (Table 2) are independent of the size of the crystal and depend only weakly on its shape. Thus, all the information about the size and shape of the crystal is essentially contained in $L(\hat{\mathbf{k}})$. Hence it follows, with the help of (3.19), that for $j \geq 0$,

$$E^{(2j+1)} = A(\mu + gQ) \frac{\psi^{2j}}{(2j+1)!}, \qquad (5.9)$$

in which

$$\psi = 2gQ / [B(\mathbf{k}_0)B(\mathbf{k}_h)]. \qquad (5.10)$$

The multiple scattering expansion (4.7) can therefore be summed to give

$$E = A(\mu + gQ) \frac{\sinh \psi}{\psi}. \qquad (5.11)$$

Let us first consider an infinite plane slab (see Appendix) for which the parameters in the factor model are given by

$$L(\hat{\mathbf{k}}_0) = d \csc \varphi, \quad p = \tfrac{3}{4},$$
$$L(\hat{\mathbf{k}}_h) = d \csc \varphi', \quad q = \tfrac{2}{3}. \qquad (5.12)$$

The coefficients a_S in equation $(A.5)$ of the Appendix can be obtained for the factor model by noting that $E = R/gQt$. The resulting values of a_s are those labelled 'approximate' in Table 3. Comparing these approximate values with the corresponding exact values, we note first that a_S is given correctly by the factor model for $s \leq 1$ in the Bragg case and for $s \leq 2$ in the Laue case. Although discrepancies occur for larger values of s, it is evident that (at least up to $s = 3$) the factor model is asymptotically exact in the limit $\zeta \ll 1$, where $a_s = 1/(s+1)!$, and also in the limit $\zeta \gg 1$, where $a_s = \zeta^s/(s+1)!$.

The factor model is least accurate for symmetric reflexions where $\zeta = 1$. Fig. 3 shows a comparison of the factor model with the exact results for symmetric reflexions obtained in the Appendix and with the first-

Table 2. Numerical values of the parameters p and q in the factor model (5.8)

The values for the cylinder apply only to equatorial reflexions where the plane of scattering is perpendicular to the axis.

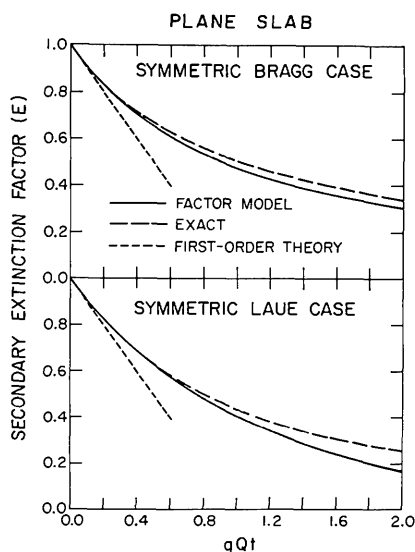| Crystal shape	p	q
plane slab	0.750	0.667
cylinder	0.644	0.659
sphere	0.592	0.633

PLANE SLAB

Fig. 3. Secondary extinction factor for an infinite plane slab with a step-function mosaic for the case of zero absorption and symmetric reflexion geometry. The figure shows a comparison of the factor model (5.11) with the exact result obtained from $(A.6)$ and with the first-order theory (4.13).

order theory (4.13). It is evident that the first-order theory is accurate for $gQt \lesssim 0\cdot1$ and the factor model for $gQt \lesssim 0\cdot5$. For larger values of gQt the factor model underestimates E and, hence, overestimates the amount of secondary extinction.

For equatorial reflexions from a cylinder of radius r the parameters in the factor model are given by

$$L(\hat{k}_0) = L(\hat{k}_h) = 2r, \quad p = \frac{16}{9\pi^2 - 64}, \quad q = \frac{3\pi}{4} - \frac{16}{3\pi}. \quad (5.13)$$

Fig. 4 shows a comparison of the factor model with the results obtained by Hamilton (1963) from a numerical solution of the Darwin equations for equatorial reflexions from a cylinder. The results of the first-order theory (4.13) are also shown. These results refer, again, to the case of zero absorption and a step-function mosaic. The discrepancies in Fig. 4 are very similar to those in Fig. 3.

For all reflexions from a sphere of radius r the parameters in the factor model are given by

$$L(\hat{k}_0) = L(\hat{k}_h) = 2r, \quad p = \tfrac{45}{76}, \quad q = \tfrac{19}{30}. \quad (5.14)$$

Fig. 5 shows a comparison of the factor model with the approximate theory of Becker & Coppens (1974a) for a sphere. These results also refer to the case of zero absorption. In both Fig. 4 and Fig. 5, the factor $A(gQ)$ in (5.11) was obtained from International Tables for X-ray Crystallography (Kasper & Lonsdale, 1959). Becker & Coppens's results are for a Gaussian mosaic whereas the factor model results are, as before, for a step-function mosaic. The results of the first-order

theory (4.13) are also shown. The discrepancies are larger in Fig. 5 than in Figs. 3 and 4. It is evident from Fig. 2 that the larger discrepancies can reasonably be attributed to the fact that Becker & Coppens's results refer to a Gaussian mosaic while all the others are for
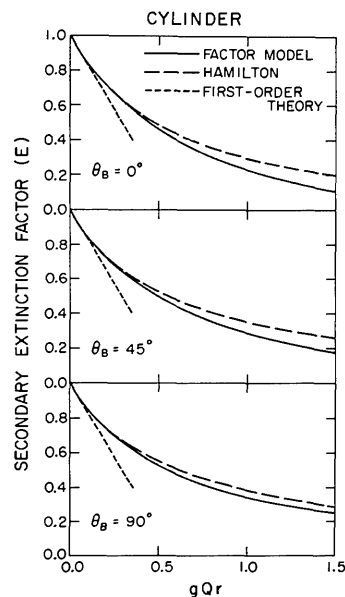
CYLINDER

Fig. 4. Secondary extinction factor for a cylinder of radius r with a step-function mosaic for the case of zero absorption. The figure shows a comparison of the factor model (5.11) with the results of Hamilton (1963) and with the first-order theory (4.13).
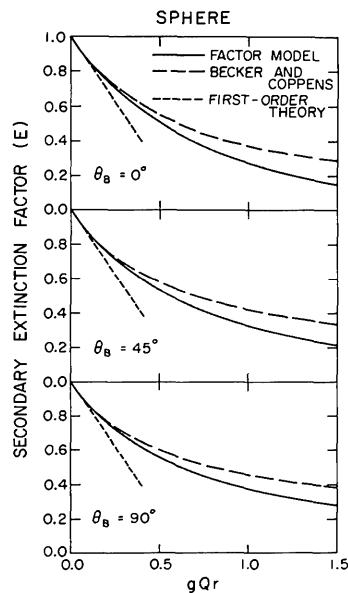
SPHERE

Fig. 5. Secondary extinction factor for a sphere of radius r for the case of zero absorption. The figure shows a comparison of the factor model (5.11) for a step-function mosaic with the results of Becker & Coppens (1974a) for a Gaussian mosaic and with the first-order theory (4.13).

a step-function mosaic. Otherwise, the results in Fig. 5 are very similar to those in Figs. 3 and 4.

It is apparent from Figs. 3, 4 and 5 that as long as the secondary extinction is moderately weak ($E \gtrsim 0.6$, say), which is usually the case for the small crystals employed in crystal-structure determinations, the factor model provides an accurate estimate of the secondary extinction factor regardless of the shape of the crystal. The error is typically $\lesssim 4\%$. The main advantage of the factor model is that it provides a simple analytical expression for E rather than simply a table of numerical values. This may be especially useful for computing purposes in structure refinements.

For severe secondary extinction ($E < 0.6$) the factor model consistently overestimates the amount of secondary extinction although it remains qualitatively correct. In this region the secondary extinction factor is increasingly dependent on the detailed shape of $W(\theta')$ so that existing tables of secondary extinction factors, which are calculated on the basis of a specific model for $W(\theta')$, are likewise of limited usefulness for quantitative purposes (see Fig. 2). On the other hand, such severe secondary extinction is normally encountered only in neutron-monochromator crystals. Such crystals are usually in the form of plane slabs for which analytical solutions of the Darwin equations are available.

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APPENDIX
Infinite plane slab

The transmission factors H_j, which govern the multiple scattering expansions for both diffuse scattering

and Bragg reflexion, can be calculated exactly for an infinite plane slab for all j. The results are given in a recent article (Sears, 1975a) in the form of an algebraic recursion relation. With increasing j, the explicit expressions for H_j rapidly become unwieldly and we shall therefore confine our attention to H_1 and H_3 which determine the first two terms in (3.13). The results are:

$$H_1 = \frac{1 - \exp\left[-(\zeta+1)x\right]}{(\zeta+1)x} \quad \text{(B)},$$

$$= \frac{e^{-x} - e^{-\zeta x}}{(\zeta-1)x} \quad \text{(L)} \qquad (A.1)$$

and

$$H_3 = \frac{\zeta}{(\zeta+1)^3 x \Sigma^2}\left\{1 - 2(\zeta+1)x \exp\left[-(\zeta+1)x\right]\right.$$
$$\left. - \exp\left[-2(\zeta+1)x\right]\right\} \quad \text{(B)},$$

$$= \frac{\zeta}{(\zeta-1)^3 x \Sigma^2}\left\{\left[(\zeta-1)x-2\right]e^{-x}\right.$$
$$\left. + \left[(\zeta-1)x+2\right]e^{-\zeta x}\right\} \quad \text{(L)}. \qquad (A.2)$$

Here (B) denotes the Bragg case (reflexion geometry) and (L) the Laue case (transmission geometry). Also, $\zeta = \sin\varphi/\sin\varphi'$ where φ and φ' are the angles which the incident and reflected beams make with the surface of the slab. Finally, $x = \Sigma d \operatorname{cosec}\varphi$ where $\Sigma = \mu + \Sigma_h$ and d is the thickness of the slab. Hence it follows from (3.22) that in the case of zero absorption, where $\mu = 0$ so that $\Sigma = \Sigma_h$ and $x = R_k$,

$$R^{(1)} = \frac{1}{\zeta+1}\left\{1 - \exp\left[-(\zeta+1)R_k\right]\right\} \quad \text{(B)},$$

$$= \frac{1}{\zeta-1}\left\{\exp\left(-R_k\right) - \exp\left(-\zeta R_k\right)\right\} \quad \text{(L)}, \qquad (A.3)$$

Table 3. *The coefficients a_s in the expansion $(A.5)$ of the reflectivity of an infinite plane slab in the case of zero absorption*

The exact values are from $(A.6)$ and the approximate values from the factor model ($\S 5$).

Reflexion type	s	Bragg case		Laue case	
		exact	approximate	exact	approximate
asymmetric	0	1	1	1	1
	1	$\frac{1}{2!}(\zeta+1)$	$\frac{1}{2!}(\zeta+1)$	$\frac{1}{2!}(\zeta+1)$	$\frac{1}{2!}(\zeta+1)$
	2	$\frac{1}{3!}(\zeta^2+4\zeta+1)$	$\frac{1}{3!}(\zeta^2+3\zeta+1)$	$\frac{1}{3!}(\zeta+1)^2$	$\frac{1}{3!}(\zeta+1)^2$
	3	$\frac{1}{4!}(\zeta+1)(\zeta^2+10\zeta+1)$	$\frac{1}{4!}(\zeta+1)(\zeta^2+\frac{16}{3}\zeta+1)$	$\frac{1}{4!}(\zeta+1)^3$	$\frac{1}{4!}(\zeta+1)(\zeta^2+\frac{10}{3}\zeta+1)$
symmetric ($\zeta=1$)	0	1	1	1	1
	1	1	1	1	1
	2	1	5/6	2/3	2/3
	3	1	11/18	1/3	4/9

and

$$R^{(3)} = \frac{\zeta}{(\zeta+1)^3} \{1 - 2(\zeta+1)R_k \exp[-(\zeta+1)R_k]$$
$$- \exp[-2(\zeta+1)R_k]\} \quad (B),$$

$$= \frac{\zeta}{(\zeta-1)^3} \{[(\zeta-1)R_k-2]\exp(-R_k)$$
$$+ [(\zeta-1)R_k+2]\exp(-\zeta R_k)\} \quad (L). \quad (A.4)$$

Since $R^{(2j+1)} = O(R_k^{2j+1})$ the expansions of $R^{(1)}$ and $R^{(3)}$ in powers of R_k can be substituted into (3.13) to determine the coefficients a_s for $s \le 3$ in the expansion

$$R = \sum_{s=0}^{\infty} (-)^s a_s R_k^{s+1}. \quad (A.5)$$

The resulting values of a_s are those labelled 'exact' in Table 3. (The other entries in this table are from the approximate theory in §5). It will be noted that the difference between the Bragg and Laue cases begins at the $s=2$ term.

On the other hand, the Darwin equations (3.1) can be solved directly for an infinite plane slab. In the case of zero absorption the resulting expressions for the reflectivity are

$$R = \frac{\exp[(1-\zeta)R_k]-1}{\exp[(1-\zeta)R_k]-\zeta} \quad (B),$$

$$= \frac{1}{1+\zeta}\{1-\exp[-(1+\zeta)R_k]\} \quad (L). \quad (A.6)$$

When these expressions are expanded in the form $(A.5)$ we find the same coefficients a_s as before. This verifies that the multiple-scattering solution of the integral form of the Darwin equations is equivalent to the direct solution of the corresponding differential equations. For symmetric reflexions ($\zeta=1$) equation $(A.6)$ reduces to the well-known results of Bacon & Lowde (1948).

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