Acta Cryst. (1965). **18**, 184

The Effect of Experimental Resolution on Crystal Reflectivity and Secondary Extinction in Neutron Diffraction

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(*Received 3 February* 1964 *and in revised form* 16 *March* 1964)

The reflectivity for neutrons of a plane slab crystal is calculated in the transmission case when the crystal is placed between two Soller collimators. The calculations indicate that the crystal reflectivity, as well as the secondary extinction coefficient, depends significantly on the angular resolution of the collimators. Curves are given for the extinction of the crystal with different crystal and collimator parameters.

1. Introduction

The interaction between a beam of thermal neutrons and a single free nucleus can result in either absorption or isotropic scattering processes (in the centre of mass system).

If several equal nuclei are present, arranged in a lattice, interference will occur between the scattered beams. The only directions around which the elastic scattered beams have non-vanishing intensities are given by the Bragg condition,

$$n\lambda = 2d \sin \theta \,, \tag{1·1}$$

n being a positive integer called the scattering order, λ the neutron wavelength, d the lattice spacing, and θ the Bragg angle (2θ the angle between the direct and the scattered beams).

The ratio between the number of neutrons with wavelength λ in the elastic scattered beam and in the incoming beam is called the reflectivity. This is a function of two independent variables, such as λ and the incoming direction, or θ and the crystal setting. Further the reflectivity depends on the order of reflexion, crystal shape, *etc.* The calculations in this article deal with the transmission or Laue case for a crystal having the form of a plane parallel slab. In the transmission case the neutrons leave the crystal from the side opposite to that of their arrival. This case has previously been dealt with by Zachariasen (1945) for X-ray diffraction, by Bacon & Lowde (1948) and by Holm (1955) for neutron diffraction. There appear to be some discrepancies in the calculations by Bacon & Lowde and Holm. Some of the calculations made by Holm, which we permit ourself to criticize, have been adopted by other investigators (Haas & Shore, 1959; Hautecler & Pollak, 1958).

In § 2 some introductory remarks on the problem of extinction are made. The reflectivity of a plane slab crystal in the transmission case is calculated in § 3 as a function of the direction of the incident neutrons. Though such calculations have been published earlier (Bacon & Lowde, 1948; Holm, 1955), it was found reasonable to go into some detail and point out the discrepancies mentioned. The total or integrated reflectivity evaluated by the authors cited is obtained by integration of the reflectivity calculated in § 3. In relation to experimental situations this integrated reflectivity would be measured either by rotating the crystal in a narrow incoming neutron beam or by keeping the crystal fixed in a wide open beam. By narrow and wide open beams is meant beams with angular spreads much less and much higher respectively than the mosaic spread of the crystal. In neutron diffraction experiments the angular spread of the neutron beam is often comparable to the mosaic spread. In this case the integrated reflectivity and also the secondary extinction become dependent on the angular spread of the collimation. We have investigated this dependence in the special case with two Soller collimators placed in front of and behind a crystal in a fixed position. This is described in § 4.

2. Extinction

An infinitesimal volume element δV of a perfect single crystal (crystallite) irradiated in a neutron beam flux I neutrons cm^{-2} sec^{-1} will scatter $IQ\delta V$ neutrons sec^{-1}, provided the number of atoms in the volume element is so large that the coherence is sharper than the angular spread of the neutron beam. The crystallographic quantity Q, evaluated by Zachariasen (1945), is given by

$$Q = \lambda^3 N_c^2 F^2 / \sin 2\theta \,, \tag{2·1}$$

N_c being the number of unit cells per unit volume in the crystal and F the structure factor, *i.e.*

$$F = \sum_j b_j e^{-W} \exp\left[2\pi i(\mathbf{k}-\mathbf{k}_0)\cdot \mathbf{r}_j\right] \,, \tag{2·2}$$

where the summation is taken over all atoms (at positions $\mathbf{r}_j$) in the unit cell. $\mathbf{k}_0$ and $\mathbf{k}$ are the incident and scattered wave vectors respectively and e^{-W} is the square root of the Debye–Waller factor originating from the thermal vibrations of the atoms. W has been evaluated, for instance, by James (1948). The analytical expression for W used in the following calculations is

$$W = \frac{6h^2 \sin^2 \theta}{m_A k \theta_D \lambda^2} \left[\frac{\varphi(x)}{x} + \frac{1}{4} \right] . \tag{2·3}$$

Here h is Planck's constant, m_A is the nuclear mass, k is Boltzmann's constant, θ_D is the Debye temperature of the crystal, and x is equal to θ_D/T, where T is the absolute temperature of the crystal. $\varphi(x)$ is a function of x defined by

$$\varphi(x) \equiv \frac{1}{x} \int_0^x \frac{y dy}{e^y - 1} = x - \frac{x^2}{4} + \frac{x^3}{36} - \frac{x^5}{3600} + \frac{x^7}{211680} - \dots . \tag{2·4}$$

If the crystal scattering the neutron beam is not infinitesimal in dimensions, damping of the neutron intensity over the crystal will take place, giving unequal illumination of different parts of the crystal. The damping due to diffraction inside a crystallite is called the *primary extinction*.

Real single crystals are not perfect, but are assumed to consist of small crystallites stacked together with small, random, angular displacements Δ. The angular distribution, $W(\Delta)$, of the 'mosaic blocks' is normally assumed to have a Gaussian shape, *i.e.*

$$W(\Delta) = \frac{1}{\eta \sqrt{(2\pi)}} \exp(-\Delta^2/2\eta^2) , \tag{2·5}$$

where η, the 'mosaic spread', is the standard deviation of the distribution. The validity of this assumption is discussed by James (1948).

Two mosaic blocks, a distance apart and both in position for Bragg reflexion, will be differently irradiated, the intensity being diminished from the first to the second block owing to diffraction in the first block, and possibly from absorption between the blocks. The part of the intensity damping due to diffraction is called the *secondary extinction*.

In the following calculations the actual intensity variation inside the crystal is approximated by a smoothed curve (Fig. 1), for which a differential equation can be set up and solved. This approximation is good when the intensity damping inside a crystallite is small compared with the total intensity variation in the crystal. A crystal in which this condition is fulfilled is known as an 'ideal imperfect crystal'.

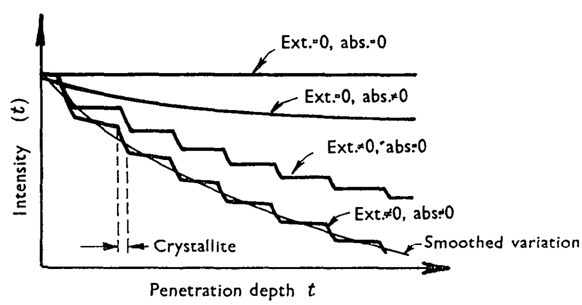

Fig. 1. Showing in principle how the intensity variation depends upon penetration depth for various combinations of extinction and absorption. When the relative damping of the intensity inside a crystallite is small, the crystal is said to be 'ideal imperfect', and the smoothed variation gives a good approximation to the real variation.

3. Reflectivity of a plane slab in the transmission case

Fig. 2 shows the unsymmetrical transmission case for a plane infinite slab of thickness t_0. χ denotes the angle between the normal to the crystal surface and the crystal plane under consideration. The direction cosines of the incident beam of wave length λ and the scattered beam with respect to the inward normal to the crystal surface are called γ_0 and γ_H respectively,

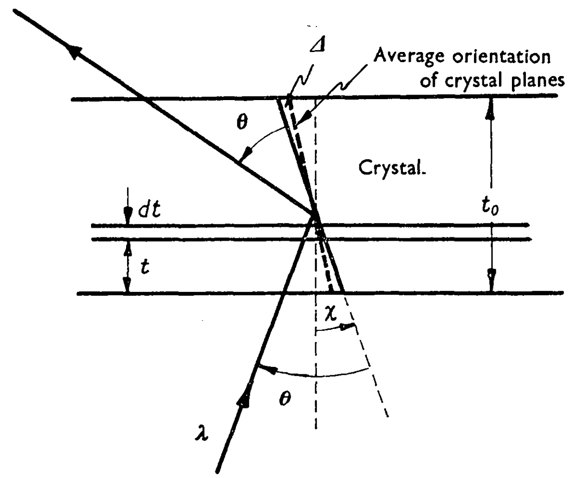

Fig. 2. Transmission path in a plane slab crystal.

i.e. $\gamma_0 = \cos(\theta - \chi)$, $\gamma_H = \cos(\theta + \chi)$. Through a layer of thickness dt, the incident beam path length is dt/γ_0 and the reflected beam path length is dt/γ_H.

We will assume the crystal azimuthally orientated in such a way that multiple scattering does not occur; that is neither the incident nor the diffracted beam can be scattered by more than one set of crystal planes.

The fraction of the mosaic blocks in a position to diffract the beam (as shown in Fig. 2) is $W(\Delta)d\Delta$, which means that the reflectivity per unit path length is

$$S(\Delta)d\Delta \equiv QW(\Delta)d\Delta . \tag{3·1}$$

If the linear absorption coefficient is denoted by μ, the change in the incident beam intensity $P_0(\Delta, t)$ over the layer dt at depth t is

$$dP_0(\Delta, t) = \left(-\mu \frac{P_0(\Delta, t)}{\gamma_0} - S \frac{P_0(\Delta, t)}{\gamma_0} + S \frac{P_H(\Delta, t)}{\gamma_H} \right) dt , \tag{3·2}$$

the last term giving a gain in intensity from a double diffracted beam. Similarly the change in the diffracted beam intensity $P_H(\Delta, t)$ is

$$dP_H(\Delta,t) = \left(-\mu\frac{P_H(\Delta,t)}{\gamma_H} - S\frac{P_H(\Delta,t)}{\gamma_H} + S\frac{P_0(\Delta,t)}{\gamma_0}\right)dt\,. \quad (3\cdot3)$$

These coupled differential equations can be integrated and solved with the boundary conditions: $P_H(0)=0$ and $P_0(t=0)=P_0(0)$, and the reflectivity (from now on termed $P(\theta, \Delta)$) can be found to be

$$P(\theta,\Delta) = \frac{P_H(\Delta,t_0)}{P_0(\Delta,0)} = \frac{S}{\gamma_0\cdot\varepsilon}\exp\left(-\frac{\mu+S}{\Gamma}t_0\right)\sinh(\varepsilon t_0) \quad (3\cdot4)$$

where

$$\varepsilon = \sqrt{\left(\frac{(\mu+S)^2}{G^2} + \frac{S^2}{\gamma_0\gamma_H}\right)}\,, \quad (3\cdot5)$$

and

$$\frac{1}{\Gamma} = \frac{1}{2}\left(\frac{1}{\gamma_0} + \frac{1}{\gamma_H}\right);\ \frac{1}{G} = \frac{1}{2}\left(\frac{1}{\gamma_0} - \frac{1}{\gamma_H}\right)\,. \quad (3\cdot6)$$

Formula (24) of Bacon & Lowde (1948) giving the reflectivity for the unsymmetrical transmission case differs from the same quantity derived in (3·4). The deviation is due to a misinterpretation, by these authors, of an earlier equation (4·21) of Zachariasen (1945). This latter equation (4·21), giving the differential change in beam intensities similar to (3·2) and (3·3), is in fact, as stated by Zachariasen for the symmetrical case, *i.e.* $\gamma_0=\gamma_H$. This misunderstanding has been furthered by the existence of both γ_0 and γ_H in the Zachariasen formula, though in wrong positions. Unfortunately, a recent article by Stehr (1963) has been partly based on the erroneous Bacon & Lowde formula.

To simplify calculation of the reflectivity, ε can be approximated by S/Γ. This approximation is valid for

$$\frac{\Gamma^2}{G^2}\left(\frac{2\mu}{S} + \frac{\mu^2}{S^2}\right) \ll 1\,. \quad (3\cdot7)$$

Here $\Gamma/G<1$, and hence for crystal planes with small absorption to diffraction ratio or for symmetrical reflection ($1/G=0$),

$$\begin{aligned} P(\theta,\Delta) &= \frac{\Gamma}{\gamma_0}\exp\left(-\frac{\mu+S}{\Gamma}t_0\right)\sinh\left(\frac{S}{\Gamma}t_0\right) \\ &= \frac{\Gamma}{2\gamma_0}\exp\left(-\frac{\mu}{\Gamma}t_0\right)\sum_{j=1}^{\infty}(-1)^{j+1}\frac{(2St_0/\Gamma)^j}{j!} \\ &= \frac{\Gamma}{2\gamma_0}\exp(-\mu t_0/\Gamma)\sum_{j=1}^{\infty}(-1)^{j+1}\frac{(C)^j}{j!}\exp\left(-\frac{j\Delta^2}{2\eta^2}\right) \end{aligned} \quad (3\cdot8)$$

with

$$C = 2Qt_0/\sqrt{(2\pi)}\eta\Gamma\,.$$

Holm (1955) calculates a reflectivity for the symmetrical transmission case corresponding to (3·8) for $\gamma_0=\gamma_H$. His result deviates from the reflectivity derived here, first because the linear damping coefficient has been used for μ, instead of the linear absorption coefficient (*i.e.* the diffraction has been included in μ), and secondly because the Debye–Waller factor has been placed in front of the whole expression instead of in the structure factor, where it actually belongs. In this way the calculations give too high a secondary extinction, because the Debye–Waller factor will in fact tend to diminish the magnitude of C. This implies further that according to Holm the secondary extinction is independent of temperature, whereas our calculations give a decrease of the extinction with the temperature.

4. Effect of experimental resolution

It is necessary to take the finite resolution of the incoming and outgoing beams into consideration when comparing the calculated reflectivity with measured reflectivities.

Fig. 3 shows a situation in which a white beam impinges on a crystal. Path I indicates the beam from which neutrons with wave length λ_B (corresponding to Bragg angle θ_B) are reflected from mosaic blocks with the average orientation. Path II indicates a beam reflected from mosaic blocks turned through an angle Δ from the average orientation. These reflected neutrons have wavelength λ (corresponding to Bragg angle θ). The angle between I and II before reflexion is δ and after reflexion β, where

$$\delta = (\theta-\theta_B) - \Delta \quad \text{and} \quad \beta = \delta + 2\Delta = (\theta-\theta_B) + \Delta\,. \quad (4\cdot1)$$

If the incident beam has passed through a collimator with acceptance function $n_i(\delta)$ and the diffracted beam has to pass through a collimator with acceptance function $n_d(\beta)$, the resolution function

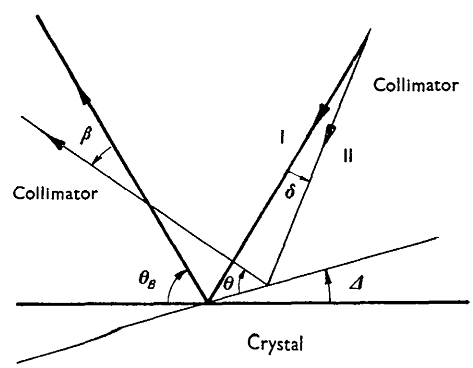

Fig. 3. Geometry for calculation of the experimental resolution effect.

$R(\theta-\theta_B)$ will be

$$\begin{aligned} R(\theta-\theta_B) &= \text{constant}\cdot\int_{-\infty}^{\infty} n_i(\delta)P(\theta,\Delta)n_d(\beta)d\Delta \\ &= \text{constant}\cdot\int_{-\infty}^{\infty} n_i((\theta-\theta_B)-\Delta) \\ &\quad \times P(\theta,\Delta)n_d((\theta-\theta_B)+\Delta)d\Delta\,. \end{aligned} \quad (4\cdot2)$$

We will confine ourselves to the case where the first and second collimators are identical Soller collimators, and for calculational convenience the acceptance function will be approximated by a Gaussian with standard deviation $\alpha/\sqrt{2}$, *i.e.*

$$n(\varphi)=\exp(-\varphi^2/\alpha^2) \tag{4·3}$$

with $\alpha=s/2L\sqrt{(\ln 2)}$, s being the width and L the length of the collimator and φ the angular divergence from the central passage through the collimator. The constant in (4·2) takes account of the normalization of the acceptance functions. To determine absolute intensities it is necessary to evaluate this constant as performed by Sailor, Foote, Landon & Wood (1956) in a special case. However, when dealing with crystal reflectivity the constant need not be considered.

The acceptance function for a Soller collimator is in fact a triangle. The Gaussian approximation is discussed by Sailor *et al.* (1956). For the product of the two acceptance functions in (4·2) we find, in the Gaussian approximation

$$n_i((\theta-\theta_B)-\Delta)n_d((\theta-\theta_B)+\Delta)=n^2(\theta-\theta_B)n^2(\Delta)\,. \tag{4·4}$$

From (4·2) and (4·4), therefore

$$R(\theta-\theta_B)=\text{constant}\cdot n^2(\theta-\theta_B)\int_{-\infty}^{\infty} n^2(\Delta)P(\theta,\Delta)d\Delta\,. \tag{4·5}$$

The integral in (4·5) is called the integrated reflectivity $P_{\text{int}}(\theta)$. Using (3·8), (4·3) and (4·4) (interchanging integration and summation), gives

$$\begin{aligned}P_{\text{int}}(\theta)&=\frac{\Gamma}{2\gamma_0}\exp(-\mu t_0/\Gamma)\sum_{j=1}^{\infty}(-1)^{j+1}\frac{(C)^j}{j!}\\&\quad\times\int_{-\infty}^{\infty}\exp\left(-\Delta^2\left(\frac{2}{\alpha^2}+\frac{j}{2\eta^2}\right)\right)d\Delta\\&=\sqrt{\left(\frac{\pi}{2}\right)}\frac{\eta\Gamma}{\gamma_0}\exp(-\mu t_0/\Gamma)\sum_{j=1}^{\infty}(-1)^{j+1}\frac{(C)^j}{j!\sqrt{(j+4\eta^2/\alpha^2)}}\,.\end{aligned} \tag{4·6}$$

The intensity $I(\theta_B)$ after the second collimator is found by multiplying (4·5) by the incident wavelength distribution $f(\lambda)$ and integrating over θ. $n^2(\theta-\theta_B)$ is normally so sharply peaked that $f(\lambda)$ can be approximated by the constant $f(\lambda_B)$ and similarly $P_{\text{int}}(\theta)$ by $P_{\text{int}}(\theta_B)$. Thus

$$I(\theta_B)\propto P_{\text{int}}(\theta_B) \tag{4·7}$$

revealing that the intensity is approximately proportional to the integrated reflectivity (4·6), corresponding to the average neutron wavelength.

5. Discussion

It is often of interest in neutron diffraction experiments to minimize the extinction effect and possibly to correct for it. The extinction coefficient, E_s, is defined as the ratio between the scattered intensity and the intensity one would get without

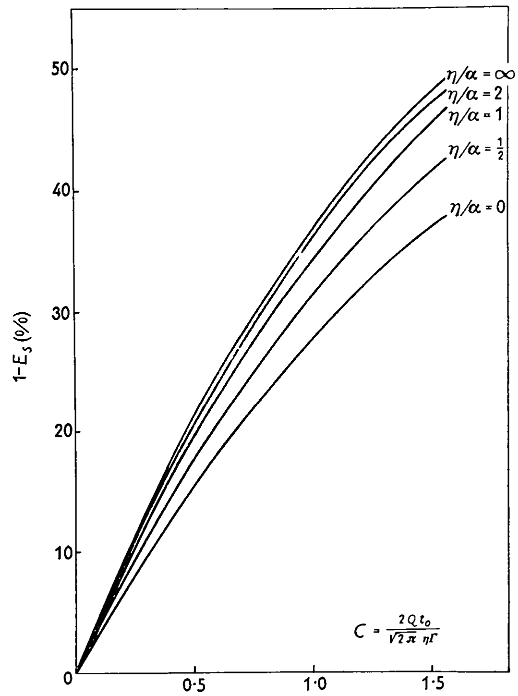

Fig. 4. The effect of the experimental resolution from two Soller collimators on the secondary extinction coefficient E_s. η is the mosaic spread of the crystal and α is the standard deviation for the collimator acceptance function divided by $\sqrt{2}$.

extinction. The latter intensity is represented by the linear, first term in the sum (4·6). In our notation therefore E_s is equal to the ratio of $P_{\text{int}}(\theta)$ to the first term in the sum (4·6). $(1-E_s)$ is shown in Fig. 4 (in %) as a function of C. The extinction depends on the experimental resolution through η/α. Curves are shown for several values of η/α. As seen from Fig. 4, the extinction will lie in a band. The results of Bacon & Lowde and Holm correspond for a fixed crystal to wide open incoming and outgoing beams, *i.e.* $\eta/\alpha=0$. Bacon has introduced a criterion for a 'thin' crystal, defined as a crystal with extinction $<5\%$. Incorporating the resolution effect, this criterion roughly approximates to

$$\frac{Qt_0}{\eta\Gamma}<\frac{1}{8}\sqrt{\left(\frac{2+4\eta^2/\alpha^2}{1+4\eta^2/\alpha^2}\right)}\,. \tag{5·1}$$

For decreasing values of C the integrated reflectivity will tend to approach the linear decrease of the first term in (4·6), *i.e.*

$$P_{\text{int}}(\theta_B)\xrightarrow[C\to 0]{}\exp(-\mu t_0/\Gamma)\frac{Qt_0}{\gamma_0\sqrt{(1+4\eta^2/\alpha^2}}\,. \tag{5·2}$$

When C increases, the integrated intensity will reach a maximum value followed by a decrease due to the absorption factor.

An example of the behaviour of the integrated intensity is shown in Fig. 5. The curves are reflectivities for Be (100) planes, calculated from (4·6) on a digital computer as a function of the Bragg angle. The specifications for the crystal and the collimators are given in the figure. The mosaic spread for the crystal was determined by measuring the rocking curve halfwidth for the crystal in a parallel double-reflexion set-up (Compton & Allison, 1935).

The reflectivity is proportional to θ^2 for small values of θ. For increasing θ the reflectivity reaches a plateau. This is a special property of the symmetric transmission ($\chi=0$) with small linear absorption coefficient. In general, the factors $(\Gamma/\gamma_0)\exp(-\mu t_0/\Gamma)$ will perturb this plateau. A special example of this kind was chosen to indicate that the higher order reflectivities, as expected, reach the same maximum value as the first order reflectivity. This would not be true for reflectivities calculated from the formulas of Holm.

The curves in Fig. 5 were used to determine higher order contamination for the Be 100 reflexion. The calculated contamination was in good agreement with measured values (Dietrich & Als-Nielsen, 1964).

In the approximation (3·7) the extinction is independent of the absorption. If (3·7) is not fulfilled, the extinction will decrease with increasing absorption to diffraction ratio and in the limit $\mu \gg S$ the extinction will vanish.

We have confined ourselves to the transmission case for an infinite plane slab, because this case is the simplest to treat. The reflexion, or Bragg case, for an infinite plane slab does not give an analytical expression for the reflectivity as simple as the expression in the transmission case but can be treated numerically. The problem of an arbitrary crystal shape has been investigated by Hamilton (1957) by use of numerical procedures. Hamilton has not included the experimental resolution effect, which, according to Fig. 4, appears to be rather significant for the extinction.

Thanks are due to our colleagues H. Bjerrum Møller and T. Brun for valuable discussions, and to Mrs Jennifer Starcke for assistance with the text.

We are grateful to Prof. O. Kofoed-Hansen, Head of the Physics Department at Risø, for providing a fruitful research atmosphere.

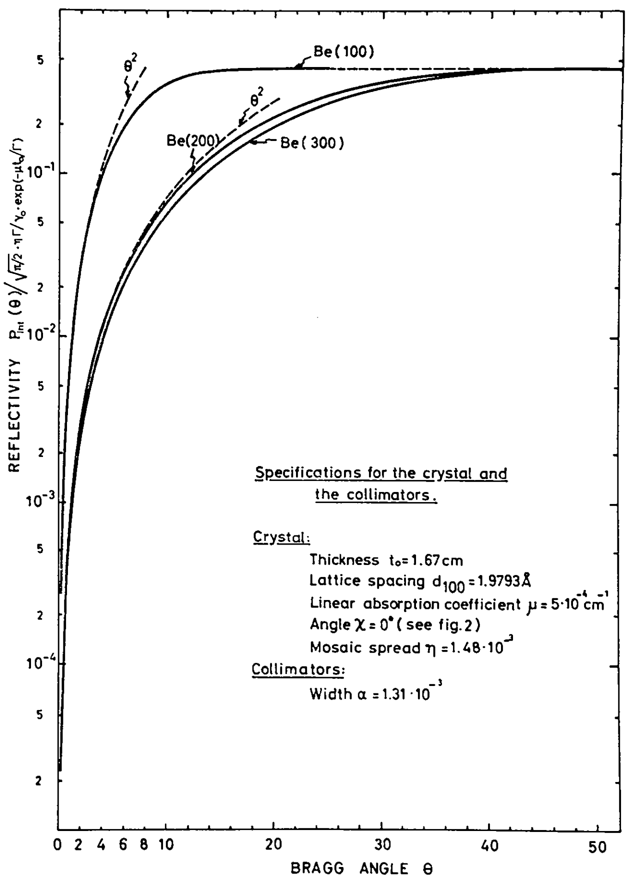

Fig. 5. The reflectivity, $P_{\rm int}(\theta)$, calculated from (4·6) as a function of Bragg angle for Be 100 reflexions. For small Bragg angles, the reflectivities are proportional to θ^2. The digital computer used for calculations was unable to evaluate the dotted section of the Be 100 curve.

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