

Estimate of the Contribution of Multiple Diffraction to Observed Intensities in Single-Crystal X-ray and Neutron Diffraction

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The likelihood of the occurrence of multiple-diffraction effects is discussed. The number and distribution of Umweganregung peaks are calculated from geometrical considerations. The effect of multiple diffraction on integrated intensities taken under conditions when many reflexions are simultaneously excited is estimated within the framework of the secondary-extinction theory.

Introduction

Considerable attention has been paid in recent years to the effects of multiple diffraction on intensity measurements in single-crystal X-ray and neutron diffractometry. In their most striking manifestation, these effects give rise to reflexions that are space-group forbidden by the Umweganregung process first described by Renninger (1937). The effects on normal reflexions are less dramatic but may still produce appreciable errors in observed intensities (Lipson & Cochran, 1953; Speakman, 1965).

Multiple diffraction occurs when more than one reciprocal-lattice point lies very close to the surface of the Ewald sphere. Geometrical aspects of the problem have been considered by Santoro & Zocchi (1964), Willis (1962), Burbank (1965), and others. Cole, Chambers & Dunn (1962) have derived the mathematical conditions that must be satisfied for multiple diffraction to occur; their procedure for indexing Umweganregung peaks in simple cases can be easily extended to indexing multiple diffraction scans in general.

The intensities of these effects have been discussed by Moon & Shull (1964) and Zachariasen (1965). Moon & Shull obtained good agreement between theory and their experimental results for neutron diffraction, from specimen crystals in the form of plane parallel plates. These authors have shown that the errors due to multiple diffraction are proportional to the secondary-extinction corrections; for example when the reflexions involved are all equally strong, corrections for single, double, triple and quintuple diffraction are in the ratios 1:1.5:2:3 (Zachariasen).

Multiple-diffraction effects may be frequently encountered in crystallographic studies. They may lead to appreciable errors in experimental structure factors (Panke & Wölfel, 1968). Consequently, procedures should be devised to eliminate these effects or at least to estimate their magnitude. With the four-circle diffractometer it is often possible to avoid multiple diffraction by exploiting the degree of freedom that remains, once a specified reciprocal-lattice point has been

constrained to lie on the surface of the Ewald sphere. The crystal may then be rotated about the scattering vector of this reflexion to obtain an optimal azimuth, *i.e.* one for which multiple-diffraction effects are minimal or, in favourable cases, absent (Santoro & Zocchi). Coppens (1968) has described a procedure for finding azimuthal positions at which measurements free from multiple-diffraction perturbations due to strong reflexions may be made. The necessity for weakening the constraint on the crystal's orientation to positions free only from perturbations due to strong reflexions is a result of the decrease, with increasing cell volume, of the probability of finding a position entirely free from any perturbations.

In the following paragraphs we discuss multiple diffraction in the case of crystals with unit-cell dimensions that are large compared to the wavelength. The statistical probabilities governing the occurrence of multiple diffraction are then high, and we can obtain statistically averaged estimates for the errors likely to be incurred in intensity measurements.

Multiple diffraction probabilities

Consider a crystal oriented with respect to a monochromatic beam such that a nominated set of planes corresponding to the reciprocal-lattice point H is in the diffracting position. Now consider that the direction of incidence (unit vector \mathbf{u}_0) precesses about the scattering vector \mathbf{H} so that the Bragg condition for the reflection H is continuously satisfied: the centre of the Ewald sphere generates a circle C , while the surface of the Ewald sphere sweeps out a volume of reciprocal space v^* (see Fig. 1). Every reciprocal lattice point K_i within this volume will have fallen on the surface of the Ewald sphere for two orientations; thus, it will have satisfied the geometrical conditions for simultaneous diffraction by the planes H and K_i .

When the wavelength is small compared with the unit-cell dimensions of the crystal, the approximate number of possible multiple-diffraction situations may be calculated from a knowledge of the wavelength, cell

volume, and Bragg angle of the reflexion H :

$$\begin{aligned} N &= 2v^*/V^* \\ &= 4\pi^2 V \lambda^{-3} \cos \theta_H, \end{aligned} \quad (1)$$

where $V^* = 1/V$ is the reciprocal cell volume. The argument is unaffected if the direction of incidence is fixed while the crystal is rotated about H .

Considering only a representative member of the set K_i and dropping the subscript, let us refer to K as the secondary or operative reflexion and H as the primary reflexion. Multiple diffraction between H and K implicitly involves a third set of planes, the cooperative reflexion K' , whose reciprocal-lattice vector is given by

$$\mathbf{K}' = \mathbf{H} - \mathbf{K}.$$

A further condition for multiple diffraction to occur is that at least two of H , K and K' have non-zero structure factors; the condition for the effect to be significant is that at least two are moderately intense reflexions. Thus, the number of possible multiple-diffraction peaks suggested by equation (1) must be reduced by a factor (a_H) that accounts for the various types of forbidden reflexions, which have been discussed by Kottwitz (1968). For example, in the diamond structure (space group $Fd\bar{3}m$), if H corresponds to a rigorously forbidden reflexion of the type $hk0$ where h and k are even and $h+k=4n+2$, or to a 'forbidden' reflexion of the type hkl where h , k and l are all even and non-zero, and $h+k+l=4n+2$, then N must be multiplied by $\frac{1}{2}$. This value results from restricting operative reflexions to the type hkl where h , k and l are all odd; therefore, we rewrite equation (1) in the form

$$N_H = a_H \cdot 2v^*/V^*. \quad (2)$$

Table 1 shows, for three common X-ray wavelengths, the number of Umweganregung peaks that might be observed in a complete rotation of a silicon crystal about the scattering vectors of several forbidden or 'forbidden' reflexions: calculated from equation (2), and computed by a procedure similar to that of Cole, Chambers & Dunn. Peaks that are degenerate in the sense that two or more operative reflexions are simultaneously favoured – Zachariasen's triple, quadruple, quintuple, *etc.* diffraction – have been counted as many times as they are degenerate.

Based on the assumption that N_H is large and the cell dimensions are similar, we have derived the probability density function which determines the distribu-

tion of reciprocal-lattice points of potentially operative reflexions as a function of radial distance from the origin:

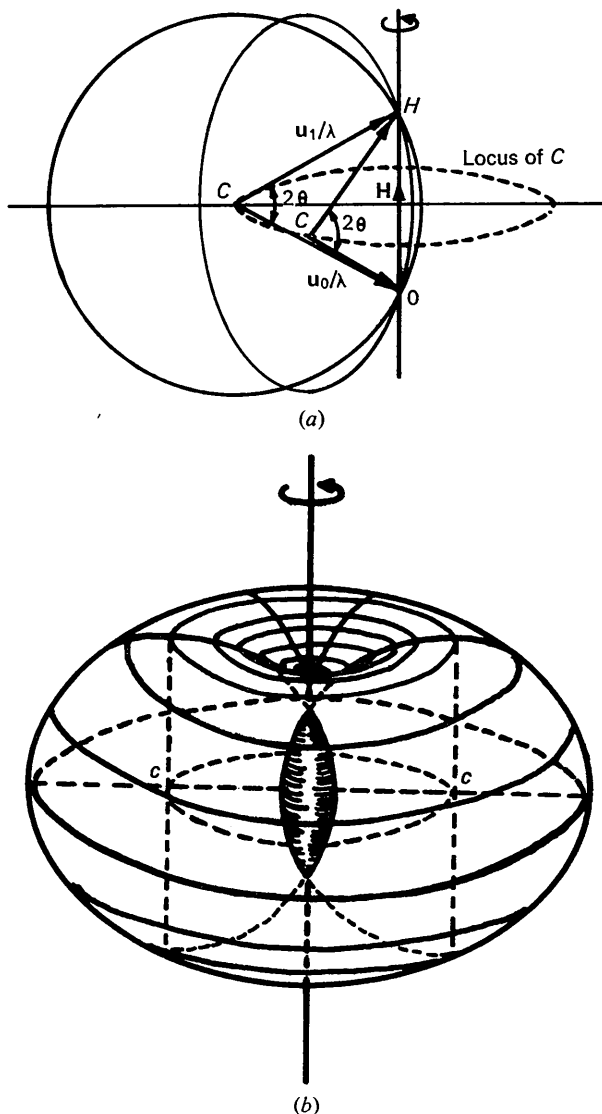


Fig. 1. Rotation of Ewald sphere about scattering vector H . (a) Trace of the Ewald sphere in the diffraction plane and beam directions at two instants. (b) Volume $v^* = 2\pi^2 \lambda^{-3} \cos \theta_H$ swept out by the surface of the Ewald sphere during a full rotation. Shaded axial region is excluded.

Table 1. Number of multiple diffraction peaks possible for silicon

N_s estimated by means of equation (3); N_c computed by exhaustion procedure. Operative and cooperative reflexions have odd Miller indices.

Primary reflexion	Cu $K\alpha_1$ $\lambda = 1.5405 \text{ \AA}$		Mo $K\alpha_1$ $\lambda = 0.70926 \text{ \AA}$		Ag $K\alpha_1$ $\lambda = 0.55936 \text{ \AA}$	
	N_s	N_c	N_s	N_c	N_s	N_c
H						
200	202	192	2192	2136	4486	4424
222	196	180	2152	2220	4438	4500
600	108	104	2036	2008	4290	4136
666	–	–	1620	1644	3810	3888

$$p(r) = 8\pi r^2 a_H V \cos \theta_H [1 - (r\lambda/2)^2]^{1/2} \quad (3)$$

where $r = 2 \sin \theta_K / \lambda$. This may be written in the form

$$p(2 \sin \theta_K / \lambda) = 32\pi a_H V \lambda^{-2} \cos \theta_H \cos \theta_K \sin^2 \theta_K.$$

Thus, the number of possible operative reflexions between $\sin \theta_K$ and $\sin \theta_K + d(\sin \theta_K)$ is

$$dN_H = 64\pi a_H V \lambda^{-2} \cos \theta_H \cos \theta_K \sin^2 \theta_K d(\sin \theta_K), \quad (4)$$

and it may be verified that

$$N_H = \int_0^{2\lambda^{-1}} p(r) dr.$$

Computation of the actual distribution for several of the primary reflexions of Table 1 yielded satisfactory agreement with the predictions of equation (4).

The overwhelming importance of angular divergence in multiple diffraction has been emphasized by Post (1969), and is illustrated by the work of Williamson & Fankuchen (1959). For fairly perfect crystals the width of Umweganregung peaks is dominated by the vertical divergence (Colella & Merlini, 1966). If the plane wave previously considered is replaced by a beam having vertical divergence δ , we may expect that for an arbitrary azimuth different rays will exactly satisfy the geometrical conditions for different operative reflexions. The number of operative reflexions that will be excited should be approximately

$$N_H(\delta) = (\delta \sec \theta_H / 2\pi) N_H.$$

For divergences of $1-2^\circ$, $N_H(\delta)$ may still be large; therefore, if the distribution in azimuth is fairly uniform it may be impossible to find a setting of the crystal for which there is no multiple diffraction, and indeed the number of operative reflexions simultaneously excited may be large.

Intensity of multiple diffraction effects

We assume that diffraction may be described in terms of the usual secondary-extinction theory. For single diffraction by a crystal of arbitrary shape, Zachariasen obtains the following approximate expression for the integrated intensity of the diffracted beam:

$$\bar{P}_1 \simeq I_0 \nu A [Q_1 p_1 - g Q_1^2 p_{11}(0) \bar{T}] \quad (5)$$

where I_0 is the incident intensity of the monochromatic X-ray beam, ν the irradiated volume of the crystal, A the transmission factor, Q_1 the effective reflectivity, and p_1 and $p_{11}(0)$ are polarization factors for the once- and twice-scattered beams; $g = \int [W(\Delta)]^2 d\Delta$, where $W(\Delta)$ is the distribution function of mosaic blocks in the crystal; $\bar{T} = A dA^* / d\mu$ is the mean-path length. For multiple diffraction the expression obtained by Zachariasen (ignoring polarization) is

$$\bar{P}_i \simeq I_0 \nu A [Q_i + C_i g \bar{T}]$$

where C_i involves the effective reflectivities of all the simultaneously excited reflexions, which for most cases he treats are symmetry-related.

We consider the specific case of double diffraction by sets of planes unrelated by symmetry, so that the structure factors $|F_H|$, $|F_K|$ and $|F_{K'}|$ are unrelated. The solution for the integrated intensity of the primary beam is then

$$\bar{P}_H \simeq I_0 \nu A [Q_H - \frac{1}{2} g (Q_H^2 \bar{T}_{HH} - Q_H Q_K \bar{T}_{HK} - Q_H Q_{K'} \bar{T}_{HK'} + Q_K Q_{K'} \bar{T}_{KK'})]. \quad (6)$$

Lorentz and polarization factors have been temporarily neglected. The subscription of mean-path lengths signifies that they are not necessarily equal, being dependent in principle on the different scattering angles associated with the several terms. However, we shall assume the crystal to be spherical and absorption to be small or moderate, so that \bar{T}_i is only weakly dependent on scattering angles: then the subscript may be dropped and the value of \bar{T} for forward scattering can be used throughout.

The change in the integrated intensity of the primary reflexion caused by double diffraction is

$$\Delta \bar{P}_H \simeq I_0 \nu A \frac{1}{2} g \bar{T} [-Q_H Q_K - Q_H Q_{K'} + Q_K Q_{K'}]. \quad (7)$$

The relative change is obtained by dividing equation (7) by the single diffraction expression, which we approximate by its zero-order (kinematic) term, $I_0 \nu A Q_H$. Thus the relative change is

$$R = \Delta \bar{P}_H / \bar{P}_H = \frac{1}{2} g \bar{T} \left[-Q_K - Q_{K'} + \frac{Q_K Q_{K'}}{Q_H} \right]. \quad (8)$$

R corresponds to the ratio R_D in equation (19) of Moon & Shull for the case where only one secondary reflexion is excited. In their original notation the result obtained by these authors is

$$R_D = \frac{1}{2} \left[\frac{Q_{0i} I_0}{(2\pi)^{1/2} \eta} \right] \sum_i \left[-\{1 + (K_{0i}^\theta)^2\}^{-1/2} \left(\frac{Q_{0i}}{Q_{0i}} \right) - \{1 + (K_{1i}^\theta)^2\}^{-1/2} \left(\frac{Q_{1i}}{Q_{0i}} \right) \left(\frac{l_i}{l_0} \right) + \{(K_{0i}^\theta)^2 + (K_{1i}^\theta)^2\}^{-1/2} \left(\frac{Q_{0i} Q_{1i}}{Q_{0i}^2} \right) \left(\frac{l_i}{l_0} \right) \right], \quad (9)$$

where the summation extends over all secondary beams. Accordingly, when several secondary reflexions are simultaneously excited, each one can be treated independently as regards its effect on R_D . Therefore, if this result may be assumed to hold for spherical crystals, it is sufficient hereafter to treat only double diffraction, where convenient, on the understanding that approximate results for higher-order diffraction may be obtained by summing over secondary reflexions.

We note that R_D is obtained in principle by measuring rocking curves at two azimuths — for one of which multiple diffraction is favoured; for the other, precluded. Hence it represents the proportional error due to multiple diffraction in a rocking-curve measurement performed under conditions that fail to preclude multiple diffraction.

Lorentz and polarization factors

In double diffraction three beams exist within the crystal, and we denote their directions by unit vectors \mathbf{u}_0 , \mathbf{u}_1 and \mathbf{u}_2 . To incorporate the correct Lp factors we must account for three scattering angles: $\cos^{-1}(\mathbf{u}_0 \cdot \mathbf{u}_1)$, $\cos^{-1}(\mathbf{u}_0 \cdot \mathbf{u}_2)$ and $\cos^{-1}(\mathbf{u}_1 \cdot \mathbf{u}_2)$ denoted by $2\theta_H$, $2\theta_K$ and $2\theta_{K'}$ respectively. These three angles are independent; however if the angle φ (Fig. 2) between the diffraction planes $(\mathbf{u}_0, \mathbf{u}_1)$ and $(\mathbf{u}_0, \mathbf{u}_2)$ is known, then $2\theta_{K'}$ is determined through the relationship:

$$\cos 2\theta_{K'} = \cos 2\theta_H \cos 2\theta_K + \sin 2\theta_H \sin 2\theta_K \cos \varphi.$$

On incorporating Lp factors, equation (8) takes the form

$$R = \frac{1}{2} g \bar{T} p_H^{-1} \left[-p_{HK}(K') K_{HK} Q_K - p_{HK'}(K) K_{HK'} Q_{K'} \right. \\ \left. + p_{KK'}(H) K_{KK'} \frac{Q_K Q_{K'}}{Q_H} \right], \quad (10)$$

where

$$p_i = \frac{1}{2} [1 + \cos^2 2\theta_i]; \quad p_{ij}(k) = \frac{1}{2} [\cos^2 2\theta_i + \cos^2 2\theta_j \\ + (\cos 2\theta_k - \cos 2\theta_i \cos 2\theta_j)^2];$$

and

$$K_{ij} = [K_i^2 + K_j^2]^{-1/2} \text{ with } K_H = 1, \quad K_K = [\cos 2\theta_{K'} \\ - \cos 2\theta_H \cos 2\theta_K] / 2 \sin 2\theta_H \sin 2\theta_K$$

and

$$K_{K'} = -[\cos 2\theta_K - \cos 2\theta_{K'} \cos 2\theta_H] / 2 \sin 2\theta_{K'} \sin 2\theta_K.$$

Beam divergence and mosaic spread

The derivation of equation (8) rests on the implicit assumptions that the incident beam is perfectly collimated and the alignment is such that the operative reflexion appearing in equation (6) is precisely satisfied. For a divergent incident beam one set of rays satisfies the Bragg condition for the planes H , another set sat-

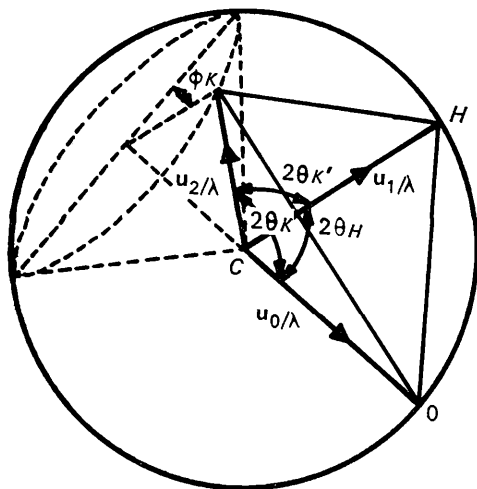


Fig. 2. Relationship between scattering angles and φ , the angle between diffraction planes $(\mathbf{u}_0, \mathbf{u}_1)$ and $(\mathbf{u}_0, \mathbf{u}_2)$.

isfies that for planes K and, effectively, a third satisfies that for planes K' . Only rays common to two sets can be subject to diffraction by two planes simultaneously. Therefore, if the sets do not coincide the same I_0 will not be applicable to all terms in equations (5) and (6). Consider the incident beam to have uniform intensity over an angular range of divergence δ about the central ray, and let the mosaic distribution of the crystal be of the form

$$W(\Delta) = \begin{cases} 1 & (|\Delta| \leq \eta/2) \\ 0 & (|\Delta| > \eta/2). \end{cases}$$

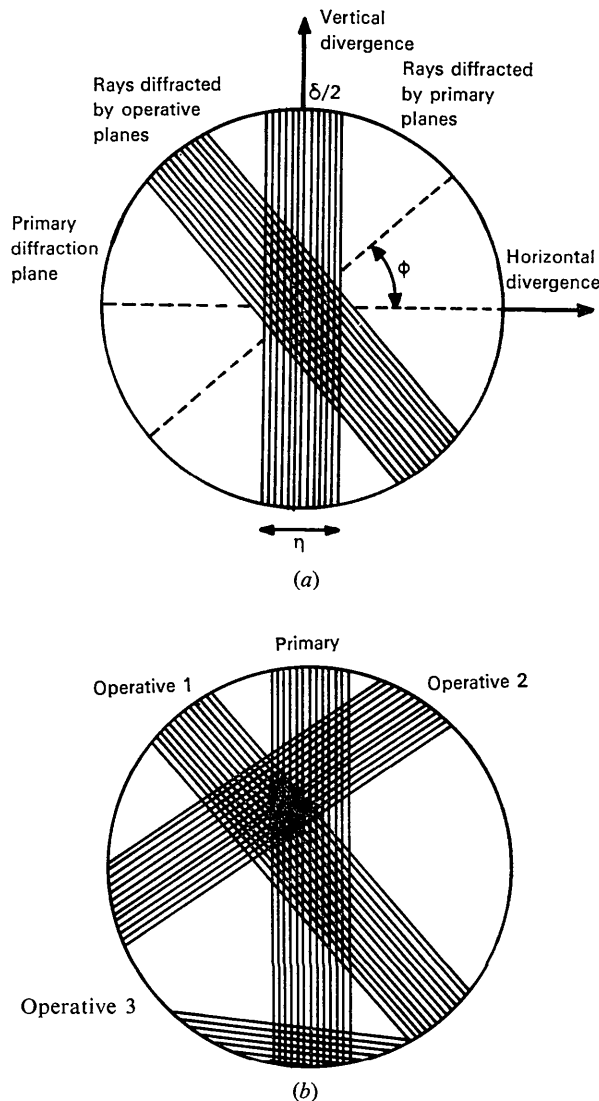


Fig. 3. Schematic depiction of incident beam of uniform intensity distribution over a range of divergence δ , showing rays subject to diffraction by primary and operative planes. (a) Double diffraction. The central ray satisfies the Bragg condition for both sets of planes. (b) Higher-order diffraction, primary reflexion and operative reflexion 1 being precisely satisfied, while operative reflexions 2 and 3 are partially satisfied.

If $\delta \ll \eta$ and the Bragg conditions for H and K are simultaneously satisfied by the central incident ray, then the sets of rays will be identical; hence, I_0 will apply to all terms of equations (5) and (6). If however, $\delta \gg \eta$, the sets of rays will in general overlap incompletely, the extent of overlap depending on the angles φ between

pairs of diffraction planes. The latter situation is illustrated in Fig. 3(a). The overlap between sets of rays involved in diffraction by primary and operative planes is only complete in this case when $\varphi = 0$, or equivalently, when \mathbf{u}_0 , \mathbf{u}_1 and \mathbf{u}_2 are coplanar.

If the operative and co-operative reflexions are not precisely satisfied (*i.e.* not satisfied by the central ray), they may still be satisfied by some rays, provided $|\alpha - \alpha_0| < \delta/2$, where α is the actual azimuth and α_0 is the correct azimuth. Where several operative reflexions are at least partially satisfied, some rays may be common to more than two reflexions and the situation illustrated in Fig. 3(b) may arise. Here the primary reflexion and operative reflexion 1 are precisely satisfied while operative reflexions 2 and 3 are partially satisfied. A detector in position to accept the primary beam would receive sets of rays that had undergone single, double and triple diffraction. We have stated, however, that each operative reflexion may be treated independently of others that are simultaneously excited.

In the case $\delta \gg \eta$ we take $I_0(\eta/\delta)$ as the value of I_0 applicable to the last three terms in equation (6). This approximation implies that, whereas primary diffraction occurs over a range η in the horizontal plane and δ in the vertical plane, multiple diffraction is restricted to a range η in both planes. (Deviations from $\varphi = \eta/2$ have been ignored.) When the mosaic distribution is Gaussian, *i.e.* when

$$W(\Delta) = [(2\pi)^{1/2}\eta]^{-1} \exp[-\Delta^2/2\eta^2]$$

as shall be assumed hereafter, we replace η , above, by $1/g$. (A multiple-diffraction method obtaining the distribution parameter η has been recently discussed by Caticha-Ellis, 1969.) It follows that R , equation (9), must be multiplied by $1/g$; it is therefore independent of g but inversely proportional to the divergence range δ .

Expectation value of R

We now calculate the expectation value of R as a function of the strength and location of the primary reflexion. We assume the intensities of operative and cooperative reflexions to be determined entirely by their distances from the origin of reciprocal space. A plausible assumption of this form is that all reflexions (except the primary reflexion) fall on the straight line of an auxiliary Wilson plot, (Rogers, 1965). The structure factors are then given by

$$|F|^2 = q \exp[-s \sin^2 \theta] \tag{11}$$

where s , the slope of the plot, depends on the wavelength temperature factor and the (Gaussian) unitary scattering factor profile, and q is the y intercept of the plot.

The average is obtained by treating the distribution of operative reflexions as continuous, and then integrating R , weighted by the normalized probability function $(\delta \sec \theta_H / 2\pi) p(r)$, over the entire range $r = 0 \rightarrow 2\lambda^{-1}$. A complication arises from the fact that, as men-

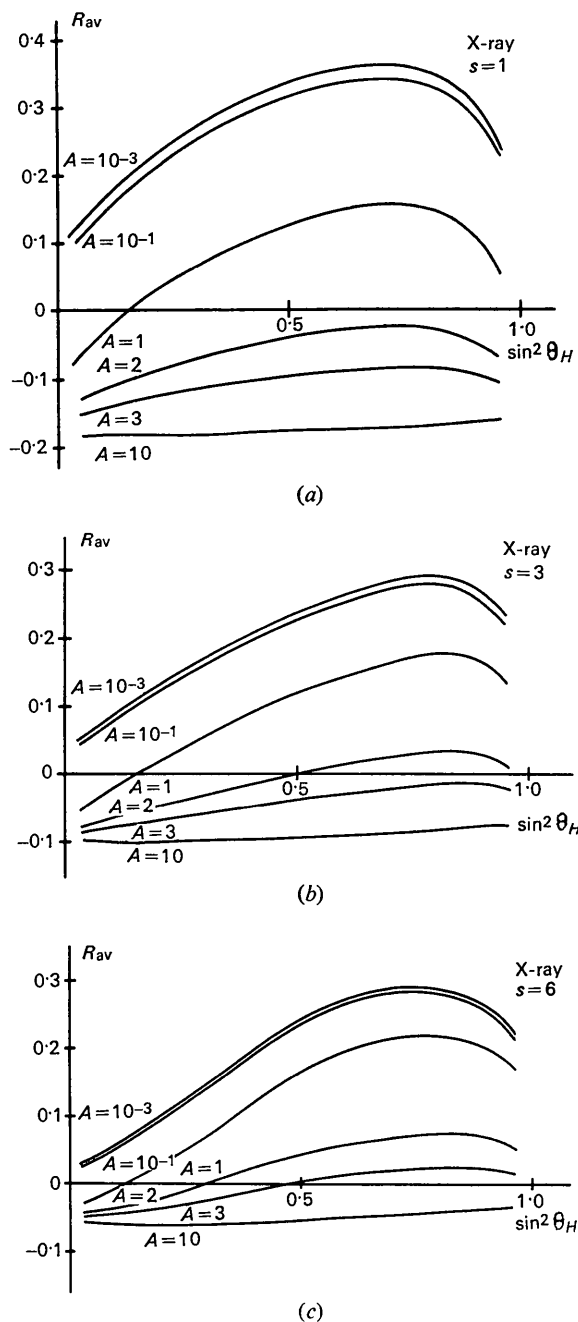


Fig. 4. Proportional error, due to multiple diffraction, in rocking-curve measurements, as a function of the location of the primary reciprocal-lattice point. Parameter A governs the strength of the primary reflexion. For $A = 10^{-3}$ indicated value of R_{av} must be multiplied by 10^{-3} ; for $A = 10^{-1}$, by 10. Diffraction: X-ray. (a) $s = 1$, (b) $s = 3$, (c) $s = 6$.

tioned previously, $\theta_{K'}$ is not determined by θ_H and θ_K ; therefore, we reasonably assume that the values of φ are randomly distributed, and that for each H, K we may average over φ . For $\delta \gg \eta$ we obtain:

$$R_{av} = \int_0^{2\lambda^{-1}} (\delta/2\pi)p(r) \sec \theta_H \left[\frac{1}{\pi} \int_0^\pi \frac{1}{g\delta} R d\varphi \right] dr. \quad (12)$$

To exclude divergences we must place bounds on θ_K and $\theta_{K'}$: lower bounds assert that reciprocal-lattice points are at a finite distance from the origin, and upper bounds correspond to the denial of reflexions with $\theta \rightarrow \pi/2$. Note that R_{av} is now independent of δ : while the intensity of each contribution to R_{av} is proportional to δ^{-1} , the number of contributing reflexions is proportional to δ .

R_{av} represents the effect of multiple diffraction in the measurement of a rocking curve only in so far as the number of operative reflexions 'sampled' at a given azimuth is representative of the distribution of operative reflexions. The validity of this calculation with respect to experiment would be improved if rocking curves were taken at a large number of randomly chosen azimuths, or if a single rocking curve were taken stepwise, the crystal being spun about the scattering vector \mathbf{H} at each step. In the case of a powder the azimuthal orientation of diffracting crystallites is expected to be random.

Results and discussion

R_{av} was evaluated by numerical integration, as a systematic function of the strength and location of the primary reflexion. Typical results are shown in Fig. 4. Each curve corresponds to a different strength of the primary reflexion relative to other reflexions; all other reflexions are assumed to conform to equation (11) and the exceptional primary reflexion is given by

$$|F_H|^2 = Aq \exp[-s \sin^2 \theta_H], \quad (13)$$

which is 'weak' or 'strong' according to whether $A < 1$ or $A > 1$. Apart from constants affecting only the ordinate scale of Fig. 4, the only factor upon which R_{av} depends is the slope s of the auxiliary Wilson plot. The variation of R_{av} with s is shown in the sequence (a), (b), (c) of Fig. 4.

Comparison of curves $A=10^{-1}$ and $A=10^{-3}$ shows that for weak reflexions R_{av} is nearly proportional to A^{-1} . This result follows from the dominance of the third (Umweganregung) term over the first two (Aufhellung) terms in equation (8).

Fig. 5 is a graph of the integrand of equation (12) versus $\sin \theta_K$, plotted for several values of $\sin^2 \theta_H$ and corresponding to points on the curve $A=1$ of Fig. 4(c). It illustrates how an 'average' primary reflexion tends to relinquish intensity to outer reflexions - reflexions of the same strength but located further from the origin - and to gain intensity from inner reflexions.

In plotting Figs. 4 and 5 we have omitted constants, and factors that depend on the crystal. To obtain ab-

solute values of R_{av} and $dR_{av}/d \sin \theta_K$, we multiply the ordinate scale by

$$C = 16 \left(\frac{e^2}{mc^2} \right)^2 a_H \bar{T} \frac{1}{V} \sum_i [f_i(0)]^2, \quad (14)$$

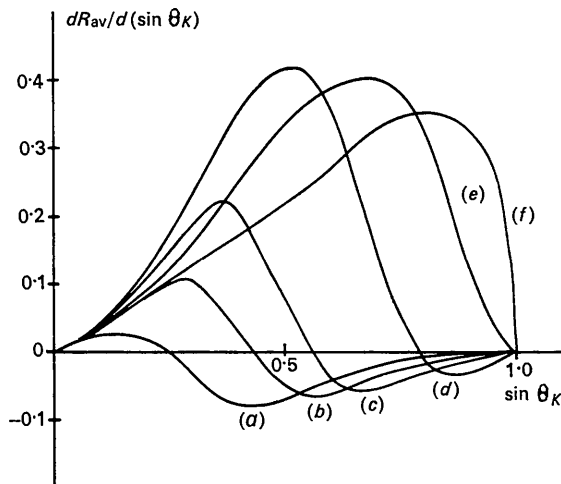


Fig. 5. Curves showing the distribution in reciprocal space of contributions to R_{av} for a primary reflexion of medium strength whose location is given by: (a) $\sin^2 \theta_H = 0.05$, (b) $\sin^2 \theta_H = 0.15$, (c) $\sin^2 \theta_H = 0.25$, (d) $\sin^2 \theta_H = 0.50$, (e) $\sin^2 \theta_H = 0.75$, (f) $\sin^2 \theta_H = 0.90$. Integrals under the curves correspond to points on the curve $A=1$ of Fig. 4(a).

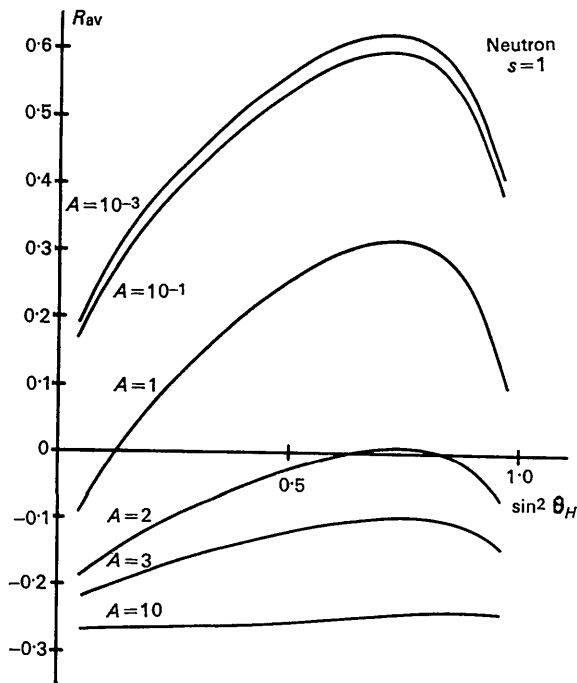


Fig. 6. Proportional error, due to multiple diffraction, in rocking-curve measurements, as a function of the location of the primary reciprocal-lattice point. Parameter A governs the strength of the primary reflexion. For $A=10^3$ indicated value of R_{av} must be multiplied by 10^3 ; for $A=10^{-1}$, by 10. Diffraction: neutron. $s=1$, $q=10$.

where f_i is the atomic scattering factor of the i th atom in the unit cell. For $V \sim 10^{-22} \text{ cm}^3$, $a_H \sim 1$, $\sum f_i^2 \sim 10^3$ and $T \sim 10^{-2} \text{ cm}$ we obtain $C \sim 10^{-2}$. Referring to Fig. 4, the maximum value of $|R_{av}|$ is then less than 1% for strong and medium reflexions, while for weak reflexions it may easily exceed 100%. For instance, we have calculated that the value of R_{av} for the inordinately 'weak' 002 reflexion in CaF_2 might be about 100%, while the values for other 'weak' reflexions might be from 2 to 5% (Cooper, 1970). Note that the values are almost independent of wavelength; for whereas the relative change in intensity due to a single operative reflexion [R of equation (8) is proportional to λ^{-3}], the number of operative reflexions contributing to R_{av} is proportional to $\lambda^3 \cos^{-1} [1 - (\lambda/2d_H)^2]^{1/2}$, where d_H is the spacing of the primary planes. In other words, the wavelength does not affect the scale of Fig. 4 but determines only $\sin^2\theta_H$ for the primary reflexion under consideration.

Similar calculations were made for neutron diffraction, in which case polarization factors are unity, the assumption of weak absorption is usually well justified, s is determined by the wavelength and the temperature factor, and C of equation (14) is written in terms of neutron scattering lengths. Fig. 6 shows the result of the neutron calculation performed with the same value of s as applies to Fig. 4(a).

For a crystal with a known structure the approximations inherent in equations (11) and (13) may be improved; also, calculations that treat the effect of various types of reflexions on primary reflexions, whose 'strength' is consonant with the type to which they belong, may be performed with greater consistency than has been the case here. The procedure to be fol-

lowed then, is to calculate independently, and then add, the contributions of the several types of reflexions on primary reflexions of a particular type. The correct statistics are introduced by changing a_H of equation (3) to $a_{H,K,K'}$, where H , K and K' represent the types of the primary, operative and cooperative reflexions.

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Determination of the Static Displacement of Atoms in a Binary Alloy System using Anomalous Scattering

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It is shown that the anomalous scattering of either X-rays or thermal neutrons provides a method of separating the individual static displacements due to AA and BB pairs of atoms in a solid solution.

Introduction

It is well known that the static displacement of the atoms from the nodes of the average lattice causes diffuse scattering of X-radiation. The effect of the root mean square of the static displacements is to reduce the intensity of the Bragg reflexions in a manner

similar to thermal diffuse scattering. The intensity lost in the Bragg reflexions is conserved by the resultant Huang (1947) diffuse scattering which is distributed close to the reciprocal-lattice points. The presence of short-range order (SRO) in a solid solution manifests itself as modulations in intensity of the Laue monotonic diffuse scattering with broad peaks at positions