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Simultaneous Reflexion: Its Detection and Correction for Intensity Perturbation

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The geometrical condition under which simultaneous reflexions occur with a general setting of a crystal has been formulated in three equations in terms of reciprocal-lattice vectors. A procedure is described to correct the intensity data for structure analysis for the intensity perturbation due to simultaneous reflexion. The following practical experimental conditions were taken into account: the effect due to the circumstance that the primary and secondary reflexions do not always occur exactly at the same time, the divergence and insufficient monochromatization of the incident beam, and a finite size and mosaicity of crystal specimen. The correction for simultaneous reflexion was applied to the X-ray intensity data from diformylhydrazine. It was shown that non-equal intensities among equivalent reflexions could be corrected reasonably by this method.

Introduction

The accuracy of measured intensities of X-ray diffraction has recently been improved so appreciably that the errors due to simultaneous reflexion should not be ignored in accurate intensity measurements.

Simultaneous reflexion occurs when a single crystal is so oriented that two or more reciprocal-lattice points lie on the sphere of reflexion at the same time. The simultaneous reflexion problem separates into two parts: determining the crystal orientation at which the simultaneous reflexion occurs, and determining its effects on the intensities. As to the orientation problem, Cole, Chambers & Dunn (1962) proposed a graphical method which is useful especially for crystals of higher symmetry. However, their method is cumbersome and involves the possibility of ignoring some effective secondary reflexions. Santoro & Zocchi (1964) proposed a method for calculating a setting angle for a single crystal on a four-circle diffractometer and suggested a procedure to find out an optimum azimuthal angle accompanied by minimum simultaneous reflexion effects for each reflecting plane.

The magnitude of intensity perturbation by simultaneous reflexion was estimated by Moon & Shull (1964) and by Zachariasen (1965). Moon & Shull pointed out that it is comparable to that of secondary extinction and that this effect is enhanced especially when a strong reflexion acts as a secondary reflexion, while the primary reflexion is weak.

The effect of simultaneous reflexion is mitigated to some extent in normal X-ray data collection, owing to the divergence and insufficient monochromatization of the incident beam and to the finite size and mosaicity of the crystal. However, simultaneous reflexion occurs more frequently than commonly supposed, and sometimes the change in intensity of the primary reflexion amounts to as much as 10%. Non-equal intensities between equivalent reflexions are partly due to this effect.

In this paper, the orientation problem is treated first and then a practical procedure is described to correct the intensity perturbation due to simultaneous reflexion.

Geometrical condition for simultaneous reflexion

A primary reflexion, say $h_1^0h_2^0h_3^0$, is measured after proper rotations of the crystal to its reflecting position. The geometrical condition for secondary reflexion $h_1h_2h_3$ can be described in terms of the reciprocal-lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ whose orientations with respect to the Cartesian coordinate system attached to the laboratory are assumed to be known for each primary reflexion $h_1^0h_2^0h_3^0$ at its reflecting position.

Three orthogonal unit vectors, $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{e}_3$ forming a right-handed system are defined as follows:

$$\mathbf{e}_3=\frac{\mathbf{b}_1\times\mathbf{b}_2}{|\mathbf{b}_1\times\mathbf{b}_2|}\,,\quad \mathbf{e}_2=\frac{\mathbf{e}_3\times\mathbf{b}_1}{|\mathbf{e}_3\times\mathbf{b}_1|}\,,\quad \mathbf{e}_1=\frac{\mathbf{b}_1}{|\mathbf{b}_1|}\,. \tag{1}$$

In Fig. 1 are illustrated a sphere of reflexion, the reciprocal-lattice vectors and the vectors $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{e}_3$; O is the origin of the reciprocal lattice. Consider a plane P perpendicular to $\mathbf{e}_3$ that passes through the reciprocal-lattice point G whose coordinates are given as $(0,0,h_3)$ with reference to $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$. Let AB a line through the centre of the sphere of reflexion C and parallel to $\mathbf{e}_3$. This line intersects the plane P at A, and also the plane defined by $\mathbf{e}_1$ and $\mathbf{e}_2$ at B. The plane P cuts the sphere of reflexion if

$$|\overrightarrow{CA}|\le R\equiv 1/\lambda\,,$$

where R is the radius of the sphere of reflexion. Obviously,

$$\overrightarrow{CA}=\overrightarrow{CB}+\overrightarrow{BA}=[\mathbf{e}_3\,.\,(R\mathbf{j}+h_3\mathbf{b}_3)]\mathbf{e}_3\,,$$

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therefore

$$|\mathbf{e}_3 \,.\, (R\mathbf{j}+h_3\mathbf{b}_3)| \le R\,, \tag{2}$$

where **j** is the unit vector parallel to the direction of the incident beam. From this equation the upper and lower limits of h_3 can be evaluated. Next let us take a plane Q which passes through a reciprocal-lattice point with coordinates $(0,h_2,0)$ with references to $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ and is perpendicular to $\mathbf{e}_2$. Let a line DAE on P be perpendicular to the intersection FF' of the plane Q with P. Q passes across the circle of intersection between P and the sphere of reflexion if

$$|\overrightarrow{AE}| \le r_3\,,$$

where r_3 is the radius of the circle of intersection and given by

$$r_3 = \sqrt{R^2-|\overrightarrow{CA}|^2} = [R^2-\{\mathbf{e}_3 \,.\, (R\mathbf{j}+h_3\mathbf{b}_3)\}^2]^{1/2}.$$

Noting that $\overrightarrow{AC}$ and $\overrightarrow{GD}$ are perpendicular to $\mathbf{e}_2$, we obtain

$$\begin{aligned}|\overrightarrow{AE}| = |\overrightarrow{AE} \,.\, \mathbf{e}_2| &= |(\overrightarrow{AC}+\overrightarrow{CO}+\overrightarrow{OG}+\overrightarrow{GD}+\overrightarrow{DE}) \,.\, \mathbf{e}_2| \\ &= |(\overrightarrow{CO}+\overrightarrow{OG}+\overrightarrow{DE}) \,.\, \mathbf{e}_2| \\ &= |(R\mathbf{j}+h_2\mathbf{b}_2+h_3\mathbf{b}_3) \,.\, \mathbf{e}_2|\,.\end{aligned}$$

Thus, we have

$$|\mathbf{e}_2 \,.\, (R\mathbf{j}+h_2\mathbf{b}_2+h_3\mathbf{b}_3)| \le r_3\,. \tag{3}$$

The upper and lower limits of h_2 can thus be evaluated for each h_3 from equation (3).

Now we ask whether a point F, at which a line through E and parallel to $\mathbf{e}_1$ intersects with the sphere of reflexion, is a reciprocal-lattice point or not. Noting that $\overrightarrow{BA}$ and $\overrightarrow{AE}$ are perpendicular to $\mathbf{e}_1$,we obtain

$$\begin{aligned}\mathbf{e}_1 \,.\, \overrightarrow{OF} = \mathbf{e}_1 \,.\, (\overrightarrow{OB}+\overrightarrow{BA}+\overrightarrow{AE}+\overrightarrow{EF}) &= \mathbf{e}_1 \,.\, (\overrightarrow{OB}+\overrightarrow{EF}) \\ &= -R(\mathbf{e}_1 \,.\, \mathbf{j}) \pm r_2\end{aligned}$$

where

$$\begin{aligned}r_2 = |\overrightarrow{EF}| &= \sqrt{r_3^2-|\overrightarrow{AE}|^2} \\ &= [r_3^2-\{\mathbf{e}_2 \,.\, (R\mathbf{j}+h_2\mathbf{b}_2+h_3\mathbf{b}_3)\}^2]^{1/2}\,.\end{aligned}$$

We can also put

$$\overrightarrow{OF} = h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3\,.$$

Hence

$$\pm r_2 = \mathbf{e}_1 \,.\, (R\mathbf{j}+h_1\mathbf{b}_1+h_2\mathbf{b}_2+h_3\mathbf{b}_3)\,. \tag{4}$$

The value of h_1 can be evaluated from equation (4) for each h_2 and h_3. The point (h_1,h_2,h_3) is decided to be a lattice point if h_1 is an integer.

The procedure described above can be used to check whether any lattice point lies on a sphere of reflexion for a known crystal orientation giving a primary reflexion, so that we can tell when the condition for the simultaneous reflexion occurs.

Intensity effects

When two or more reciprocal-lattice points are on the sphere of reflexion at the same time, the change in the power of the primary beam $\Delta P_1(T)$ is given by the expression

$$-\frac{\Delta P_1(T)}{P_0(0)} = \tfrac{1}{2}\sum_i(-r_{01}l_0r_{0i}l_0-r_{01}l_0r_{1i}l_1+r_{0i}l_0r_{i1}l_i) \tag{5}$$

(Moon & Shull, 1964). This equation is valid when the crystal may be considered as a flat plate with a thickness T and large compared with the incident-beam cross section. Here $P_0(0)$ is the power of the incident beam, l_i is the path length of the ith beam and r_{ij}, called the linear reflexion coefficient, stands for the exchange of power from i to j per unit path length. It is assumed that the angular width associated with the incident-beam collimation and wavelength spread is much larger than the width of a perfect-crystal reflexion curve, but is much smaller than the width of the mosaic distribution. r_{ij} is given by

$$r_{ij} = Q_{ij}W(\Delta\theta_{ij})\,,$$

where Q_{ij} stands for the integrated reflectivity per unit volume of a small crystallite, and $W(\Delta\theta_{ij})$ is the mosaic distribution function which is usually assumed to be of Gaussian form:

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

where $\Delta\theta_{ij}$ is the deviation in Bragg angle from the mean of the distribution and η is the mosaic spread. It can be shown that

$$\Delta\theta_{ij} = (\sin\psi\cos\chi\cos\xi/\sin 2\theta)_{ij}\Delta\varepsilon = K^{\varepsilon}_{ij}\Delta\varepsilon\,,$$

where $\Delta\varepsilon$ is a small change in angle about the rotation axis and the other angles ψ, χ and ξ as defined in Fig. 2 in the same way as those of Moon & Shull (1964).

The distribution function W may now be written in terms of the rotation angle $\Delta\varepsilon$. The renormalized form is given by

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

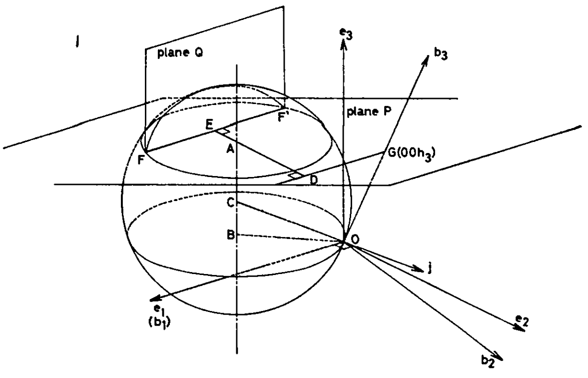

Fig. 1. Illustrating the condition of simultaneous reflexion in reciprocal space. FF' and DE are parallel to $\mathbf{e}_1$ and $\mathbf{e}_2$ respectively.

and the reflectivity expression becomes

$$r_{ij}=Q_{ij}[(2\pi)^{1/2}\eta]^{-1}\exp\left[-(K^{\varepsilon}_{ij}\Delta\varepsilon)^2/2\eta^2\right].$$

In applying equation (5), the following points should be taken into account.

(*a*) The primary and secondary reflexions do not always occur exactly at the same time. The delay between the two reflexions can be expressed in terms of the angle ζ about the rotation axis to bring the secondary reciprocal-lattice point onto the sphere after the primary one has passed it. In Fig. 3, a reciprocal-lattice point S near the sphere of reflexion is shown. The reciprocal-lattice point S reaches T on the surface of the sphere after the rotation ζ around the axis of rotation OV. ζ is expressed as

$$\cos\zeta=\overrightarrow{VS}\,.\,\overrightarrow{VT}/|\overrightarrow{VS}|^2.$$

We must replace $\Delta\varepsilon$ in r_{0i} and r_{1i} in (5) by $\Delta\varepsilon+\zeta$ in order to take this delay into account.

(*b*) Because of the divergence of the incident beam, finite size and the mosaicity of the crystal and wavelength spread, the surface of the sphere of reflexion should be considered as having finite thickness. However, in place of directly taking account of this circumstance, we consider the function $W(\Delta\varepsilon)$ not as a distribution function of mosaicity but as a function representing the broadening of a peak profile. Thus the mosaic spread η is replaced by $x/2\sqrt{2\ln 2}$ where x is the half width of the reflexion peak concerned. When x cannot be measured for each reflexion, we assume that x equals to $A+B\times\sin{}^2\theta$; A and B are determined by a least-squares procedure based on the peaks of known half width.

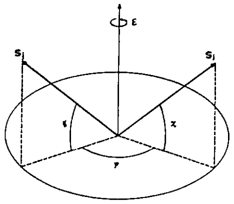

Fig. 2. Definition of angles ψ, χ and ξ. The plane in which ψ is measured is perpendicular to the rotation axis of the crystal. $\mathbf{s}_i$ and $\mathbf{s}_j$ denote the directions of the ith and jth beams, respectively (Moon & Shull, 1964).

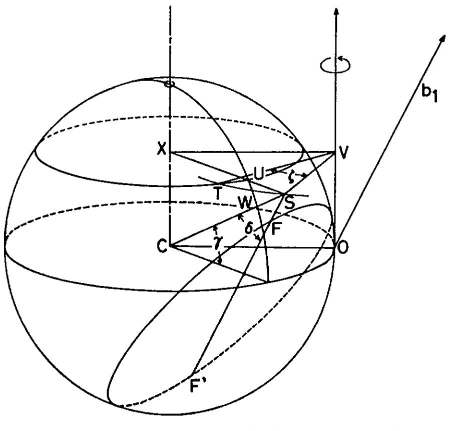

Fig. 3. Illustrating the definition of ζ in (8). A reciprocal-lattice point S is rotated around the rotation axis OV of the crystal and reaches T on the reflexion sphere after the rotation ζ. SX and SC intersect the sphere at U and W respectively.

(*c*) Since a crystal specimen is usually neither a flat plate nor large compared with the incident-beam cross section, we assume that the crystal is a sphere which is small enough compared with the incident-beam cross section and replace the path lengths l_i by $\pi r/2$, the mean path length of a sphere of radius r.

(*d*) In the case of X-ray diffraction, the polarization factor p_{ij} should be considered as introduced by Zachariasen (1965).

With the effects mentioned above combined equation (5) takes the form:

$$\frac{\Delta P_1(T)}{P_0(0)}=\frac{\pi^2r^2}{8}\sum_i(-p_{01}r_{01}p_{0i}r_{0i}-p_{01}r_{01}p_{1i}r_{1i}+p_{0i}r_{0i}p_{i1}r_{i1})\,,\quad(6)$$

where

$$r_{ij}r_{mn}=\frac{Q_{ij}Q_{mn}}{2\pi\eta_{ij}\eta_{mn}}\exp\left[-\frac{K^{\varepsilon2}_{ij}}{2\eta^2_{ij}}\Delta\varepsilon^2-\frac{K^{\varepsilon2}_{mn}}{2\eta^2_{mn}}(\Delta\varepsilon+\zeta)^2\right]\quad(7)$$

and from (*b*), η_{ij} is expressed in terms of x_{ij}

$$\eta_{ij}=\frac{x_{ij}}{(8\ln 2)^{1/2}}\,.\quad(8)$$

The equation (6) can be easily integrated to give

$$\begin{aligned}\frac{\Delta I_1}{I_1}&=\frac{\sqrt{\pi r^2}}{8}Q_{01}\sum_i(-G_{01;0i}-G_{01;1i}+G_{0i;i1})\\&=\frac{\sqrt{\pi r^2}}{8}Q_{01}\sum_i\left[-g_{01;0i}\left(\frac{Q_{0i}}{Q_{01}}\right)-g_{01;1i}\left(\frac{Q_{1i}}{Q_{01}}\right)+g_{01;i1}\left(\frac{Q_{0i}}{Q_{01}}\right)\left(\frac{Q_{i1}}{Q_{01}}\right)\right],\end{aligned}\quad(9)$$

where

$$G_{ij;mn}=g_{ij;mn}\left(\frac{Q_{ij}}{Q_{01}}\right)\left(\frac{Q_{mn}}{Q_{01}}\right),$$

$$g_{ij;mn}=\frac{p_{ij}}{\eta_{ij}}\cdot\frac{p_{mn}}{\eta_{mn}}f\left(\frac{K^{\varepsilon2}_{ij}}{2\eta^2_{ij}},\frac{K^{\varepsilon\,2}_{mn}}{2\eta^2_{mn}}\right)$$

and

$$\begin{aligned}f(a,b)&=\int_{-\infty}^{\infty}\exp\left[-\{a\Delta\varepsilon^2+b(\Delta\varepsilon+\zeta)^2\}\right]d\Delta\varepsilon\\&=\sqrt{\frac{\pi}{a+b}}\exp\left(-\frac{ab}{a+b}\zeta^2\right).\end{aligned}\quad(10)$$

The first and the second terms of equation (9) represent a diminution, and the third one an increase in the primary intensity respectively. $g_{ij;mn}$ is the damping term mentioned above.

Detection of secondary reflexions

A program was written in Fortran to detect the secondary reflexions on the basis of equations (2) to (4). Indexing of secondary reflexions around the scattering vector in the case of Ge 222 reflexion was also carried out by Cole, Chambers & Dunn (1962). The present calculation was done for Cu $K\alpha_1$, at every 0·01° around the scattering vector, assuming that the crystal specimen at 20 °C is so mounted on a four-circle diffractometer that the directions of the reciprocal-lattice vectors $\mathbf{b}_2$ and $\mathbf{b}_3$ coincide with those of the incident beam and of the axis of rotation respectively; in other words, the **U** matrix (Busing & Levy, 1967) becomes a unit matrix. The results, listed in Table 1, agree well with those obtained by Cole *et al.*, (1962).

Table 1. *Calculated secondary reflexions*

ψ is the rotation angle around the scattering vector. Primary reflexion: Ge 222, λ = 1·54051 Å

Secondary reflexion	ψ	Secondary reflexion	ψ	Secondary reflexion	ψ
220	180·00	$\bar{4}24$	190·95	153	201·87
002	180·00	$\bar{4}44$	191·00	151	202·08
$\bar{5}31$	182·10	$\bar{3}35$	193·83	004	202·22
$15\bar{1}$	183·48	$\bar{3}5\bar{1}$	193·97	$\bar{3}15$	202·33
240	184·11	$13\bar{1}$	194·16	$\bar{1}\bar{1}3$	205·18
$02\bar{2}$	184·12	$\bar{5}33$	195·73	$\bar{1}\bar{1}1$	208·21
113	185·43	$\bar{2}04$	195·77	$\bar{4}40$	209·14
$04\bar{2}$	186·02	$\bar{2}60$	196·85	$\bar{2}62$	209·14
$\bar{1}35$	187·74	$\bar{4}02$	198·17	$\bar{3}\bar{1}3$	209·53
$\bar{2}2\bar{2}$	190·85	$\bar{1}15$	198·31	$\bar{5}13$	209·90
$\bar{2}4\bar{2}$	190·85	$\bar{1}5\bar{1}$	198·56	$\bar{3}3\bar{1}$	210·47
060	190·85	062	200·05	$\bar{5}31$	210·10
242	190·85	$\bar{3}1\bar{1}$	201·87		

Intensity correction

X-ray and neutron diffraction analyses of diformylhydrazine have been carried out. The crystal data (from Tanaka & Saito, 1975) are space group $P2_1/a$, a = 8·9874 (15), b = 6·2617 (7), c = 3·5846 (7) Å, β = 113·05 (2)° at 23 °C, Z = 2. A program written in Fortran was used to correct the intensity perturbation, as follows.

Experimental

The crystal was shaped into a sphere of radius 0·33 mm on a sheet of wet filter paper. The path length of the incident beam between the source and the graphite monochromator was 50 mm, and the distance between the monochromator and the crystal was 225 mm. A collimator, 0·25 mm in radius, was placed at a distance of 196·5 mm from the monochromator.

As the magnitude of perturbation due to the simultaneous reflexion effect was expected to be small in this case, the correction for the simultaneous reflexion effect is meaningful only when other errors, in particular those due to statistical counting, are at low levels. Thus each reflexion was repeatedly measured using Mo $K\alpha$ radiation (λ = 0·7107 Å) to reduce statistical counting errors to less than one per cent of the observed structure factor except for very weak reflecions. The maximum number of repetitions was ten. Intensities of Friedel pairs were averaged since the geometrical conditions for the simultaneous reflexion effect are the same for the two reflexions in the pair.

It was found, as an important feature revealed after the correction, that intensity differences between symmetry-related reflexions larger than the statistical counting error can be mainly ascribed to the effect of simultaneous reflexion, though small differences remained unexplained. Some typical examples for which the perturbation is more than twice its statistical counting error are listed in Table 2, where σ_F represents the largest value among statistical errors and the difference between the observed structure factors of Friedel's pair. ΔF is $(F_o - F_{o_{\rm cor}})/F_o$, and hkl and $h\bar{k}l$ are symmetry-related reflexions. The maximum value of correction is as large as 17%. The number of Friedel pairs perturbed more than one per cent is 83, out of 2888 pairs, and those perturbed more than S per cent of its σ_F are tabulated in Table 3. The fluctuation between the symmetry-related reflexions could be definitely reduced for about 60% of the reflexions. The remaining 40% may be affected by uncertainties in η and in the setting parameters. In the final difference synthesis, bonding electron density as well as lone-pair electron density was clearly visible.

Table 2. *Primary reflexions for which the perturbations are more than twice their statistical errors*

hkl and $h\bar{k}l$ are symmetry-related reflexions. Data are for diformylhydrazine (X-ray diffraction).

hkl	F_o	$F_{o_{\rm cor}}$	σ_F	$\Delta F\times 10^2$*
$\bar{5}32$	186·54	180·51	2·49	3·34
$\bar{5}\bar{3}2$	178·77	178·81	1·18	−0·01
$\bar{4}\bar{2}2$	131·22	130·21	0·56	0·78
$\bar{4}22$	129·70	129·71	0·57	−0·01
$\bar{4}\bar{4}2$	95·60	93·51	0·50	2·22
$\bar{4}42$	94·12	94·13	0·74	−0·01
$1\bar{4}1$	67·77	66·43	0·48	2·02
141	65·95	65·97	0·40	−0·03
041	55·81	54·87	0·92	1·71
$0\bar{4}1$	55·24	55·35	0·51	−0·19
232	48·25	44·79	1·11	7·72
$2\bar{3}2$	41·69	41·69	0·67	−0·00
432	45·39	43·65	0·73	3·98
$4\bar{3}2$	44·39	44·40	0·32	−0·02
$6\bar{4}2$	41·27	39·59	0·44	4·25
642	38·61	38·69	0·41	−0·21
$4\bar{4}1$	29·30	25·16	0·77	16·44
441	25·28	25·28	0·40	−0·02
$\bar{4}\bar{6}3$	17·12	14·60	0·75	17·32
$\bar{4}63$	15·14	15·14	0·86	−0·02
261	14·14	12·15	1·60	16·43
$2\bar{6}1$	10·16	10·16	2·10	−0·03

* $\Delta F = (F_o - F_{o_{\rm cor}})/F_o$

Table 3. *Numbers of reflexions which are perturbed by more than S percent of their statistical errors*

S		S		S		S	
10	634	50	96	80	60	150	29
20	296	60	86	90	54	200	19
30	187	70	72	100	48	300	9
40	119						

Discussion

From (5) the following criterion has been drawn by Coppens (1968). Significant intensity changes due to simultaneous reflexion will be avoided when no reciprocal-lattice points representing strong reflexions are located on either the sphere of reflexion corresponding to the incident beam, or that corresponding to the primary diffracted ray. Therefore, if the lattice points corresponding to strong reflexion are on the sphere of reflexion, the large simultaneous-reflexion effect can be avoided by rotating the crystal around the scattering vector. However, all simultaneous-reflexion effects cannot be avoided in this way, especially for a crystal of large unit cell and in the case of neutron diffraction. This effect occurs so frequently that its elimination is not only impossible but the accumulation of the effects may become significant. In the case of neutron diffraction the divergence of the incident beam, wavelength spread and the size of the crystal are very large, so that the chance of a simultaneous-reflexion effect occurring is very high and the damping term $g_{ij;mn}$ in (10) becomes small. In addition, a long path length may contribute directly to this effect, as seen in (10). This is one reason why we have proposed a practical method to correct this effect.

In the case of Ge 222 described above, it takes no more than one second on a FACOM 270-30 computer to calculate the secondary reflexions at a given angle around the scattering vector. The computing time can be greatly reduced in our method, since only the reciprocal-lattice points in the vicinity of the surface of the sphere of reflexion are checked.

There are a few remarks concerning the correction procedure.

(*a*) Generally, h_1 calculated from (4) is not an integer. Let the value of h_1 be $H_1+\varDelta H_1$, where H_1 is an integer and $-0{\cdot}5<\varDelta H_1\le 0{\cdot}5$. If $\varDelta H_1$ is small, the reciprocal-lattice point $S(H_1h_2h_3)$ lies close to the surface of the sphere of reflexion. The criterion used to decide whether or not $S(H_1h_2h_3)$ takes part in the simultaneous reflexion is as follows; if

$$\zeta_{H_1h_2h_3}\le\zeta^0$$

$S(H_1h_2h_3)$ is assumed to cause the simultaneous reflexion, where ζ^0 was fixed to 0·03 radian in this case. This value is slightly larger than the peak widths $\varDelta\omega_{h_1^0h_2^0h_3^0}$ of most of the primary beams with 2θ below 120°. The delay angle $\zeta_{H_1h_2h_3}$ can be obtained as a function of $\varDelta H$ as follows: since S is near the surface of the sphere of reflexion as illustrated in Fig. 3, we have

$$|\overrightarrow{SU}|=\varDelta R\sec\gamma\approx r\zeta_{H_1h_2h_3}\cos\alpha\,,$$

where r is the distance between S and the axis of rotation OV, $\varDelta R=|\overrightarrow{SW}|=||\overrightarrow{CS}|-R|$ is the distance between S and the surface of the sphere and $\alpha=\angle TSU$. Since S lies on FF' which is parallel to $\mathbf{b}_1$ and is close to F, we obtain

$$|FS|=|b_1|\varDelta H_1\approx\varDelta R\sec\delta\,.$$

From the above two equations we have

$$\varDelta H_1=(r\cos\gamma\cos\alpha/|\mathbf{b}_1|\cos\delta)\zeta_{H_1h_2h_3}\equiv K_S\zeta_{H_1h_2h_3}\,. \quad (11)$$

Thus if

$$\varDelta H_1\le K_S\zeta^0\,, \quad (12)$$

the correction for intensity perturbation due to simultaneous reflexion was carried out.

(*b*) We have approximated the peak shape as Gaussian. It has a long tail around the peak due to the exponential character of this function. Consequently, even when the delay angle ζ was large and the simultaneous reflexion effects were expected to be negligible, the calculated perturbation became significant if Q_{0i} or Q_{1i} was large compared with Q_{01}. In order to avoid this overestimation, the correction was not made when the delay angle ζ was greater than $C\times(\eta_{01}/K^{\varepsilon}_{01}+\eta_{01}/K^{\varepsilon}_{0i})$ *etc.*, where C is a constant and $(2\ln 2)^{1/2}\eta_{ij}/K_{ij}$ is an effective half width of the reflexion ij. The difference between equivalent reflexions became smallest when C was 0·375 in this case, though most of the corrected values did not vary with C.

(*c*) When the half widths of most of the reflexions were measured and used for correction, it turned out that the results were much improved compared with the results calculated by $A+B\times\sin^2\theta$ for the half width. This fact indicates that the method of correction is most successful when an observed half width is used as well as accurate setting parameters.

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