larization factor for double diffraction with one monochromator is therefore:

$$P(\xi_1,\xi_2,\theta,\theta_M)=\{Q(\cos^2\chi+\sin^2\chi\,\cos^2\xi_2)+\cos^2\xi_1(\sin^2\chi+\cos^2\chi\,\cos^2\xi_2)+(1-Q)\cos^2\varphi(\cos^2\chi\,\sin^2\chi\,\cos^2\xi_1-\sin^2\chi\,\cos^2\xi_2-\cos^2\chi\,\cos^2\xi_1\,\cos^2\xi_2)\}/2\,. \quad (A9)$$

Including the effect of the second monochromator yields:

$$P(\xi_1,\xi_2,\theta,\theta_M)=[D\{\cos^2\gamma\,\cos^2\chi+\sin^2\gamma\,\sin^2\chi\,\cos^2\xi_2\}+B[\cos^2\gamma\,\sin^2\chi\,\cos^2\xi_1+\sin^2\gamma\,\cos^2\chi\,\cos^2\xi_1\,\cos^2\xi_2]+Q\{D[\sin^2\gamma\,\cos^2\chi+\cos^2\gamma\,\sin^2\chi\,\cos^2\xi_2]+B[\sin^2\gamma\,\sin^2\chi\,\cos^2\xi_1+\cos^2\chi\,\cos^2\gamma\,\cos^2\xi_1\,\cos^2\xi_2]\}]/2 \quad (A10)$$

where:

$$D=Q+(1-Q)\cos^2\varphi$$
$$B=1-(1-Q)\cos^2\varphi\,.$$

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Theory of X-Ray Diffraction In Crystals With Stacking Faults

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(*Received* 28 *June* 1966)

X-ray diffraction in a crystal with stacking disorder is studied theoretically. It is assumed that the layers are identical and equidistant. If $\mathbf{a}_2$ is the stacking direction, diffraction occurs when the scattering vector $\mathbf{s}$ satisfies the condition $\mathbf{s}=2\pi[H_1\mathbf{b}_1+y\mathbf{b}_2+H_3\mathbf{b}_3]$, where H_1, H_3 are integers, but y may have any value. As to intensity of scattering, the observable quantity is the integrated intensity $P_{H_1H_3}(y)$, and the detailed expression for this function is deduced. For an ordered crystal the integrated intensity is invariant under the symmetry operations of the crystal as applied to the indices $H_1H_2H_3$, but this is not true in general of $P_{H_1H_3}(y)$. Thus $P_{H_1H_3}(y)\neq P_{H_1H_3}(-y)$ when $\mathbf{b}_2$ is the normal to a mirror plane. It is shown how the precise nature of the stacking disorder can be deduced by means of a detailed analysis of the experimental curves $P_{H_1H_3}(y)$.

Introduction

A structure study of a single crystal of β-$Ca(BO_2)_2$ was recently begun by the writer. The crystal is orthorhombic with periods $a_1=8{\cdot}369\pm0{\cdot}001$, $a_2=13{\cdot}816\pm0{\cdot}001$, $a_3=5{\cdot}007\pm0{\cdot}001$ Å; but the X-ray diffraction patterns are unusual. Diffraction occurs for integral values of the Miller indices H_1 and H_3, and when H_3 is even also for integral values of H_2. However, diffraction takes place for any value y of the second index when H_3 is odd. In other words, the diffraction conditions are those of a three-dimensional lattice if H_3 is even, those of a two-dimensional lattice if H_3 is odd. The diffraction vectors $\mathbf{s}$ are thus of the form

$$H_3 \text{ even: } \mathbf{s}=2\pi[H_1\mathbf{b}_1+H_2\mathbf{b}_2+H_3\mathbf{b}_3]$$
$$H_3 \text{ odd: } \mathbf{s}=2\pi[H_1\mathbf{b}_1+y\mathbf{b}_2+H_3\mathbf{b}_3] \quad (1)$$

where y may have any value.

Extensive integrated intensity measurements have been made for zones $[H_1yH_3]$ with H_3 odd, using both Cu $K\alpha$ radiation with a 'normal beam' counter spectrometer and Mo $K\alpha$ radiation with a 'goniostat' spectrometer. As an illustration Table 1 shows the measured values of the integrated intensity $P_{H_1H_3}(y)$ for the reciprocal lattice row $[2y1]$ at intervals of 0·1 for y over the range $-9\leq y\leq+9$. Intensity maxima occur at integral and half-integral values of y, but about eighty per cent of the scattering is in the background between the maxima. The most remarkable feature of Table 1 is the experimental fact that the integrated intensities $P_{H_1H_3}(y)$ and $P_{H_1H_3}(\bar{y})$ are different. The symmetry of the crystal being centrosymmetric orthorhombic, one has $|F_{H_1H_3}(y)|=|F_{H_1H_3}(\bar{y})|$, and it is, therefore, startling to find that the integrated intensity is not invariant under the symmetry operations of the crystal.

The observed diffraction geometry as expressed in equation (1) is explained by stacking disorder in the $\mathbf{a}_2$ direction with a choice between displacements Δ and $\Delta+\frac{1}{2}\mathbf{a}_3$ normal to $\mathbf{a}_2$.

The X-ray diffraction effects in a crystal with stacking disorder have been studied theoretically by several workers, and the expression for the scattered intensity $J_{H_1H_3}(y)$ as function of position in the reciprocal lattice has been derived. This function does exhibit the symmetry of the crystal, and hence does not explain the lack of symmetry in the experimental data of Table 1.

Experimentally one does not measure $J_{H_1H_3}(y)$, but the integrated intensity function $P_{H_1H_3}(y)$ which represents the total power of the diffracted beam entering the counter with a convergent beam incident on the crystal. A detailed interpretation of experimental data requires a knowledge of the dependence of $P_{H_1H_3}(y)$ on $J_{H_1H_3}(y)$, but this relationship has not been established.

It is the purpose of the present paper to derive the general expression for the integrated intensity function $P_{H_1H_3}(y)$. For the sake of completeness the formula for the intensity distribution in the reciprocal lattice, $J_{H_1H_3}(y)$, will be derived again.

In a subsequent paper the theoretical results of the present article will be applied to the specific case of β-$Ca(BO_2)_2$, and it will be shown that all experimental data [including the difference between $P_{H_1H_3}(y)$ and $P_{H_1H_3}(\bar{y})$] are in quantitative agreement with theory.

The intensity distribution in the reciprocal lattice, $J_{H_1H_3}(y)$

The atomic positions in a crystal with stacking faults in the $\mathbf{a}_2$ direction are of the form $\mathbf{r}_f+L_1\mathbf{a}_1+L_2\mathbf{a}_2+L_3\mathbf{a}_3+\Delta_{L_2}$, where Δ_{L_2} is not periodic in L_2. It will be assumed that the layers are stacked equidistantly, *i.e.* that $\Delta_{L_2}\,.\,\mathbf{b}_2=0$. As to the shape of the crystal, it is convenient to set $0\leq L_i\leq N_i-1$ with N_i a larger integer. The volume of the crystal, δV, is thus $\delta V=N_1N_2N_3V$ with $V=\mathbf{a}_1\,.\,\mathbf{a}_2\times\mathbf{a}_3$ the volume of the unit cell.

Imagine a plane wave of X-rays with propagation direction $\mathbf{u}_0$ incident upon the crystal and consider a scattering direction $\mathbf{u}$, so that $\mathbf{s}=2\pi\lambda^{-1}(\mathbf{u}-\mathbf{u}_0)$ is the scattering vector. In the kinematical approximation the intensity of the scattered X-rays is

$$I(\mathbf{s})=I_e|F|^2S_1S_3|T|^2\,. \tag{2}$$

$I_e=I_0(e^2/mc^2R)^2p$, with p the polarization factor, is the J.J.Thomson scattering for a single electron. $F=\Sigma f_j\exp(i\mathbf{s}\,.\,\mathbf{r}_j)$, and the symbols S_i and T have the following meanings:

$$S_i=\sin^2(\tfrac{1}{2}N_i\mathbf{s}\,.\,\mathbf{a}_i)/\sin^2(\tfrac{1}{2}\mathbf{s}\,.\,\mathbf{a}_i)\,, \tag{2a}$$

$$T=\sum_0^{N_2-1}\exp[i\mathbf{s}\,.\,(L_2\mathbf{a}_2+\Delta_{L_2})]\,. \tag{2b}$$

If $\mathbf{s}\,.\,\Delta_{L_2}$ is periodic in L_2 (which is possible for some values of $\mathbf{s}$ even though Δ_{L_2} is not periodic) with period K, it is convenient to introduce a new vector $\mathbf{a}_2'=K\mathbf{a}_2$.

Table 1. *Integrated intensities*,* $P_{21}(y)$ and $P_{21}(\bar{y})$

y	$P_{21}(y)$	$P_{21}(\bar{y})$	y	$P_{21}(y)$	$P_{21}(\bar{y})$	y	$P_{21}(y)$	$P_{21}(\bar{y})$
0	13	13	3·0	560	459	6·0	1474	926
0·1	15	18	3·1	269	221	6·1	1178	571
0·2	20	19	3·2	193	151	6·2	979	501
0·3	22	28	3·3	150	127	6·3	931	456
0·4	33	31	3·4	115	98	6·4	966	499
0·5	39	42	3·5	97	74	6·5	1146	581
0·6	57	54	3·6	55	45	6·6	1127	550
0·7	57	63	3·7	36	31	6·7	1063	510
0·8	78	79	3·8	27	20	6·8	1146	535
0·9	123	118	3·9	16	11	6·9	1364	649
1·0	281	277	4·0	7	6	7·0	1914	990
1·1	172	159	4·1	9	6	7·1	1531	617
1·2	175	172	4·2	10	16	7·2	1156	479
1·3	186	179	4·3	26	23	7·3	956	410
1·4	225	215	4·5	49	34	7·4	896	399
1·5	273	262	4·4	98	67	7·5	873	387
1·6	259	234	4·6	122	83	7·6	742	318
1·7	278	251	4·7	142	106	7·7	652	262
1·8	318	292	4·8	199	135	7·8	638	246
1·9	393	369	4·9	311	209	7·9	698	258
2·0	787	711	5·0	609	436	8·0	741	335
2·1	436	374	5·1	479	293	8·1	582	181
2·2	369	320	5·2	475	279	8·2	370	134
2·3	347	301	5·3	463	290	8·3	273	99
2·4	351	301	5·4	545	340	8·4	208	74
2·5	407	363	5·5	678	406	8·5	150	57
2·6	354	300	5·6	640	378	8·6	118	44
2·7	309	269	5·7	638	373	8·7	73	27
2·8	320	274	5·8	735	440	8·8	34	14
2·9	353	301	5·9	914	538	8·9	18	8
3·0	560	459	6·0	1474	926	9·0	12	5

* The data were obtained with a goniostat spectrometer, using Mo $K\alpha$ radiation, a 2° take-off angle and the balanced-filter technique.

Equation (2) then reduces to the familiar expression for a structure periodic in three dimensions

$$I(s)=I_e|F|^2S_1S_2S_3 \tag{3}$$

with S_2 and F now referring to the cell $\mathbf{a}_1$, $\mathbf{a}_2'$, $\mathbf{a}_3$.

When $\mathbf{s}\,.\,\Delta_{L_2}$ is not periodic in L_2, it will be assumed that the scattering from the crystal specimen under consideration is the same as for a statistical sample of the disordered crystal. With this assumption one has

$$|T|^2=N_2+\sum_1^{N_2-1}(N_2-M)[W_M\exp(iM\mathbf{s}\,.\,\mathbf{a}_2) + W_M^*\exp(-iM\mathbf{s}\,.\,\mathbf{a}_2)], \tag{4a}$$

$$W_M=\langle\exp[i\mathbf{s}\,.\,(\Delta_{L_2+M}-\Delta_{L_2})]\rangle\,. \tag{4b}$$

The correlation coefficient, W_M, is the expectation value for the interference of two layers M spacings apart.

If stacking disorder is present as postulated, no correlation exists between the displacements of layers very far apart, *i.e.* $W_M\neq 0$ only for $|M|\ll N_2$. Thus equation (4) may be approximated as follows

$$|T|^2=N_2\,\Sigma\,W_M\exp(iM\mathbf{s}\,.\,\mathbf{a}_2) \tag{5}$$

where $W_0=1$, $W_{-M}=W_M^*$, and the summation extends over positive and negative integers. The basic intensity expression for the study of the assumed stacking disorder is accordingly

$$I(s)=I_e|F|^2S_1S_3N_2\,\Sigma\,W_M\exp(iM\mathbf{s}\,.\,\mathbf{a}_2)\,. \tag{6}$$

The product S_1S_3 vanishes unless the corresponding Laue equations are exactly or very nearly satisfied, *i.e.* $\mathbf{s}=2\pi[(H_1+\varepsilon_1)\mathbf{b}_1+y\mathbf{b}_2+(H_3+\varepsilon_3)\mathbf{b}_3]$ and $I(\mathbf{s})=0$ unless $|\varepsilon_i|\ll 1$. $I(\mathbf{s})$, regarded as function of position in reciprocal space, is thus different from zero only in the immediate vicinity of the reciprocal lattice rows $[H_1yH_3]$, and for a particular row one may set $I(\mathbf{s})=I_{H_1H_3}(\varepsilon_1,y,\varepsilon_3)$. The total intensity associated with the point y on a given row, $J_{H_1H_3}(y)$, is given by $J_{H_1H_3}=\iint I_{H_1H_3}d\varepsilon_1d\varepsilon_3$. Since I_e and F are slowly varying functions of $\mathbf{s}$, they can be treated as constants over the integration range, and one has in consequence

$$J_{H_1H_3}(y)= I_e|F_{H_1H_3}(y)|^2V^{-1}\delta V\,\Sigma\,W_M^{H_1H_3}\exp(i2\pi My)\,, \tag{7}$$

where $F_{H_1H_3}$ and $W_M^{H_1H_3}$ are the values of F and W_M for $\mathbf{s}=2\pi[H_1\mathbf{b}_1+y\mathbf{b}_2+H_3\mathbf{b}_3]$.

The formula for $J_{H_1H_3}$ given in equation (7) has been derived before (see *e.g.* Zachariasen, 1947, 1948). It can be put in the form

$$J_{H_1H_3}=Cp|F_{H_1H_3}|^2D_{H_1H_3}\,, \tag{7a}$$

where C is a constant and

$$D_{H_1H_3}\equiv\Sigma\,W_M^{H_1H_3}\exp(i2\pi My)\,.$$

$D_{H_1H_3}$ is periodic in y with period unity and satisfies the condition

$$\int_y^{y+1}D_{H_1H_3}dy=1\,. \tag{8}$$

Since $p|F_{H_1H_3}|^2$ is a slowly varying function of y, it is in general possible to find both functions $|F_{H_1H_3}|$ and $D_{H_1H_3}$ once $J_{H_1H_3}$ is known, and accordingly also the correlation coefficients $W_M^{H_1H_3}$.

It is seen from equation (7) that $J_{H_1H_3}(y)$ has the symmetry of the crystal. Specifically one has $J_{H_1H_3}(y)=J_{H_1H_3}(\bar{y})$ if $|F_{H_1H_3}(y)|=|F_{H_1H_3}(-y)|$.

The integrated intensity, $\mathbf{P}_{\mathrm{H_1H_3}}(\mathbf{y})$

In experiments a convergent incident beam is used, and one measures the total power of the diffracted beam as recorded in the counter.

Let the incident beam and the line focus of the X-ray tube lie in the horizontal plane with $\mathbf{u}_0^0$ the direction of the central ray of incidence. If the height of the line focus is neglected, the direction of a neighboring ray of incidence is $\mathbf{u}_0=\mathbf{u}_0^0+\Delta\mathbf{u}_0$, where $\Delta\mathbf{u}_0$ has one degree of freedom. It is convenient to use a cartesian set of unit vectors, $\mathbf{i}$, $\mathbf{j}$, $\mathbf{k}$ such that $\mathbf{i}=\mathbf{u}_0^0$ and $\mathbf{k}$ is vertical. Then $\mathbf{u}_0=\mathbf{u}_0^0+\Delta\mathbf{u}_0=\mathbf{i}+\alpha_1\mathbf{j}$ with $-\frac{1}{2}\Delta_1\leq\alpha_1\leq\frac{1}{2}\Delta_1$, Δ_1 being the total convergence. It will be assumed that the incident intensity, I_0, is constant over the range of α_1.

The diffraction direction $\mathbf{u}^0$ which corresponds to the incidence direction $\mathbf{u}_0^0$ satisfies the condition $\mathbf{u}^0-\mathbf{u}_0^0=\lambda[H_1\mathbf{b}_1+y\mathbf{b}_2+H_3\mathbf{b}_3]$, and one imagines the counter to be set so that its axis coincides with such a direction $\mathbf{u}^0$. For a neighboring ray entering the counter the direction is $\mathbf{u}=\mathbf{u}^0+\Delta\mathbf{u}$, and one has

$$\Delta\mathbf{u}-\Delta\mathbf{u}_0=\lambda[\varepsilon_1\mathbf{b}_1+\varepsilon_2\mathbf{b}_2+\varepsilon_3\mathbf{b}_3]\,. \tag{9}$$

The orientation of the counter can be described by the two angles ψ and φ which represent the horizontal and vertical projections of the scattering angle 2θ. Thus $\cos 2\theta=\cos\psi\cos\varphi$ and

$$\mathbf{u}^0=\cos\psi\cos\varphi\mathbf{i}+\sin\psi\cos\varphi\mathbf{j}+\sin\varphi\mathbf{k} \tag{10}$$

while the neighboring scattering direction $\mathbf{u}$ corresponds to angles $\psi+\alpha_2$, $\varphi+\alpha_3$. The vector $\Delta\mathbf{u}-\Delta\mathbf{u}_0$ of equation (9) may hence also be expressed in terms of the three variables α_1, α_2, α_3 as follows:

$$\Delta\mathbf{u}-\Delta\mathbf{u}_0=-(\alpha_2\sin\psi\cos\varphi+\alpha_3\cos\psi\sin\varphi)\mathbf{i} -(\alpha_1-\alpha_2\cos\psi\cos\varphi+\alpha_3\sin\psi\sin\varphi)\mathbf{j} +\alpha_3\cos\varphi\mathbf{k}\,. \tag{11}$$

The total power recorded in the counter is the integrated intensity $P_{H_1H_3}(y)$ given by

$$P_{H_1H_3}(y)=\int\!\!\int\!\!\int I_{H_1H_3}(\varepsilon_1,y+\varepsilon_2,\varepsilon_3)d\alpha_1dS\,, \tag{12}$$

where $dS=R^2\cos\varphi\,d\alpha_2d\alpha_3$ is an elementary area of the counter aperture and R is the distance from the crystal. The integrand is given by equation (6) with

$$\mathbf{s}=2\pi[(H_1+\varepsilon_1)\mathbf{b}_1+(y+\varepsilon_2)\mathbf{b}_2+(H_3+\varepsilon_3)\mathbf{b}_3]\,.$$

If the counter aperture is circular with maximum angular divergence Δ_2, one has

$$-\tfrac{1}{2}\Delta_2\leq\sqrt{\alpha_2^2\cos^2\varphi+\alpha_3^2}\leq\tfrac{1}{2}\Delta_2\,. \tag{13}$$

The integral of equation (12) is readily evaluated by using the Jacobians from equations (9) and (11), and the result is

$$P_{H_1H_3}(y)=\frac{R^2\lambda^3}{V\sin\psi\cos\varphi}\int J_{H_1H_3}(y+\varepsilon_2)d\varepsilon_2\,. \qquad (14)$$

Let the variable ε_2 range from $-\frac{1}{2}\Delta y$ to $+\frac{1}{2}\Delta y$. If Δy is so small that $J_{H_1H_3}$ does not change appreciably over the range, one has

$$\int J_{H_1H_3}(y+\varepsilon_2)d\varepsilon_2\simeq J_{H_1H_3}(y)\Delta y\,. \qquad (15)$$

However, this assumption is not usually valid, so that the exact expression must be used and this is

$$\int J_{H_1H_3}(y+\varepsilon_2)d\varepsilon_2=I_e|F_{H_1H_3}(y)|^2\Delta y V^{-1}\delta V\,\Sigma\, W_M^{H_1H_3}\times\frac{\sin\pi M\Delta y}{\pi M\Delta y}\exp(i2\pi My). \qquad (16)$$

The detailed formula for the integrated intensity is thus

$$P_{H_1H_3}(y)=I_0(e^2)/(mc^2V)^2\lambda^3\delta V|F_{H_1H_3}|^2\times\frac{1+\cos^2 2\theta}{2}\frac{\Delta y}{\sin\psi\cos\varphi}D'_{H_1H_3}$$

$$D'_{H_1H_3}(y)=\Sigma\, W_M^{H_1H_3}\frac{\sin\pi M\Delta y}{\pi M\Delta y}\exp(i2\pi My)\,, \qquad (17)$$

where $p=(1+\cos^2 2\theta)/2$ corresponds to unpolarized incident radiation. In deriving equation (17) it is assumed that absorption is negligible. However, absorption effects are readily included. Relative intensity measurements are usually made, and one may set

$$P_{H_1H_3}(y)=CApL'|F_{H_1H_3}|^2D'_{H_1H_3}\,, \qquad (18)$$

where C is a scale factor, A is the transmission factor and $L'\equiv\Delta y/\sin\psi\cos\varphi$ may suitably be called the two-dimensional Lorentz factor.

The two-dimensional Lorentz factor, L'

In order to apply equation (17) or (18) to experimental data it is necessary to know the expressions for Δy and L'.

The physical meaning of Δy (which is a function of y and of the geometry) becomes apparent when one considers the diffraction condition $\lambda^{-1}[\mathbf{u}-\mathbf{u}_0]=H_1\mathbf{b}_1+y\mathbf{b}_2+H_3\mathbf{b}_3$ in the reciprocal lattice. The value of y in this relation is determined by the requirement that $|\mathbf{u}|=|\mathbf{u}_0|=1$. If the sphere of reflection corresponding to a direction $\mathbf{u}_0$ is drawn, $\lambda^{-1}\mathbf{u}$ will be the radius vector to the intersection point of the sphere with the lattice row $[H_1yH_3]$.

In the incident beam all directions $\mathbf{u}_0=\mathbf{i}+\alpha_1\mathbf{j}$ with $-\frac{1}{2}\Delta_1\le\alpha_1\le\frac{1}{2}\Delta_1$ are present. This is indicated in Fig. 1 by the two spheres corresponding to the extreme values $\mathbf{u}_0=\mathbf{i}\pm\frac{1}{2}\Delta_1\mathbf{j}$. If the counter aperture is wide enough to admit the entire diffracted beam, then $b_2\Delta y$ is simply the segment of the lattice row lying between the two spheres as shown in Fig. 1.

However, if the divergence δ of the diffracted beam exceeds the angular divergence Δ_2 of the counter aperture only the fraction Δ_2/δ of the diffracted beam will enter the counter, and the value of Δy obtained from Fig. 1 must be reduced by this factor.

The function $I_{H_1H_3}(\varepsilon_1,y+\varepsilon_2,\varepsilon_3)$ is a delta function in ε_1 and ε_3. For the present purpose it is, therefore, justifiable in equation (9) to neglect ε_1 and ε_3 relative to ε_2, and by combination of equation (9) with equation (11) one finds the following set of equations relating ε_2 to α_1, α_2, α_3:

$$\frac{|\varepsilon_2|}{\sin\psi\cos\varphi}=\frac{|\alpha_1|}{\lambda|\mathbf{b}_2\,.\,\mathbf{u}^0|}=\frac{|\alpha_2|}{\lambda|\mathbf{b}_2\,.\,\mathbf{i}+\mathbf{b}_2\,.\,\mathbf{k}\cos\psi\tan\varphi|}=\frac{|\alpha_3|}{\lambda|\mathbf{b}_2\,.\,\mathbf{k}|\sin\psi} \qquad (19)$$

where $2|\alpha_1|\le\Delta_1$ and $2\sqrt{\alpha_2^2\cos^2\varphi+\alpha_3^2}\le\Delta_2$.

The divergence δ of the diffracted beam associated with the maximum convergence Δ_1 of the incident beam is

$$\delta=\left|\frac{\Delta_1}{\mathbf{b}_2\,.\,\mathbf{u}^0}\right|\sqrt{(\mathbf{b}_2\,.\,\mathbf{i}\cos\varphi+\mathbf{b}_2\,.\,\mathbf{k}\cos\psi\sin\varphi)^2+(\mathbf{b}_2\,.\,\mathbf{k}\sin\psi)^2}\,. \qquad (20)$$

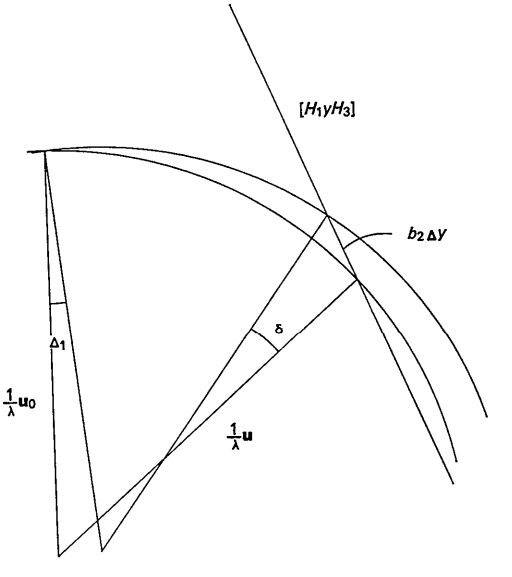

Fig. 1. The construction of $b_2\Delta y$ in the reciprocal lattice. For simplicity the lattice row $[H_1yH_3]$ is assumed to lie in the plane of the drawing, but in general this is not true.

Accordingly, the general expressions for Δy and L' become

$$\delta<\Delta_2 \quad L'=\frac{\Delta y}{\sin\psi\cos\varphi}=\frac{\Delta_1}{\lambda|\mathbf{b}_2\,.\,\mathbf{u}^0|} \tag{21a}$$

$$\delta>\Delta_2 \quad L'=\frac{\Delta y}{\sin\psi\cos\varphi}= \frac{\Delta_2}{\lambda\sqrt{(\mathbf{b}_2\,.\,\mathbf{i}\cos\varphi+\mathbf{b}_2\,.\,\mathbf{k}\cos\psi\sin\varphi)^2+(\mathbf{b}_2\,.\,\mathbf{k}\sin\psi)^2}}. \tag{21b}$$

(Suppose that $\mathbf{b}_2$ is a twofold symmetry axis. Then $|F_{H_1H_3}(y)|=|F_{H_1H_3}(\bar{y})|$ and the angles ψ, φ are the same for y and $-y$. If the diffraction condition is first satisfied for $[H_1yH_3]$ and next for $[H_1\bar{y}H_3]$, the crystal must be rotated through an angle $2\tan^{-1}(b_2yd_{H_1}0_{H_3})$ about the axis $H_3\mathbf{a}_1-H_1\mathbf{a}_3$. This rotation transforms the vector $\mathbf{b}_2$ into $\mathbf{b}_2'$ having a different orientation in the **i**, **j**, **k** system and the value of Δy is inevitably altered. Hence $\Delta y(y)\neq\Delta y(\bar{y})$ and $P_{H_1H_3}(y)\neq P_{H_1H_3}(\bar{y})$, as illustrated in Table 1).

It is useful to give the specific expressions for L' and Δy for the two commonly used counter techniques: the normal-beam and the goniostat methods. In the former procedure the counter orientation has two degrees of freedom, ψ and φ, while the crystal orientation is varied with one degree of freedom, ζ, representing the angle of rotation about the fixed vertical axis **k**.

The goniostat technique provides for one degree of freedom for the counter, $\psi=2\theta$ and $\varphi=0$, while the crystal has two degrees of freedom, Φ and χ, such that 2θ, Φ, χ form a set of Eulerian angles.

The normal beam technique

When this method is used, it is convenient to mount the crystal either with the disorder axis $\mathbf{a}_2$ or one of the other axes vertical. For the sake of convenience it will be assumed that the crystal axes are orthogonal so that $\mathbf{a}_i\|\mathbf{b}_i$, $a_ib_i=1$.

Case A. $\mathbf{a}_2\|\mathbf{k}$.

In this case the angles φ, θ, ψ are obtained from the relations $\sin\varphi=\lambda y/a_2$, $\sin\theta=\lambda/2d_{H1yH3}$ and $\cos\psi=\cos 2\theta/\cos\varphi$.

Substitution in equations (20) and (21) gives $\delta=\Delta_1\sin 2\theta$ and

$$\delta<\Delta_2 \quad L'=\frac{\Delta y}{\sin\psi\cos\varphi}=\frac{a_2\Delta_1}{\lambda\sin\varphi}, \tag{22a}$$

$$\delta>\Delta_2 \quad L'=\frac{\Delta y}{\sin\psi\cos\varphi}=\frac{a_2\Delta_2}{\lambda\sin 2\theta}. \tag{22b}$$

Case B. $\mathbf{a}_3\|\mathbf{k}$.

The angle φ is now given by $\sin\varphi=\lambda H_3/a_3$.

Let the zero point for the angle ζ be so chosen that $\mathbf{a}_2\|\mathbf{i}$ when $\psi=0$. Accordingly

$$\mathbf{b}_2/b_2=\mathbf{a}_2/a_2=\mathbf{i}\cos(\tfrac{1}{2}\psi-\zeta)+\mathbf{j}\sin(\tfrac{1}{2}\psi-\zeta), \tag{23}$$

$$\delta=\Delta_1\cos(\tfrac{1}{2}\psi-\zeta)/\cos(\tfrac{1}{2}\psi+\zeta). \tag{24}$$

The expression for the angle ζ is

$$\zeta=\tfrac{1}{2}\psi-\eta+\Phi, \tag{25a}$$

$$\tan\eta=\frac{1-\cos 2\theta}{\sin\psi\cos\varphi}, \tag{25b}$$

$$\tan\Phi=\frac{ya_1}{H_1a_2}. \tag{25c}$$

These formulas simplify for the equatorial plane ($H_3=0$), giving $\tfrac{1}{2}\psi=\eta=\theta$ and $\zeta=\Phi$).

From equation (21) one has

$$\delta<\Delta_2 \quad L'=\frac{\Delta y}{\sin\psi\cos\varphi}=\frac{a_2\Delta_1}{\lambda\cos(\psi-\eta+\Phi)\cos\varphi} \tag{26a}$$

$$\delta>\Delta_2 \quad L'=\frac{\Delta y}{\sin\psi\cos\varphi}=\frac{a_2\Delta_2}{\lambda\cos(\eta-\Phi)\cos\varphi}. \tag{26b}$$

According to equation (25c) the angle Φ changes sign with y and with H_1. For the orthorhombic crystal under consideration one has in consequence

$$P_{H_1H_3}(y)=P_{\bar{H}_1H_3}(\bar{y})\neq P_{H_1H_3}(\bar{y})=P_{\bar{H}_1H_3}(y),$$

and if $\delta<\Delta_2$ for $-y$ as well as y

$$P_{H_1H_3}(y)/P_{H_1H_3}(\bar{y})=\cos(\psi-\eta-|\Phi|)/\cos(\psi-\eta+|\Phi|).$$

The goniostat technique

In this method $\varphi=0$, $\psi=2\theta$, and $\sin\theta=\lambda/2d_{H_1yH_3}$. Suppose the crystal (assumed to be orthorhombic) is mounted with $\mathbf{a}_3$ along the Φ axis. If $\chi\leq\pi/2$, only positive values of H_3 can be obtained. Let the zero point be so chosen that $\mathbf{a}_2\|\mathbf{i}$ when $2\theta=\Phi=\chi=0$.

The angle Φ is then given by equation (25c) and the angle χ by

$$\sin\chi=H_3d_{H_1yH_3}/a_3=H_3\lambda/2\,a_3\sin\theta. \tag{27}$$

In terms of the angles θ, Φ, χ the unit vector along the disorder axis and the divergence δ become

$$\begin{aligned}\mathbf{b}_2/b_2=\mathbf{a}_2/a_2=&(\cos\theta\cos\Phi+\sin\theta\sin\Phi\cos\chi)\mathbf{i}\\&+(\sin\theta\cos\Phi-\cos\theta\sin\Phi\cos\chi)\mathbf{j}\\&+\sin\Phi\sin\chi\,\mathbf{k},\end{aligned} \tag{28}$$

$$\delta=\Delta_1\sqrt{\frac{(\cos\theta\cos\Phi+\sin\theta\sin\Phi\cos\chi)^2+(\sin 2\theta\sin\Phi\sin\chi)^2}{\cos\theta\cos\Phi-\sin\theta\sin\Phi\cos\chi}}. \tag{29}$$

Substitution in equation (21) gives

$$\delta<\Delta_2 \quad L'=\frac{\Delta y}{\sin 2\theta}= \frac{a_2\Delta_1}{\lambda(\cos\theta\cos\Phi-\sin\theta\sin\Phi\cos\chi)} \tag{30a}$$

$$\delta>\Delta_2 \quad L'=\frac{\Delta y}{\sin 2\theta}= \frac{a_2\Delta_2}{\lambda\sqrt{(\cos\theta\cos\Phi+\sin\theta\sin\Phi\cos\chi)^2+(\sin 2\theta\sin\Phi\sin\chi)^2}}. \tag{30b}$$

Again one has $P_{H_1H_3}(y)=P_{\bar{H}_1H_3}(\bar{y})\neq P_{H_1H_3}(\bar{y})=P_{\bar{H}_1H_3}(y)$, while the result for the integrated intensity ratio when $\delta<\Delta_2$ becomes

$$\frac{P_{H_1H_3}(y)}{P_{H_1H_3}(\bar{y})}=\frac{\cos\theta\cos\Phi+\sin\theta\sin|\Phi|\cos\chi}{\cos\theta\cos\Phi-\sin\theta\sin|\Phi|\cos\chi}. \tag{31}$$

Discussion

The experimental conditions are usually such that $\Delta_2\gg\Delta_1$. However, even so it is frequently true that $\delta>\Delta_2$ implying that equation (21*b*) rather than (21*a*) must be used. This situation will arise whenever the lattice row $[H_1yH_3]$ is nearly tangent to the sphere of reflection.

In order to get good resolution in the experimental curve $P_{H_1H_3}(y)$ it is desirable to have Δy small, particularly when the coefficients $W_M^{H_1H_3}$ decrease slowly with increasing $|M|$, and this suggests the use of small values for Δ_1.

The equations obtained for Δy show this quantity to be nearly independent of wave length for large values of $d_{H_1yH_3}$. However, a longer wavelength is preferable at smaller values of $d_{H_1yH_3}$ since Δy is smaller for the longer wavelength. The use of a longer wavelength also has the advantage that the scattering angles are larger with a corresponding gain in the precision with which the counter and the crystal can be set.

The greater simplicity of the expressions for L' favors the 'normal beam' over the 'goniostat' technique, but this point is not important if electronic computers are available.

If the structure of the layer is known, the quantity $ApL'|F_{H_1H_3}|^2$ on the right side of equation (18) can be calculated, and hence the function $CD'_{H_1H_3}(y)$ can be obtained from the experimental curve $P_{H_1H_3}(y)$. (It is obvious, however, that the precision is poor for such regions of y where $P_{H_1H_3}$ and $|F_{H_1H_3}|$ are small). The function Δy varies slowly with y and can usually be treated as a constant over the range y to $y+1$. Accordingly, one has

$$\int_y^{y+1} D'_{H_1H_3}=1, \tag{32}$$

which will serve to determine the scale factor C. The function $D'_{H_1H_3}$ is thus derived from the experimental function $P_{H_1H_3}$, and by Fourier inversion one has

$$W_M^{H_1H_3}\frac{\sin\pi M\Delta y}{\pi M\Delta y}\simeq\int_{y_0-\frac{1}{2}}^{y_0+\frac{1}{2}} D'_{H_1H_3}\exp(-i2\pi My)dy, \tag{33}$$

where, on the left of the equation, Δy is the mean value over the integration range. Since $\Delta y\simeq\Delta y(y_0)$, which can be calculated, the various correlation coefficients $W_M^{H_1H_3}$ can thus be obtained from experiment.

Once the correlation coefficients have been found, the nature of the stacking disorder can be deduced. Usually the stacking faults are such that the relative displacements $\Delta_{L_2+M}-\Delta_{L_2}$ can assume only a small set of discrete values Δ_j, where the components of Δ_j are simple rational numbers. (As an illustration: in stackings of hexagonal close-packed layers three values are possible for Δ_j, namely $\Delta_1=0$, $\Delta_2=\frac{1}{3}\mathbf{a}_1+\frac{2}{3}\mathbf{a}_3$, $\Delta_3=-\Delta_2$). These discrete values Δ_j are readily found by observing the conditions under which three-dimensional rather than two-dimensional diffraction occurs. (For the hexagonal example given above the condition is that $H_1-H_3=3n$).

The correlation factor W_M of equation (4*b*) can be written in the form

$$W_M=\sum_j p_{Mj}\exp(i\mathbf{s}\,.\,\Delta_j), \tag{34}$$

where p_{Mj} is the probability of finding a relative displacement Δ_j between layers M spacings apart. If $\Delta_j=\Delta x_j\mathbf{a}_1+\Delta z_j\mathbf{a}_3$ the expression for the observable quantities $W_M^{H_1H_3}$ becomes

$$W_M^{H_1H_3}=\sum_j p_{Mj}\exp\{i2\pi[H_1\Delta x_j+H_3\Delta z_j]\}, \tag{35}$$

and the probabilities p_{Mj} can thus be found.

When the structure of the layer is unknown, it is necessary first to find the function $|F_{H_1H_3}|^2$. As a consequence of equations (18) and (32) one has

$$C\int_{y-\frac{1}{2}}^{y+\frac{1}{2}}|F_{H_1H_3}|^2dy=\int_{y-\frac{1}{2}}^{y+\frac{1}{2}}\frac{P_{H_1H_3}}{ApL'}dy=Y(y), \tag{34}$$

where Y is a known function obtained from the experimental data. Clearly Y is the first approximation to the sought function $|F_{H_1H_3}|^2$. Further approximations are readily obtained by expansion in power series, the second approximation being

$$|F_{H_1H_3}(y)|^2\simeq Y(y)-\tfrac{1}{6}[Y(y+\tfrac{1}{2})+Y(y-\tfrac{1}{2})-2Y(y)]. \tag{35}$$

References

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