Calculation of Dimensions of Ordered Regions in Triclinic and Monoclinic Pseudosymmetric Crystals from the Intensity of Diffuse Scattering

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II. CALCULATION OF DIMENSIONS OF ORDERED REGIONS IN TRICLINIC AND MONOCLINIC PSEUDOSYMMETRIC CRYSTALS FROM THE INTENSITY OF DIFFUSE SCATTERING

By H. D. FLACK

CONTENTS

Mathematical relations are obtained giving the X-ray scattering for a crystal the unit cell of which contains one or two asymmetric molecules, each of which can adopt either of two centrosymmetrically-related orientations, giving pseudocentrosymmetry. It is shown that measurements of the integral breadth of maxima of the diffuse 'disorder' scattering can give the dimensions of the short-range order regions. The temperature variation of intensity of such diffuse scattering is different from that of thermal diffuse scattering.

NOTATION

a, b, c	vectors representing the primitive unit-cell translations
α, β, γ	probabilities of a 'mistake' of orientation of the molecule along a, b, c respectively
M, N, Q	numbers of molecules in rows parallel to a, b, c
$R_{m,n,q}$	probability that a molecule at $ma + nb + qc$ is in the 'right' orientation
$W_{m,n,q}$	the same for the 'wrong' orientation
S	vector in reciprocal space $= s - s_0$, where
s	is a vector length $1/\lambda$ in scattered-wave direction
s_0	is a vector length $1/\lambda$ in incident-wave direction $|S| = |s - s_0| = (2\sin\theta)/\lambda$
G_0	Fourier transform of molecule (0) in the 'right' orientation at $m, n, q = 0, 0, 0$
G_0'	Fourier transform of molecule (0) in the 'wrong' orientation at $m, n, q = 0, 0, 0$
G_3	Fourier transform of the whole crystal composed of 'right' and 'wrong' molecules (0) with a 'right' molecule (0) at the origin

G_3'	as for G_3 but with a 'wrong' molecule (0) at the origin
$G_1, G_1', G_{31}, G_{31}'$	the same for molecules (1)
$G_3^*, G_3'^*$	complex conjugates of G_3, G_3' respectively
F	Fourier transform of the whole crystal structure
$\overline{F^2}$	mean-square Fourier transform for the disordered crystal
h, k, l	integral indices of a reciprocal lattice point
$H = 2\pi \boldsymbol{a} . \boldsymbol{S}$ $\quad K = 2\pi \boldsymbol{b} . \boldsymbol{S}$ $\quad L = 2\pi \boldsymbol{c} . \boldsymbol{S}$	
$y_a = 1/\{1 - 2(1 - 2\alpha)\cos H + (1 + 2\alpha)^2\}$	
y_b, y_c	the same for β, K and γ, L
w	integral breadth of a diffuse diffraction profile
$I_{\max}$	peak intensity of the diffuse diffraction profile
I	intensity of a diffuse diffraction profile at H

The 'right' orientation is the orientation dictated by the symmetry elements of the crystal as a whole given a particular orientation at the origin. Short-range order implies that successive molecules in a particular direction assume the 'right' orientation until a 'mistake' occurs giving a molecule in the 'wrong' orientation.

INTRODUCTION

The aim of this paper is to obtain mathematical relations connecting the X-ray diffraction patterns given by a crystal containing regions of a certain type of short-range order with the dimensions of those regions.

MISTAKES IN THE ORIENTATION OF MOLECULES IN A ROW

Following Wilson (1949) consider the building up of molecules into a one-dimensional lattice of translation $\boldsymbol{a}$. Assume a condition of disorder such as the following:

$$\ldots R\ R\ R\ R\ W\ W\ W\ W\ W\ R\ R\ R\ R\ R\ R\ R\ W\ W\ W\ W\ W\ W\ R\ R\ R\ W\ W\ W\ W \ldots$$

where R and W represent 'right' and 'wrong' orientations of the molecules, the orientation at the point chosen as origin being 'right' and α being the probability of a mistake occurring. Let R_m be the probability that the mth molecule from the origin is R and W_m that it is W.

Then
$$R_m + W_m = 1 \tag{1}$$

and
$$R_{m+1} = (1 - \alpha)\,R_m + \alpha W_m$$
$$= \alpha + (1 - 2\alpha)\,R_m. \tag{2}$$

MISTAKES IN THE ORIENTATION OF MOLECULES ON A THREE-DIMENSIONAL LATTICE

(a) One molecule per unit cell

The primitive lattice translations are $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$ respectively and α, β, γ are the probabilities of a 'mistake' in the molecular orientation (still confined to the two possibilities R and W), within limits defined by a total number of molecules M, N, Q along the directions $\boldsymbol{a}$, $\boldsymbol{b}$, $\boldsymbol{c}$. Let any particular molecule be defined by positive integral coordinates m, n, q where $m\boldsymbol{a} + n\boldsymbol{b} + q\boldsymbol{c}$ is the position vector of that molecule relative to a suitably selected origin. Then by an extension of (1) and (2)

$$R_{m,n,q} + W_{m,n,q} = 1, \tag{3}$$

and
$$R_{m+1,n,q} = \alpha + (1-2\alpha)\,R_{m,n,q} \tag{4a}$$

$$R_{m,n+1,q} = \beta + (1-2\beta)\,R_{m,n,q} \tag{4b}$$

$$R_{m,n,q+1} = \gamma + (1-2\gamma)\,R_{m,n,q} \tag{4c}$$

It can be shown (Flack 1968) that if $R_{0,0,0} = 1$

then
$$R_{m,n,q} = \tfrac{1}{2}\{1 + (1-2\alpha)^m\,(1-2\beta)^n\,(1-2\gamma)^q\} \tag{5}$$

and
$$W_{m,n,q} = \tfrac{1}{2}\{1 - (1-2\alpha)^m\,(1-2\beta)^n\,(1-2\gamma)^q\}, \tag{6}$$

whereas if $R_{0,0,0} = 0$ these values are reversed.

In the notation of Lipson & Taylor (1958), the Fourier transform of a three-dimensional crystal G_3 is

$$G_3 = \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} \sum_{q=0}^{Q-1} G(\boldsymbol{S}) \exp\{2\pi i(m\boldsymbol{a} + n\boldsymbol{b} + q\boldsymbol{c}) \cdot \boldsymbol{S}\}, \tag{7}$$

where $G(\boldsymbol{S})$ is the Fourier transform of the unit cell. The molecular Fourier transforms of the two possible orientations of the molecule at the origin are G_0 (for R) and G_0' (for W) respectively. Then

$$G_3 = \sum_{m=0}^{M-1} \sum_{n=0}^{N-1} \sum_{q=0}^{Q-1} (R_{m,n,q}\,G_0 + W_{m,n,q}\,G_0') \exp\{2\pi i(m\boldsymbol{a} + n\boldsymbol{b} + q\boldsymbol{c}) \cdot \boldsymbol{S}\}. \tag{8}$$

Hence, using (5) and (6) it may be shown (Flack 1968) that if $R_{0,0,0} = 1$ then

$$\begin{aligned}
G_3 = {}&\tfrac{1}{2}(G_0 + G_0')\left\{\frac{1-e^{MHi}}{1-e^{Hi}}\right\}\left\{\frac{1-e^{NKi}}{1-e^{Ki}}\right\}\left\{\frac{1-e^{QLi}}{1-e^{Li}}\right\}\\
&+ \tfrac{1}{2}(G_0 - G_0')\left\{\frac{1-(1-2\alpha)^M e^{MHi}}{1-(1-2\alpha)\,e^{Hi}}\right\}\left\{\frac{1-(1-2\beta)^N e^{NKi}}{1-(1-2\beta)\,e^{Ki}}\right\}\left\{\frac{1-(1-2\gamma)^Q e^{QLi}}{1-(1-2\gamma)\,e^{Li}}\right\},
\end{aligned} \tag{9}$$

where
$$H = 2\pi\boldsymbol{a} \cdot \boldsymbol{S}, \quad K = 2\pi\boldsymbol{b} \cdot \boldsymbol{S}, \quad L = 2\pi\boldsymbol{c} \cdot \boldsymbol{S}.$$

This is the equation that applies when the molecule at the origin is in the 'right' orientation. If, however, $R_{0,0,0} = 0$ and the molecule at the origin is in the 'wrong' orientation, then an equation (10) is obtained for G_3' similar to equation (9) but with $(G_0 - G_0')$ replaced by $(G_0' - G_0)$.

Scattering in reciprocal space

The expressions G_3 and G_3' both give rise to sharp reciprocal lattice points and to regions of diffuse intensity. Equation (9) can be written (Flack 1968) as

$$\begin{aligned}
G_3 = {}&\tfrac{1}{2}(G_0 + G_0')\,\frac{\sin\frac{1}{2}MH}{\sin\frac{1}{2}H}\frac{\sin\frac{1}{2}NK}{\sin\frac{1}{2}K}\frac{\sin\frac{1}{2}QL}{\sin\frac{1}{2}L}\exp\{\tfrac{1}{2}i[(M-1)\,H + (N-1)\,K + (Q-1)\,L]\}\\
&+ \tfrac{1}{2}(G_0 - G_0')\left\{\frac{1-2(1-2\alpha)^M\cos MH + (1-2\alpha)^{2M}}{1-2(1-2\alpha)\cos H + (1-2\alpha)^2}\right\}^{\frac{1}{2}}\left\{\frac{1-2(1-2\beta)^N\cos NK + (1-2\beta)^{2N}}{1-2(1-2\beta)\cos K + (1-2\beta)^2}\right\}^{\frac{1}{2}}\\
&\times \left\{\frac{1-2(1-2\gamma)^Q\cos QL + (1-2\gamma)^{2Q}}{1-2(1-2\gamma)\cos L + (1-2\gamma)^2}\right\}^{\frac{1}{2}}\exp\{i(\phi_1 + \phi_2 + \phi_3)\},
\end{aligned} \tag{11}$$

where
$$\phi_1 = \tan^{-1}\left\{\frac{-(1-2\alpha)^M\sin MH + (1-2\alpha)\sin H + (1-2\alpha)^{M+1}\sin(M-1)\,H}{1-(1-2\alpha)^M\cos MH - (1-2\alpha)\cos H + (1-2\alpha)^{M+1}\cos(M-1)\,H}\right\},$$

and ϕ_2, ϕ_3 are similar expressions in (β, N, K) and (γ, Q, L) respectively.

The first term in (11) is that which occurs in the case of an ordered three-dimensional crystal (Lipson & Taylor 1958). For maxima the well-known Laue conditions apply:

$$\boldsymbol{a} \cdot \boldsymbol{S} = h, \quad \boldsymbol{b} \cdot \boldsymbol{S} = k, \quad \boldsymbol{c} \cdot \boldsymbol{S} = l \quad (h, k, l \text{ integral})$$

and the structure amplitudes at the reciprocal lattice points have values proportional to $\frac{1}{2}(G_0 + G_0')$, the same as that for a structure with units at the lattice points which are the average of the two possible molecular orientations.

The second term in (11) gives rise to areas of diffuse scattering in reciprocal space. The modulus of $\exp\{i(\phi_1 + \phi_2 + \phi_3)\}$ is unity and does not affect the magnitude of the modulus of this whole second term. Since M, N and Q are of the order of 10^5 to 10^6 in a real crystal, terms of the type $(1 - 2\alpha)^M$ are very small for $0 < \alpha < 1$, and in these circumstances the second term reduces to

$$\frac{1}{2}(G_0 - G_0')\{[1 - 2(1 - 2\alpha)\cos H + (1 - 2\alpha)^2][1 - 2(1 - 2\beta)\cos K + (1 - 2\beta)^2]$$
$$\times [1 - 2(1 - 2\gamma)\cos L + (1 - 2\gamma)^2]\}^{-\frac{1}{2}} \exp\{i(\phi_1 + \phi_2 + \phi_3)\}$$

for $0 < \alpha < 1$, $0 < \beta < 1$, $0 < \gamma < 1$, or

$$\frac{1}{2}(G_0 - G_0')(y_a \times y_b \times y_c)^{\frac{1}{2}} \exp\{i(\phi_1 + \phi_2 + \phi_3)\}$$

in our notation. The function y_a has been plotted in figure 1 for values of

$$\alpha = 0, \quad 0.1, \quad 0.2, \quad 0.3, \quad 0.4, \quad 0.5$$

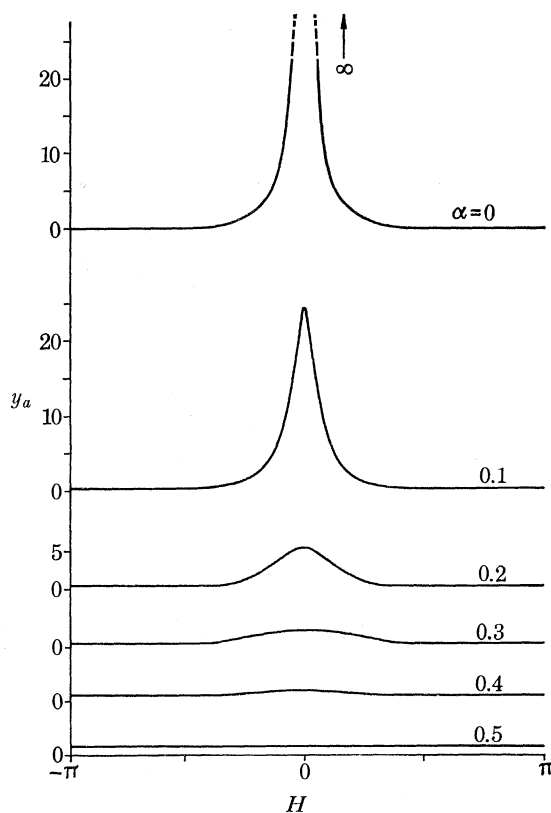against H over the range of $-\pi$ to $+\pi$ (or $(2n - 1)\pi$ to $(2n + 1)\pi$).

FIGURE 1. The function $y_a = 1/\{1 - 2(1 - 2\alpha)\cos H + (1 - 2\alpha)^2\}$ plotted for values of $\alpha = 0$, 0.1, 0.2, 0.3, 0.4, 0.5 against H over the range of $-\pi$ to $+\pi$ (or $(2n-1)\pi$ to $(2n+1)\pi$).

For values of $0.5 < \alpha < 1.0$ the function y_a shows peak heights and shapes identical with those for the corresponding value $(1 - \alpha)$ but with the peak position at $H = (2n + 1)\pi$ (n integral), whereas for $0 < \alpha < 0.5$ the peaks are at $2n\pi$. The functions y_a, y_b, y_c which modify the distribution of diffuse intensity in reciprocal space are independent of the atomic arrangement of the molecules giving rise to G_0 and G'_0. They are periodic functions, each producing layers of maximum intensity normal to the corresponding direct-lattice translation.

When $\alpha = 0.5$ the diffuse scattering function $y_a = 1$. The diffuse 'disorder' scattering is then given by $\frac{1}{2}(G_0 - G'_0)$, and so gives peaks produced by this function only. It corresponds to random disorder along or parallel to $\boldsymbol{a}$. For $0 < \alpha < 0.5$ there are maxima in the diffuse scattering for reciprocal lattice planes $h = 0, 1, 2$, etc., the maxima becoming sharper as α approaches zero. The value $\alpha = 0.1$, for instance, corresponds with an approximate molecular distribution.

$$\ldots R\,R\,R\,R\,R\,R\,R\,R\,W\,W\,W\,W\,W\,W\,W\,W\,W\,W\,R\,R\,R\,R\,R\,R\,R\,R\,R\,W\ldots$$

in the $\boldsymbol{a}$ direction.

When $0.5 < \alpha < 1$ the maxima in y_a occur for $h = n + \frac{1}{2}$ (n integral). The value $\alpha = 1$ would correspond to a superlattice having $2\boldsymbol{a}$ as its unit-cell translation. The value $\alpha = 0.9$ corresponds with an approximate distribution

$$\ldots W\,R\,W\,R\,W\,R\,W\,R\,W\,R\,W\,W\,R\,W\,R\,W\,R\,W\,R\,W\,R\,R\,W\,R\,W\,R\,W\,R\,W\,R\,W\,R\,R\,W\ldots$$

along $\boldsymbol{a}$. As α approaches the value 0.5 so the diffuse intensity maxima become broader.

There is, of course, no physical distinction between the three-dimensional arrangement having transforms G_3 and G'_3. They give identical intensity distributions in reciprocal space.

$$G_3 G_3^* = G'_3 G'^*_3 = \tfrac{1}{4}(G_0 + G'_0)^2 \frac{\sin^2 \tfrac{1}{2}MH}{\sin^2 \tfrac{1}{2}H} \frac{\sin^2 \tfrac{1}{2}NK}{\sin^2 \tfrac{1}{2}K} \frac{\sin^2 \tfrac{1}{2}QL}{\sin^2 \tfrac{1}{2}L} + \tfrac{1}{4}(G_0 - G'_0)^2 y_a y_b y_c$$

$$+ \tfrac{1}{4}J \frac{\sin \tfrac{1}{2}MH}{\sin \tfrac{1}{2}H} \frac{\sin \tfrac{1}{2}NK}{\sin \tfrac{1}{2}K} \frac{\sin \tfrac{1}{2}QL}{\sin \tfrac{1}{2}L}\,(y_a y_b y_c)^{\frac{1}{2}}, \tag{12}$$

where

$$J = (G_0 + G'_0)\,(G_0^* - G'^*_0)\exp\{\tfrac{1}{2}\mathrm{i}[(M-1)\,H + (N-1)\,K + (Q-1)\,L]\}\exp\{-\mathrm{i}(\phi_1 + \phi_2 + \phi_3)\}$$

$$+ (G_0^* + G'^*_0)\,(G_0 - G'_0)\exp\{-\tfrac{1}{2}\mathrm{i}[(M-1)\,H + (N-1)\,K + (Q-1)\,L]\}\exp\{\mathrm{i}(\phi_1 + \phi_2 + \phi_3)\}$$

neglecting the terms in $(1 - 2\alpha)^M$, $(1 - 2\beta)^N$, $(1 - 2\gamma)^Q$ as before.

The third term in (12) is zero everywhere in reciprocal space except at reciprocal lattice points and even then it becomes significant only when α, β and $\gamma \to 0$. The cases for which $\alpha, \beta, \gamma = 0$ or 1 in fact correspond with complete ordering and not with disorder or short-range order.

(b) *Two molecules per unit cell*

Let there be two molecules (numbered 0 and 1) in the unit cell, each of which occupies a definite position but in either of two orientations (see figure 2).

The whole crystal may be considered as built up of two structures, one containing type 0, the other type 1 molecules. The Fourier transform F of the whole structure is the sum of the transforms for the two individual lattices and F may be given by the four possible expressions:

$$\begin{aligned} F &= G_3 + G_{31}, \quad F = G'_3 + G_{31}, \\ F &= G_3 + G'_{31}, \quad F = G'_3 + G'_{31}, \end{aligned} \tag{13}$$

depending on the orientations of the molecules in the positions for which $m = n = q = 0$.

On the assumption that the disordered crystal is built up of blocks, each of which corresponds with one of the transforms given by (13), that these occur with an equal probability and that

there are random phase relations between the blocks, then it follows that the average value of F^2 is given by

$$\overline{F^2} = \tfrac{1}{4}|G_0 + G_0' + G_1 + G_1'|^2 \frac{\sin^2 \tfrac{1}{2}MH}{\sin^2 \tfrac{1}{2}H} \frac{\sin^2 \tfrac{1}{2}NK}{\sin^2 \tfrac{1}{2}K} \frac{\sin^2 \tfrac{1}{2}QL}{\sin^2 \tfrac{1}{2}L} + \tfrac{1}{4}\{|G_0 - G_0'|^2 + |G_1 - G_1'|^2\} y_a y_b y_c. \quad (14)$$

The first term gives sharp peaks of $\overline{F^2}$ value $\tfrac{1}{4}|G_0 + G_0' + G_1 + G_1'|^2$ at reciprocal lattice points. The second term gives diffuse regions in reciprocal space, the periodicity of which depends on y_a, y_b, y_c and hence on the values of α, β, γ.
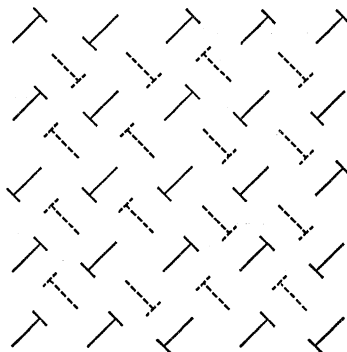

FIGURE 2. A repeat pattern of molecules occupying either of two centrosymmetrical orientations.

THE INTRODUCTION OF SYMMETRY ELEMENTS

It will be shown that equation (14), if applied to a crystal in the monoclinic system will account for the systematic space-group absences; and that the Laue symmetry of the diffuse scattering will be $2/m$.

Let there be two non-centrosymmetric molecules of a single chemical species in a monoclinic unit cell, at positions $0, 0, 0$ and $\tfrac{1}{2}, \tfrac{1}{2}, 0$. Let each of the molecules at these two positions be able to take one of two possible centrosymmetrically related orientations in such a way that there are statistical centres of symmetry at $0, 0, 0$ and $\tfrac{1}{2}, \tfrac{1}{2}, 0$. The *average* molecules at $0, 0, 0$ and at $\tfrac{1}{2}, \tfrac{1}{2}, 0$ are related by a diad screw axis parallel to $\boldsymbol{b}$ and by a glide plane parallel to (010) at $y = \tfrac{1}{4}$ having a glide $\tfrac{1}{2}\boldsymbol{a}$. The statistical space group is then $P2_1/a$ and the conditions for reflexion should be

$$
\begin{array}{ll}
hkl & \text{none} \\
0k0 & k = 2n \\
h0l & h = 2n
\end{array}
$$

corresponding to equivalent positions

$$x, y, z; \quad \bar{x}, \bar{y}, \bar{z}; \quad \tfrac{1}{2} - x, \tfrac{1}{2} + y, \bar{z}; \quad \tfrac{1}{2} + x, \tfrac{1}{2} - y, z.$$

The geometric parts of the structure factors are

$$
\left.
\begin{aligned}
G_0 &= \exp\{2\pi i(hx + ky + lz)\}, \\
G_0' &= \exp\{2\pi i(-hx - ky - lz)\}, \\
G_1 &= \exp\{2\pi i[h(\tfrac{1}{2} - x) + k(\tfrac{1}{2} + y) - lz]\} \\
&= \exp\{\pi i(h + k)\} \exp\{2\pi i(-hx + ky - lz)\}, \\
G_1' &= \exp\{2\pi i[h(\tfrac{1}{2} + x) + k(\tfrac{1}{2} - y) + lz]\} \\
&= \exp\{\pi i(h + k)\} \exp\{2\pi i(hx - ky + lz)\},
\end{aligned}
\right\}
\quad (15)
$$

whence

$$G_0 + G_0' + G_1 + G_1' = 2\cos 2\pi(hx + ky + lz) + 2\exp\{\pi i(h+k)\}\cos 2\pi(-hx + ky - lz).$$

For $h = 0$, $l = 0$:

$$G_0 + G_0' + G_1 + G_1' = 0 \quad \text{if} \quad k = 2n+1 \quad (k \text{ odd}).$$

For $k = 0$:

$$G_0 + G_0' + G_1 + G_1' = 0 \quad \text{if} \quad h = 2n+1 \quad (h \text{ odd}),$$

and there are no other systematic conditions giving zero values.

The sharp reflexions at the reciprocal lattice points in the disordered crystal have $\overline{F^2}(hkl)$ proportional to $(G_0 + G_0' + G_1 + G_1')^2$ and therefore obey these space-group $P2_1/a$ conditions.

The symmetry of the diffuse scattering is found by a consideration of the second term of (14):

$$\text{diffuse } \overline{F^2} = \tfrac{1}{4}\{|G_0 - G_0'|^2 + |G_1 - G_1'|^2\}y_a y_b y_c.$$

As before, the function $y_a y_b y_c$ is periodic in reciprocal space with the symmetry of the lattice. From (15) it follows that

$$|G_0 - G_0'|^2 + |G_1 - G_1'|^2 = 4\sin^2 2\pi(hx + ky + lz) + 4\sin^2 2\pi(-hx + ky - lz).$$

Hence diffuse $\overline{F^2}(hkl) = \overline{F^2}(\bar{h}\bar{k}l) = \overline{F^2}(h\bar{k}l) = \overline{F^2}(\bar{h}k\bar{l})$ and the diffuse scattering as a whole has the symmetry of the Laue group $2/m$.

The relation of the geometry of the diffuse scattering to the size of short-range order regions in the crystal

The expression for y_a describes analytically the shape (figure 1) of diffuse scattering in reciprocal space due to the geometry of the short-range order along $\boldsymbol{a}$, and similarly for y_b and y_c. If the experimental diffuse $\overline{F^2}$ for a disordered crystal is plotted in reciprocal space it should be possible to determine α, β, γ by a comparison of the profiles of diffuse scattering parallel to the h, k, l-constant nets with the various computed curves (as shown in figure 1). A more direct method is simply to measure the integral breadth w of the diffuse profile. According to Wilson (1949)

$$w = \left(\int_{-\pi}^{+\pi} I\,\mathrm{d}H\right)\Big/I_{\max},$$

where I is the intensity of the diffuse profile at H and $I_{\max}$ is the peak intensity of the profile. Substitution of $I = y_a$ in this equation gives

$$w = 2\pi(\alpha^{-1} - 1) \quad \text{for} \quad \alpha > 0.5. \tag{16}$$

Now if $0 < \alpha < 0.5$ the sequence of molecules is

$$\ldots \text{R R R R W W W W W R R R R R R W W W R R R R R} \ldots,$$

and if α is the probability that a mistake will occur at any one molecule, then $1/\alpha$ is the average number of molecules between mistakes (the average number of molecules along the direction $\boldsymbol{a}$ in any short-range ordered block) and a/α is the average length along $\boldsymbol{a}$ of the short-range ordered regions. Similarly for $\boldsymbol{b}$ and $\boldsymbol{c}$.

If $0.5 < \alpha < 1$ then the short-range order is of the type

$$\ldots \text{R W R W R W R W W W R W R R W R W R W R W W R W R} \ldots$$

and if α is the probability that a change of orientation will occur, then $1 - \alpha$ is the probability that no such change will occur, that is, that the R W alternation is broken. The average number

of molecules along a in a short-range ordered block is therefore $1/(1-\alpha)$ and the average length of the region in the a direction is $a/(1-\alpha)$, and similarly for b and c.

For $\alpha = 0.5$ no systematic diffuse scattering maxima parallel to the h-constant net would be found, but there would be a general increase of diffuse scattering.

THE EFFECT OF TEMPERATURE ON THE DISORDER DIFFUSE SCATTERING

Consider the effect of temperature change on the functions y_a, y_b, y_c. If the activation energy E for the reorientation of a molecule from R to W or vice versa is large, then the probability that such a change will occur is small. In fact, α, β, γ and hence y_a, y_b, y_c will not be affected by temperature unless kT is of the same order as E, which is unlikely in most cases (although not impossible).

The effect of temperature on the 'molecular' part of the diffuse scattering term,

$$\tfrac{1}{4}\{|G_0 - G_0'|^2 + |G_1 - G_1'|^2\}$$

will be similar to that on the normal Bragg reflexion appropriate to the point in reciprocal space that is under consideration since G will be of the general form

$$G = \sum_{i=1}^{N} f_i \exp\{-B_i((\sin\theta)/\lambda)^2\} \exp\{-2\pi i(hx_i + ky_i + lz_i)\},$$

where N is the number of atoms in the molecule, and B_i is the isotropic temperature factor for atom i at x_i, y_i, z_i. (Here h, k, l are not necessarily integral.) The change of temperature may, of course, involve also changes of x_i, y_i, z_i which will alter the distribution but not the peak heights of G unless the molecular geometry is changed as well as its orientation.

The value of G thus, in general, decreases with increasing temperature, the greatest effects being observed at large values of $(\sin\theta)/\lambda$.

This contrasts with the ordinary effect of temperature on the 'thermal' diffuse scattering (Lonsdale & Smith 1942; Born 1942) for which the intensity normally increases with increasing temperature. This contrast provides one means of differentiating between 'thermal' and 'disorder' diffuse scattering.

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