$A_{310} \Delta \sigma_{310} \approx E(\bar{1}, 3)$ is slightly negative and $A_{520} \Delta \sigma_{520} \approx E(\bar{2}, 5)$ is slightly positive. $\Delta \sigma'_{310}$ can become positive, and $\Delta \sigma'_{520}$ negative, if $E_a(\bar{2}, 5)$, $E_a(\bar{3}, 7)$ and $E_a(\bar{3}, 8)$ are positive, while $E_a(\bar{1}, 2)$ is nearly zero, or even slightly positive. Let us assume that $E_a(\bar{1}, 2) = 0$, so that $\theta_0 = 15° 56'$. In that case according to (23), $P_3/Q_3 = -\tan 47° 48'$ and, since $\Sigma z_i Y_i^2 = \Sigma z_i X_i Y_i = 0$, we find that $\Sigma z_j Y_j / \Sigma z_j X_j = -\tan 42° 12'$.

For the three ions A^{++}, B^- and C^- located in the sites of Ti and O atoms (see Fig. 10(b)), we find $\Sigma z_j Y_j / \Sigma z_j X_j = -\tan 47° 27'$, the line joining the centre of gravity of the negative ions with the positive ion being parallel to (010). The interaction energy of these adsorbed ions with the crystal ionic chains becomes zero for $\theta = 14° 11'$. $E_a(\bar{1}, 2)$ is slightly positive, so that these adsorbed ions fulfill the requirements for the appearance of (520).

For the face (120) to appear, $\Delta \sigma'_{120}$ should be slightly negative and $\Delta \sigma'_{130}$ should be positive. A combination of adsorbed ions in sites of crystal ions that would produce this face, could not be found.

(5) Conclusions

Up to now the appearance of crystal faces with high indices (not vicinal faces) could not be explained. The examples seem to reveal at least one of their special properties: they are all parallel (within 3°) to a direction in which the interaction energy of the crystal ionic chains is zero. For zircon and anatase it was shown that adsorption of foreign ions might produce high index faces on the equilibrium form which are not exhibited without adsorption and the appearance of which violates the law of Donnay & Harker (1937). The foreign ions were assumed to be located in sites which, if growth would proceed were to be occupied by crystal ions.

In choosing the examples among the minerals, two assumptions were made. First, that the calculations, although strictly valid at 0 °K., apply also at other temperatures. Second, that the crystals found in nature represent approximately equilibrium forms. The results obtained seem to justify these assumptions.

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On the Fourier Treatment of Distortion Broadening in X-ray Diffraction

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General expressions for the Patterson function and intensity distribution in reciprocal space of a distorted crystal are derived. It is shown that the intensity distributions of the broadened reflexions are given as sections through the six-dimensional Fourier transform of a strain distribution function. Relationship with earlier work and application to one-dimensional intensity distributions, such as powder diffractograms, are discussed.

1. Introduction

The effect of lattice distortions upon the distribution of diffracted X-ray intensity has been treated by several authors (Stokes & Wilson, 1944; Warren & Averbach, 1950; Warren, 1955) and methods have been devised to evaluate lattice strains from X-ray measurements in the case of small distortions (Warren & Averbach, 1950, 1952). It is the purpose of this paper to point out that a general description of lattice distortions may be given in reciprocal space as well as in physical space by introducing the (six-dimensional) Fourier transform $\psi(t; s)$ of the distribution function

$W(r; \mathscr{E})$ for integral strain $\mathscr{E}$ over distances r. This function $\psi(t; s)$ includes both the exact line profiles and the approximate expressions used in the references. The representation offered may thus be employed to investigate the significance of these approximations and eventually as a basis for more exact methods.

2. Intensity distribution in reciprocal space

As a starting point of our discussion, let us review the derivation of the intensity distribution for a distorted crystal. We prefer to use the 'continous representation': Let the positions p of the elements of volume

$d\tau$ in the distorted crystal be given by displacements δ from ideal positions $\mathbf{p}_0$ corresponding to an undistorted crystal:

$$\mathbf{p} = \mathbf{p}_0 + \delta(\mathbf{p}_0) \ . \tag{1}$$

The components of $\mathbf{p}_0$ can now be used as coordinates in the distorted crystal (1) being the transformation equation. The amplitude of scattering is then proportional to

$$\int \varrho(\mathbf{p}_0) \exp\left[2\pi i \mathbf{s}\mathbf{p}_0\right] \exp\left[2\pi i \mathbf{s}\delta(\mathbf{p}_0)\right] d\tau_0 \tag{2}$$

where $\mathbf{s}$ is the scattering vector and $\varrho(\mathbf{p}_0)$ the electron density of the undistorted crystal.

The intensity expression is seen to be

$$I = I_e \iint \varrho(\mathbf{p})\varrho(\mathbf{p}+\mathbf{r}) \exp\left[2\pi i \mathbf{s}\mathbf{r}\right]$$
$$\times \exp\left[2\pi i \mathbf{s}.(\delta(\mathbf{p}+\mathbf{r})-\delta(\mathbf{p}))\right] d\tau_\mathbf{p} d\tau_r \tag{3}$$

where we have omitted index zero and introduced the vector $\mathbf{r}$ in Patterson space of the undistorted crystal. I_e is the intensity scattered by an electron.

It is now profitable to define a function $A(\mathbf{r};\mathbf{s})$ analogous to the distortion Fourier coefficients A_n introduced by Warren & Averbach (1950)

$$A(\mathbf{r};\mathbf{s}) = \frac{\int \varrho(\mathbf{p})\varrho(\mathbf{p}+r)\exp\left[2\pi i\mathbf{s}(\delta(\mathbf{p}+\mathbf{r})-\delta(\mathbf{p}))\right]d\tau_\mathbf{p}}{\int \varrho(\mathbf{p})\varrho(\mathbf{p}+\mathbf{r})d\tau_\mathbf{p}} \tag{4}$$

$$I(\mathbf{s}) = I_e N \int P_0(\mathbf{r}) A(\mathbf{r};\mathbf{s}) \exp\left[2\pi i \mathbf{r}\mathbf{s}\right] d\tau_r \tag{5}$$

where $P_0(\mathbf{r})$ is the Patterson function of the undistorted crystal and N the number of unit cells.

The integrations in (4) may be performed by integrating throughout the volume of the mth unit cell and then summing over all unit cells; that is, by the substitutions

$$\int d\tau_\mathbf{p} = \sum_m \int_v d\tau_{\mathbf{p}'} \qquad \mathbf{p} = \mathbf{P}_m + \mathbf{p}'$$

where $\mathbf{P}_m$ is the lattice vector corresponding to the mth unit cell and the summation is over all unit cells.
$\varrho(\mathbf{p})$ is independent of m, and we may write:

$$A(\mathbf{r};\mathbf{s}) = \frac{1}{NP_0(\mathbf{r})}\int \varrho(\mathbf{p}')\varrho(\mathbf{p}'+\mathbf{r}) \sum_m \exp\left[2\pi i\mathbf{s}\right.$$
$$\left. \cdot (\delta(\mathbf{P}_m+\mathbf{p}'+\mathbf{r})-\delta(\mathbf{P}_m+\mathbf{p}'))\right]d\tau_{\mathbf{p}'} \ .$$

If the sum in the integral is independent of $\mathbf{p}'$ we have

$$A(\mathbf{r};\mathbf{s}) = \langle\exp\left[2\pi i\mathbf{s}(\delta(\mathbf{p}+\mathbf{r})-\delta(\mathbf{p}))\right]\rangle \ . \tag{6}$$

This is of course true when each term in the sum is independent of $\mathbf{p}'$ (undistorted unit cells). Expanding the exponential as a Fourier series in $\mathbf{p}$ we see that (6) also holds for the less rigorous condition that this expansion has no component with the period of the lattice vector, i.e. the distortions are not periodic with the same period as the lattice.

Performing the integration by $d\tau_\mathbf{r}$ in (5) in a similar way, one obtains the form derived by Warren (1955) for the intensity distribution around the reciprocal lattice-point with radius vector $\mathbf{H}$.

$$I_\mathbf{H}(\mathbf{s}) = I_e N^2 |F_\mathbf{H}|^2 \sum_n \exp\left[2\pi i\mathbf{s} \ \mathbf{R}_m\right] A_m(s)$$

where $F_\mathbf{H}$ is the structure factor and the summation is over all lattice points in Patterson space.

Equation (5) can be taken as a standard form of the intensity expression for a non-perfect crystal. For small distortions one may introduce the approximation $A(\mathbf{r};\mathbf{s}) \to A(\mathbf{r};\mathbf{H})$ for the intensity distribution around the reciprocal-lattice point $\mathbf{H}$. (Warren (1955) —referred to later in the article as the 'Warren approximation'). $A(\mathbf{r};\mathbf{H})$ is then simply the Fourier transform of this intensity distribution.

We shall now turn our attention to the general case when this approximation may not be valid, our only assumption being that an equation of the type (5) exists.

3. The distribution functions $W(r;\mathscr{E})$ and $\psi(t;s)$

Let us introduce the two Fourier expansions of $A(\mathbf{r};\mathbf{s})$

$$A(\mathbf{r};\mathbf{s}) = \int W(\mathbf{r};\mathscr{E}) \exp\left[2\pi i\mathbf{s}\mathscr{E}\right]d\tau_\mathscr{E} \tag{7}$$

$$A(\mathbf{r};\mathbf{s}) = \int \psi(t;\mathbf{s}) \exp\left[-2\pi i\mathbf{t}\mathbf{r}\right]d\tau_t \ . \tag{8}$$

We shall see that $W(r;\mathscr{E})$ and $\psi(\mathbf{t},\mathbf{s})$ describes distortion in Patterson space and intensity space respectively. The interpretation of $W(r;\mathscr{E})$ is simple if we assume (6) to be valid. $W(\mathbf{r};\mathscr{E})$ is then the distribution function for the differences

$$\mathscr{E} = \delta(\mathbf{p}+\mathbf{r})-\delta(\mathbf{p}) \tag{}$$

i.e. the integral strains between points in the structure separated through distances $\mathbf{r}$. The same result is, however, obtained without this assumption by consideration of the Patterson functions. Let us take the Fourier transform of (5) with the aid of (7) to obtain the Patterson function of the distorted crystal

$$P(r) = \int P_0(\mathbf{r}')W(\mathbf{r}';\mathbf{r}-\mathbf{r}')d\tau_\mathbf{r} \ . \tag{9}$$

$W(\mathbf{r};\mathscr{E})$ is evidently the probability that points with a separation $\mathbf{r}$ in the undistorted crystal will have a separation $\mathbf{r}+\mathscr{E}$ in the distorted crystal.

An equation similar to (9) is obtained for the intensity distribution by introducing (8) in equation (5):

$$I(\mathbf{s}) = N^2 I_e \int I_0(\mathbf{s}-\mathbf{t})\psi(\mathbf{t};\mathbf{s})d\tau_\mathbf{t} \tag{10}$$

where $N^2 I_e I_0(\mathbf{s})$ is the intensity distribution of the undistorted crystal. (10) can be written in a different form:

$$J(\mathbf{q};\mathbf{s}) = N^2 I_e \int I_0(\mathbf{s}-\mathbf{t})\psi(\mathbf{t},\mathbf{q})d\tau_\mathbf{t}$$
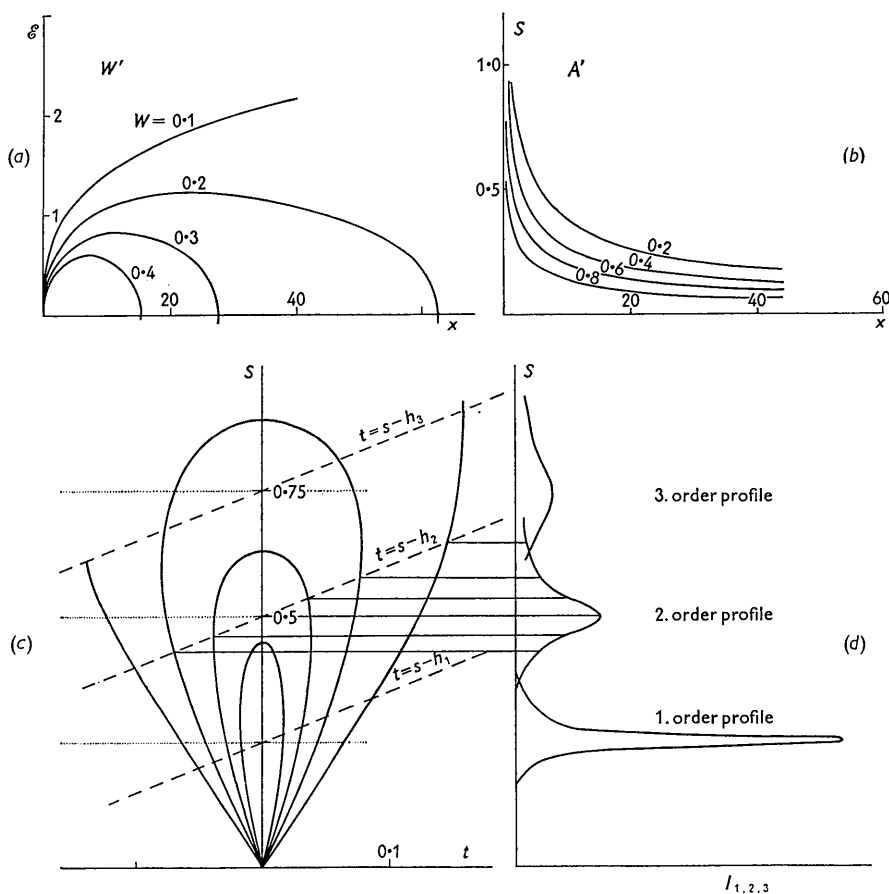$$I(\mathbf{s}) = J(\mathbf{s};\mathbf{s}) \ . \tag{10a}$$

Fig. 1. (a)–(c) Contour plot of the functions $W(x, \delta)$, $A(x, s)$ and $\psi(t, s)$ as given by the analytical example in the text ($c = 0{\cdot}2$). (d) The profiles $I_{j}(s)/KF_{j}^{2}$ as given by the sections $t = s - h_{1,2,3}$ with $h_{1} = 0{\cdot}25$. Sections corresponding to the Warren approximation are indicated by dotted lines in (c).

Here $J(\mathbf{q}; s)$ is a convolution integral of the functions I_{0} and ψ containing $\mathbf{q}$ as a parameter, and the intensity distribution $I(\mathbf{s})$ is the section $\mathbf{q} = \mathbf{s}$ through the six-dimensional coordinate space for $J(\mathbf{q}; \mathbf{s})$. Only this section of $J(\mathbf{q}; \mathbf{s})$ is determined by the intensity distribution; this indefiniteness is, of course, reflected into the functions ψ, A and W.

A considerable simplification is obtained, however, when use is made of the fact that $I_{0}(\mathbf{s})$ is a point-function, different from zero only in the reciprocal-lattice points. (10) then leads to

$$I(\mathbf{s}) = \sum_{j} N^{2} I_{e} |F_{j}|^{2} \psi(\mathbf{s} - \mathbf{H}_{j}; \mathbf{s}) \qquad (11)$$

where the sum is over all reciprocal-lattice points. F_{j} and $\mathbf{H}_{j}$ are the corresponding structure factors and reciprocal-lattice vectors.

The meaning of this equation is: The jth term in (11) represents the intensity distribution associated with the reciprocal lattice-point $\mathbf{H}_{j}$. These intensity distributions are the three-dimensional sections $\mathbf{t} = \mathbf{s} - \mathbf{H}_{j}$ through the six-dimensional coordinate space of a function $\psi(\mathbf{t}; \mathbf{s})$ which is the six-dimensional

Fourier transform of the distribution function $W(\mathbf{r}, \mathscr{E})$. ((7) and (8)). An illustration of W, ψ and A is shown in Fig. 1 (one-dimensional example).

The 'Warren approximation' is equivalent to a substitution of the sections $\mathbf{t} = \mathbf{s} - \mathbf{H}_{j}$ by the sections $\mathbf{s} = \mathbf{H}_{j}$.

The influence of crystal size may easily be taken into account by introducing a 'shape factor' (Ewald, 1940). Using the same argument as in section 2, it is found that the effect of particle size can be described by an additional factor $A_{\text{part}}(\mathbf{r})$ in the function $A(\mathbf{r}; \mathbf{s})$ (or in $W(\mathbf{r}, \mathscr{E})$). Extension to the case of a distribution of distorted crystallites offers no special difficulties.

4. Projections in reciprocal space. Analytical example

The simplest way to transfer the general results of the preceding section to the one-dimensional intensity distribution obtained from a powder is to apply the 'tangent-plane approximation' (Stokes & Wilson, 1943), that is to substitute the appropriate integration between concentric spheres in reciprocal space by one

between tangent planes.* The integration may be carried out in (5) with the aid of (7). The same result is obtained by an approximate, but possibly more instructive, argument based on the fact that a section through physical space corresponds to a projection in reciprocal space and vice versa: We consider the reflexions of orders j from a set of lattice planes, projected on to the direction of their reciprocal lattice vectors. By inspection of (9), we obtain

$$I_j(s) = K|F_j|^2 \psi'(s - h_j, s) \tag{12}$$

where K includes Lorentz and polarization factors, s and h_j are the lengths of the scattering vector and reciprocal-lattice vector respectively. The six-dimensional coordinate space for $\psi(\mathbf{t}; \mathbf{s})$ is made up of two three-dimensional ones ($\mathbf{s}$ and $\mathbf{t}$-space), and we observe that the function ψ' of (12) can be derived from the general distribution function $\psi(\mathbf{t}; \mathbf{s})$ by a projection in $\mathbf{t}$-space (on to the direction of the reciprocal lattice-vectors) and a section in $\mathbf{s}$-space (along these vectors). Its two-dimensional Fourier transform

$$W'(x, \mathscr{E}) = \iint \psi'(t, s) \exp\left[-2\pi i(tx + s\mathscr{E})\right] dt\, ds$$

is accordingly given by the general strain-distribution function $W(\mathbf{r}; \mathscr{E})$ as a section in $\mathbf{r}$-space (along the normal of the reflecting planes) and a projection in $\mathscr{E}$-space (on to this normal) $W'(x, \mathscr{E})$ is essentially the distribution $P_L(\varDelta L)$ of Warren & Averbach (1952), who discuss it in more detail. The intermediate function $A'(r, s)$ is seen to be a section of $A(\mathbf{r}; \mathbf{s})$ in both spaces.

A similar argument may be applied to sections through reciprocal space.

As an illustration we have studied a one-dimensional analytical example which may, within the tangent-plane approximation, represent the reflexions from a set of lattice planes obtained from a powder. Let the displacements be Gaussian, and randomly distributed along the normal

$$W'(x, \mathscr{E}) = (2cx)^{-\frac{1}{2}} \exp\left(-\pi \mathscr{E}^2/2cx\right)$$

from which immediately follows (cf. Campbell & Foster, 1942)

$A'(x, s) = \exp\left(-2\pi c x s^2\right)$ and $\psi'(t, s) = cs^2/\pi(c^2 s^4 + t^2)$

and the line profiles

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* A general examination of the 'tangent-plane approximation' is outside the scope of this article. Exact calculations may be carried out, however, by expanding $A(\mathbf{r}; \mathbf{s})$ in spherical harmonics and introducing the well-known Legendre series for the exponential (cf. Morse & Feshbach, 1953). The Fourier transforms (7) and (8) are then transferred into integral transforms (involving spherical Bessel functions) which combine the coefficients of $W(\mathbf{r}; \mathscr{E})$ and $\psi(\mathbf{t}; \mathbf{s})$.

$$I_j = K|F_j|^2 cs^2/\pi[c^2 s^4 + (s - h_j)^2] \,.$$

$W'(x, \mathscr{E})$, $A'(x, s)$, $\psi'(t, s)$ and the sections $I_j(s)$ are shown in Fig. 1 for the values $h_1 = 0.25$ and $c = 0.2$. (This would mean a rather heavy distortion, the line broadening being of the same order of magnitude as in organic polymers.) Notice that the lines are slightly asymmetric due to the s-dependence of ψ', whereas the sections corresponding to Warren's approximation are symmetric when W is symmetric in $\mathscr{E}$. We may examine the accuracy of this approximation in our example by differentiating ψ' with respect to s. The relative error is found to be (to the first order)

$$\varDelta I/I = 2 \cdot \frac{n^2 - 1}{n^2 + 1} \cdot \varDelta s/h_j$$

where $\varDelta s$ is the distance from the center of the line and $n/2$ is the ratio between $\varDelta s$ and the half-width.

Calculations have also been made without using the 'tangent-plane approximation' in the case of spherically symmetrical distortion broadening (i.e. to the first term in the spherical harmonics expansion). We shall only quote the results:

$$W(r, \mathscr{E}) = (2cr)^{-3/2} \exp\left(-\pi \mathscr{E}^2/2cr\right)$$
$$A(r, s) = \exp\left(-2\pi crs^2\right)$$
$$\psi(t, s) = cs^2/\pi^2(c^2 s^4 + t^2)^2$$
$$I_j(s) = K'|F_j|^2 cs/2\pi^2 h_j[c^2 s^4 + (s - h_j)^2]$$

The essential deviation from the 'tangent-plane'-result is a factor $\frac{1}{2}\pi s h_j$ to the line profile. The proportionality factor K' of the last equation will *not* contain a Lorentz factor.

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