

The Interpretation of X-ray Diffraction Intensity Distributions from Small Distorted Crystals. Definition of the Average Coherently Scattering Region

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X-ray diffraction patterns from a polycrystalline material or a small distorted crystal do not always contain enough information for the determination of the (average) geometry and the degree of distortion of the crystal(s). To avoid the consequent difficulties in the interpretation of diffraction patterns from such small distorted crystals the author introduces for the material the average lattice function $\mathcal{P}(\mathbf{x})$, that is, a repartition function. When the diffraction spots from the material can be measured separately, the $\mathcal{P}(\mathbf{x})$ function belonging to that material has certain special properties. For that case the average coherently scattering region can be defined in terms of $\mathcal{P}(\mathbf{x})$.

It is shown that the intensity distribution in such a diffraction spot can be described with the aid of the product of $C(\mathbf{x})$ and $\varphi(\mathbf{x}, \Delta\mathbf{x})$, where $C(\mathbf{x})$ is the average form function of the coherently scattering regions, $\varphi(\mathbf{x}_m, \Delta\mathbf{x})$, the special value of $\varphi(\mathbf{x}, \Delta\mathbf{x})$, is one peak of the quasiperiodic function $\mathcal{P}(\mathbf{x})$ around the m th lattice point, \mathbf{x}_m , of the average lattice. The vector \mathbf{x} represents the distance between two arbitrary unit cells in the structure; $\Delta\mathbf{x} = \mathbf{x} - \mathbf{x}_m$. Consequently the line profiles in a powder diffraction pattern can be described with the aid of $C(t) \cdot \varphi(t_m, L)$, the product of the projections of $C(\mathbf{x})$ and $\varphi(\mathbf{x}_m, \Delta\mathbf{x})$ on the perpendicular to the reflecting planes; L , t and t_m are the projections of $\Delta\mathbf{x}$, \mathbf{x} and \mathbf{x}_m respectively. It is shown that the condition $\varphi(t_m, L) = 0$ for $|L| \geq \frac{1}{2}d$ (d is the interplanar spacing) holds when the diffraction lines can be measured separately. A criterion for the applicability of the Warren-Averbach method is given.

Introduction

The geometry and degree of distortion of a small distorted crystal are often expressed by the form function $V(\mathbf{x})$ and the average strain coefficients $\langle |\Delta\mathbf{x}_m|^2 \rangle$. The form function $V(\mathbf{x})$ is the fraction of the crystal volume common to the crystal and its ghost which is displaced by \mathbf{x} with respect to the crystal.

The strain coefficients are defined by comparing the distorted crystal with an undistorted one and considering the positions of two unit cells A and B with respect to each other. Unit cell B is at a distance \mathbf{x}_m from A in the undistorted crystal; cell B is at $\mathbf{x}_m + \Delta\mathbf{x}_n$ from A in the distorted one. The strain coefficients, $\langle |\Delta\mathbf{x}_m|^2 \rangle$, are given as the mean square values of the shift $\Delta\mathbf{x}_n$ for all pairs of unit cells A and B at a distance displaced \mathbf{x}_m from each other.

The definitions of both $\langle |\Delta\mathbf{x}_m|^2 \rangle$ and $V(\mathbf{x})$ lead to difficulties in the interpretation of X-ray diffraction patterns from strongly distorted crystals: the diffraction pattern does not contain enough information for their determination.

Let us consider a crystal with bent atom rows, as in Fig. 1. When a region (a) is in the right position to scatter a parallel monochromatic X-ray beam, region (b) will not be oriented so as to scatter the same beam. Region (a) is called the coherently scattering region. It is difficult to determine the positions of the boundaries of the coherently scattering region but certainly X-ray diffraction cannot give information about the form function of the whole crystal when the distortions are

too large: it can only give information about the coherently scattering region (a).

Likewise it is impossible to determine $\langle |\Delta\mathbf{x}_m|^2 \rangle$ unambiguously from diffraction measurements. To explain this we consider the contribution to the X-ray diffraction intensity from two unit cells B and B' that have the following special positions with respect to a given unit cell A . In the undistorted crystal the position of B with respect to A is \mathbf{x}_m ; unit cell B' is at $\mathbf{x}_m + n_1\mathbf{e}_1 + n_2\mathbf{e}_2 + n_3\mathbf{e}_3$ from A in the undistorted crystal (\mathbf{e}_i are the primitive translation vectors and n_i are integers, $i=1,2,3$). In the distorted crystal B is shifted by $\Delta\mathbf{x}_n$, and B' by $\Delta\mathbf{x}_n - (n_1\mathbf{e}_1 + n_2\mathbf{e}_2 + n_3\mathbf{e}_3)$ with respect to A . Of course the positions of B and B' are identical in the distorted crystal and so their contributions to the diffraction intensity are equal. However, B and B' give different contributions to the strain coefficient, defined as above. Thus the determination of the strain coefficients from X-ray diffraction is ambiguous; the diffraction pattern does not contain enough information for their determination, especially when the distortions are too large.

In fact both the problems described above have the same origin: the size of the coherently scattering region determines the strain coefficients found and the degree of distortion determines the size of the coherently scattering region. We shall show in this paper that the above problems can be avoided by use of the average lattice function, $\mathcal{P}(\mathbf{x})$, well known in liquid diffraction and frequently used by Hosemann & Bagchi (1962) to explain the paracrystalline state; $\mathcal{P}(\mathbf{x})$ is defined below.

Definition of $\mathcal{P}(\mathbf{x})$

The average lattice function $\mathcal{P}(\mathbf{x})$ for a distorted crystalline structure is the probability density of finding the centre of a unit cell at a displacement \mathbf{x} from the centre of another arbitrary unit cell in the structure.

In principle $\mathcal{P}(\mathbf{x})$ can always be determined from a complete diffraction pattern; however, it is impossible to measure the whole pattern and it is in addition impracticable to measure it in three dimensions. In this paper it will be shown, therefore, that $\mathcal{P}(\mathbf{x})$ has special properties when the diffraction pattern is made up of discrete spots. In this case the equation that describes the intensity distribution of the individual spots can be solved in order to get information about the form function $C(\mathbf{x})$ of the average coherently scattering region and about the average distribution of atoms around the lattice points. The quantities $V(\mathbf{x})$ and $\langle |\Delta \mathbf{x}_m|^2 \rangle$, usually found from line-profile analysis, are no longer meaningful as defined above but appear as characteristics of $\mathcal{P}(\mathbf{x})$.

Derivation of the equations and definition of the coherently scattering region

In the following, derivations are given for the diffraction intensity distribution from crystals containing no stacking faults and consisting of a number of identical unit cells having approximately the same orientation. The structure factor $F(\mathbf{s})$ of such a structure is

$$F(\mathbf{s}) = f(\mathbf{s}) \sum_r \exp(2\pi i \mathbf{s} \cdot \mathbf{u}_r), \quad (1)$$

where $f(\mathbf{s})$ is the structure factor of one unit cell; \mathbf{s} is the reciprocal space coordinate and \mathbf{u}_r is the position of the centre of a unit cell. The sum is taken over all unit cells in the structure. (Unless stated otherwise the summations in the following are taken over all unit cells in the structure.)

The general formula for the intensity distribution of the diffraction pattern from this structure is

$$\begin{aligned} I(\mathbf{s}) &= F(\mathbf{s})^* F(\mathbf{s}) \\ &= f^2(\mathbf{s}) \sum_q \exp(-2\pi i \mathbf{s} \cdot \mathbf{u}_q) \sum_p \exp(2\pi i \mathbf{s} \cdot \mathbf{u}_p) \\ &= f^2(\mathbf{s}) \sum_{p,q} \exp(2\pi i \mathbf{s} \cdot \mathbf{u}_p - \mathbf{u}_q). \end{aligned} \quad (2)$$

In equation (2) $\mathbf{u}_p - \mathbf{u}_q$ is the position of unit cell p relative to unit cell q . With the aid of the primitive translation vectors \mathbf{e}_i we can express \mathbf{x}_m as

$$\mathbf{x}_m = n_1 \mathbf{e}_1 + n_2 \mathbf{e}_2 + n_3 \mathbf{e}_3, \quad (3)$$

where n_1, n_2, n_3 are integers. The points \mathbf{x}_m define the so called average lattice. We can fix the position of unit cell p relative to unit cell q unambiguously:

$$\mathbf{u}_p - \mathbf{u}_q = \mathbf{x}_m + \Delta \mathbf{x}_n = \mathbf{x}, \quad (4)$$

if we include the restriction:

$$|(\Delta \mathbf{x}_n \cdot \mathbf{e}_i)| < \frac{1}{2} |\mathbf{e}_i|^2, \quad (i=1, 2 \text{ or } 3). \quad (5)$$

The relationship (5) means that $\Delta \mathbf{x}_n$ in equation (4) is the difference between $\mathbf{u}_p - \mathbf{u}_q$ and the nearest lattice point \mathbf{x}_m .

We call $P'(\mathbf{x}_m, \Delta \mathbf{x}_n)$ the number of unit cells that are displaced by $\Delta \mathbf{x}_n$ with respect to a unit cell at a distance \mathbf{x}_m in a corresponding undistorted crystal. From equations (2), (3) and (4) the intensity distribution $I(\mathbf{s})$ can be written, with the aid of the function $P'(\mathbf{x}_m, \Delta \mathbf{x}_n)$:

$$I(\mathbf{s}) = f^2(\mathbf{s}) \sum_m \left\{ \sum_n P'(\mathbf{x}_m, \Delta \mathbf{x}_n) \exp(2\pi i \mathbf{s} \cdot \Delta \mathbf{x}_n) \right\} \times \exp(2\pi i \mathbf{s} \cdot \mathbf{x}_m), \quad (6)$$

where n and m are independent indices. The sums in equation (6) are taken over all n , including all $\Delta \mathbf{x}_n$ values that occur in the structure, and over all \mathbf{x}_m values for the structure.

If the number of unit cells in the structure is sufficiently large we can apply the continuous representation of equation (6):

$$I(\mathbf{s}) = N f^2(\mathbf{s}) \int_{-\infty}^{\infty} \sum_m \exp(2\pi i \mathbf{s} \cdot \mathbf{x}) \times \delta(\mathbf{x}_m - \mathbf{x}) d\mathbf{x} \int_{-\infty}^{\infty} \Phi'(\mathbf{x}, \Delta \mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \Delta \mathbf{x}) d\Delta \mathbf{x}, \quad (7)$$

where $\delta(\mathbf{x}_m - \mathbf{x})$ is the Dirac function; N is the total number of unit cells. The function $\Phi'(\mathbf{x}, \Delta \mathbf{x})$ is a continuous distribution function for the shift $\Delta \mathbf{x}$ that corresponds to the discontinuous function $P'(\mathbf{x}_m, \Delta \mathbf{x}_n)$. The function $\Phi'(\mathbf{x}, \Delta \mathbf{x})$ varies continuously not only with $\Delta \mathbf{x}$, but also with \mathbf{x} . However it only has real significance for the lattice when $\mathbf{x} = \mathbf{x}_m$. Then:

$$\Phi'(\mathbf{x}, \Delta \mathbf{x}) = \Phi(\mathbf{x}_m, \Delta \mathbf{x}). \quad (8)$$

Thus $\Phi'(\mathbf{x}, \Delta \mathbf{x})$ is defined as a function that has the value $\Phi(\mathbf{x}_m, \Delta \mathbf{x})$ for $\mathbf{x} = \mathbf{x}_m$. Since we have chosen $\Delta \mathbf{x}_n$ in such a way that it is the distance from the centre of a unit cell to the nearest lattice point \mathbf{x}_m , we can write

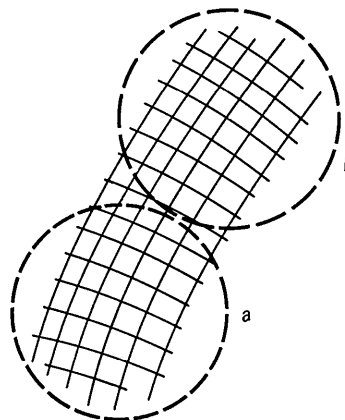


Fig.1. Diagrammatic representation of a crystal with bent rows of atoms. When region a is in the right position for scattering, region b is oriented so that it does not scatter.

for the distribution function of the displacement:

$$\Phi(\mathbf{x}_m, \Delta \mathbf{x}) = 0 \quad \text{for } |(\Delta \mathbf{x} \cdot \mathbf{e}_i)| > \frac{1}{2} |\mathbf{e}_i|^2, \quad (i=1, 2 \text{ or } 3) \quad (9)$$

The average lattice function $\mathcal{P}(\mathbf{x})$ has already been defined in the introduction. It can be expressed in terms of $\Phi(\mathbf{x}_m, \Delta \mathbf{x})$ by the relation:

$$\mathcal{P}(\mathbf{x}) = \sum_m \Phi(\mathbf{x}_m, \mathbf{x} - \mathbf{x}_m) \quad (10)$$

Of course it is always possible to express $\mathcal{P}(\mathbf{x})$ uniquely in the Fourier transform of the complete diffraction pattern $I(\mathbf{s})$. It is impossible, however, to measure the complete $I(\mathbf{s})$ pattern.

When the diffraction pattern can be separated into single broadened spots around the lattice points \mathbf{s}_n in reciprocal space, or into single diffraction lines, we can get some information about $\mathcal{P}(\mathbf{x})$ by measuring part of $I(\mathbf{s})$. For such cases $I(\mathbf{s})$ can be written as

$$I(\mathbf{s}) = \sum_n I_n(\mathbf{s} - \mathbf{s}_n) \quad (11)$$

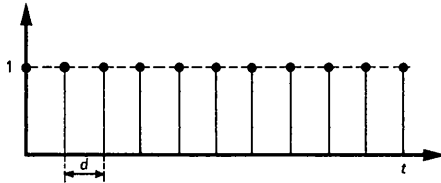


Fig.2. Integral values of the average lattice function, $\mathcal{P}(t)$, for an infinite, perfect, one-dimensional crystal.

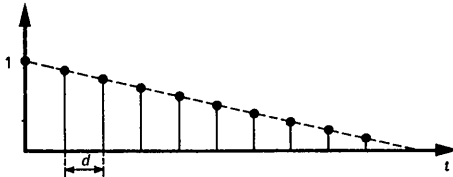


Fig.3. Integral values of the average lattice function, $\mathcal{P}(t)$, for a finite one-dimensional crystal.

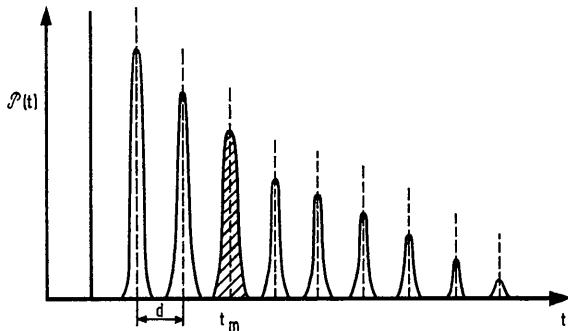


Fig.4. The average lattice function, $\mathcal{P}(t)$, for a collection of slightly distorted one-dimensional finite crystals. The (shaded) area under one peak equals $V(t)$.

$I_n(\mathbf{s} - \mathbf{s}_n)$ are the intensity distributions of the discrete diffraction spots. Equation (11) is meaningful when the crystal corresponds to a function $\mathcal{P}(\mathbf{x})$ that satisfies certain conditions, which we shall give later. Conversely it can be shown that these conditions for $\mathcal{P}(\mathbf{x})$ hold when the intensity distributions can be measured separately. To explain these properties of $\mathcal{P}(\mathbf{x})$ we give the characteristics of $\mathcal{P}(\mathbf{x})$ for some idealized cases of one-dimensional crystals. The three-dimensional analogue of the last example is the particular $\mathcal{P}(\mathbf{x})$ -function that corresponds to crystals giving separable diffraction spots.

Example 1. An infinite perfect crystal

It is clear that $\mathcal{P}(t)$ is a δ -function:

$$\mathcal{P}(t) = \sum_m \delta(t - t_m) \quad (12)$$

In Fig.2 the integral values of $\mathcal{P}(t)$ are given:

$$\int_{t_m - \Delta}^{t_m + \Delta} \mathcal{P}(t) dt = 1 \quad \text{for } t = t_m \text{ and } \Delta \rightarrow 0$$

$$= 0 \quad \text{for } t \neq t_m \text{ and } \Delta \rightarrow 0 \quad (13)$$

t is the one-dimensional lattice coordinate; t_m is the m th lattice point. When d is the net plane-distance, $t_m = dm$; $m = 0, 1, 2, \dots$

Example 2. A finite perfect crystal

When the crystal is finite, the probability of finding the centre of a unit cell at a distance t from another such centre is equal to the form function $V(t_m)$. When we look for the integral values of $\mathcal{P}(t)$ we get, therefore:

$$\int_{t_m - \frac{1}{2}d}^{t_m + \frac{1}{2}d} \mathcal{P}(t) dt = V(t_m) \quad (14)$$

$V(t_m)$ is the form function of the crystal for $t = t_m$. The integral values of $\mathcal{P}(t)$ are given in Fig.3.

Example 3. Collection of slightly distorted finite crystals of different size

For this case we can give a direct representation of $\mathcal{P}(t)$; this consists of a collection of peaks around the lattice points $t = t_m$. If we call one single peak $\varphi(t_m, L)$ and if the distortions are so small that $\varphi(t_m, L) = 0$ for $|L| \geq \frac{1}{2}d$, we can express $\mathcal{P}(t)$ by the equation

$$\mathcal{P}(t) = \sum_m V(t_m) \cdot \varphi(t_m, t - t_m) \quad (15)$$

where $L = t - t_m$. Here $V(t)$ is the average form function for the group of crystals. We have to take normalized functions for $\varphi(t_m, L)$ in order to obtain the expression

$$\int_{t_m - \frac{1}{2}d}^{t_m + \frac{1}{2}d} \mathcal{P}(t) dt = \int_{-\frac{1}{2}d}^{+\frac{1}{2}d} V(t_m) \cdot \varphi(t_m, L) dL = V(t_m) \quad (16)$$

(see Fig.4).

Example 4. Collection of slightly distorted finite crystals in a 'perfectly distorted' matrix

In example 3 a $\mathcal{P}(t)$ -function was discussed that does not correspond to a polycrystalline material. In that example $\mathcal{P}(t)$ is zero if t is larger than the crystals. In a polycrystalline material without clustering, however, the probability of finding the centre of a unit cell at a distance t from the centre of another is equal to $1/v$, when t is larger than the crystals (v is the volume of one unit cell.) Thus $\mathcal{P}(t)$ is a constant for large t ; this may be called 'perfect distortion'.

The perfectly distorted surroundings of the crystals are built up of unit cells identical with those of the crystals. Since we assume the absence of clustering in the polycrystalline material we can write

$$\mathcal{P}(t) = \sum_m V(t_m) \varphi(t_m, t-t_m) + (1/v) \{1 - V(t)\}. \quad (17)$$

Again $\varphi(t_m, t-t_m) = 0$ for $|t-t_m| \geq \frac{1}{2}d$. The term $(1/v) \{1 - V(t)\}$ describes the contribution to $\mathcal{P}(t)$ from the perfectly distorted surroundings of the crystals. The graphical representation of $\mathcal{P}(t)$ consists of peaks as in Fig. 4, superposed on the monotonically changing curve $(1/v) \{1 - V(t)\}$ (see Fig. 5). Since $V(t)$ in the interval $t_m - \frac{1}{2}d < t < t_m + \frac{1}{2}d$ may be approximated to a straight line, it can be shown that

$$\int_{t_m - \frac{1}{2}d}^{t_m + \frac{1}{2}d} \mathcal{P}(t) dt = 1 \quad (18)$$

as a consequence of the absence of clustering. The above example gives, apart from one-dimensionality, a more realistic $\mathcal{P}(t)$ function for a distorted polycrystalline material.

Example 5. A strongly distorted finite crystal in a 'perfectly distorted' matrix

It is possible to deduce the graphical representation of $\mathcal{P}(t)$ for this case from the former example: since the distortions are stronger than in example 4, the peaks from Fig. 5 are broadened and begin to overlap

each other for certain values of t . $\mathcal{P}(t)$ still consists of peaks superposed upon a monotonically changing function. Let us call the monotonic function $(1/v) \{1 - C(t)\}$; the function $C(t)$ is analogous to $V(t)$. The function $(1/v) \{1 - C(t)\}$ passes through the minima of $\mathcal{P}(t)$ so this choice leaves some ambiguity in $C(t)$, but for most cases $C(t)$ will change slowly with respect to the quasiperiodic function $\mathcal{P}(t)$; we will restrict ourselves to these cases so the ambiguity in $C(t)$ is then only small.

If we again describe the peaks of $\mathcal{P}(t)$ in terms of $\varphi(t_m, L)$, the condition $\varphi(t_m, L) = 0$ for $|L| \geq \frac{1}{2}d$ still holds, to a good approximation, if the shape of $\varphi(t_m, L)$ varies slowly with t_m . We will further restrict ourselves to these cases. It is possible to formulate $\mathcal{P}(t)$ for the above assumptions with

$$\mathcal{P}(t) = \sum_m C(t_m) \varphi(t_m, t-t_m) + (1/v) \{1 - C(t)\}. \quad (19)$$

$\varphi(t_m, t-t_m)$ are normalized functions and by formula (19) the normalization condition still holds. Formally equations (17) and (19) are identical and since $\mathcal{P}(t)$ determines the diffraction pattern uniquely, it is impossible to distinguish, by diffraction measurements, a large strongly distorted crystal from a small distorted crystal in a perfectly distorted matrix. This is the essence of the problems quoted in the introduction.

Since $C(t)$ is a slowly varying function of t and since the right hand sides of equation (19) and the one-dimensional analogue of (10),

$$\mathcal{P}(t) = \sum_m \Phi(t_m, t-t_m), \quad (20)$$

have to be identical, we may write

$$\Phi(t_m, t-t_m) = C(t_m) \varphi(t_m, t-t_m) + (1/v) \{1 - C(t_m)\}. \quad (21)$$

We now leave the one-dimensional examples and rewrite (21) for the analogous three-dimensional case:

$$\Phi(\mathbf{x}_m, \Delta \mathbf{x}) = C(\mathbf{x}_m) \varphi(\mathbf{x}_m, \Delta \mathbf{x}) + (1/v) \{1 - C(\mathbf{x}_m)\} \quad (22)$$

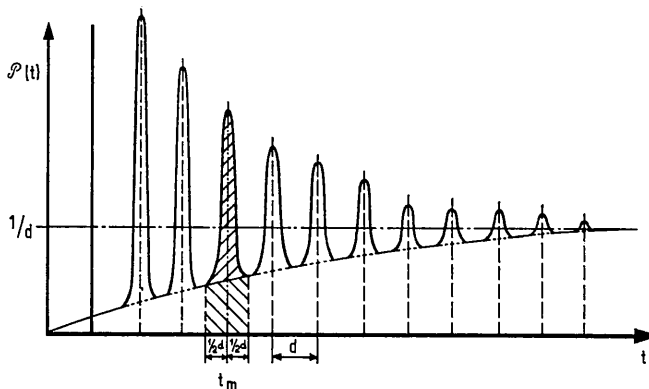


Fig. 5. The average lattice function for the same case as in Fig. 4. The crystals are now located in a completely distorted matrix of the same density as that of the crystals. The dotted line on which the peaks are superposed is $\{(1 - V(t))\} (1/d)$. The area under one peak is $V(t)$. The total area under $\mathcal{P}(t)$ around one lattice node is 1 (shaded).

with the condition

$$\varphi(\mathbf{x}_m, \Delta\mathbf{x}) = 0 \text{ for } |(\Delta\mathbf{x} \cdot \mathbf{e}_i)| \geq \frac{1}{2}|\mathbf{e}_i|^2, (i=1,2 \text{ or } 3). \quad (23)$$

$C(\mathbf{x}_m)$ and the shape of $\varphi(\mathbf{x}_m, \Delta\mathbf{x})$ vary slowly with \mathbf{x}_m . By substitution of equation (22) into equation (10) we get the $\mathcal{P}(\mathbf{x})$ function with the required properties, corresponding to crystals that give separable diffraction spots. To show this, we write for $\Phi(\mathbf{x}_m, \Delta\mathbf{x})$:

$$\Phi(\mathbf{x}_m, \Delta\mathbf{x}) = C'(\mathbf{x}_m)\varphi'(\mathbf{x}_m, \Delta\mathbf{x}) + (1/v) \{1 - C'(\mathbf{x}_m)\}. \quad (24)$$

The conditions from example 5 are not imposed upon $\varphi'(\mathbf{x}_m, \Delta\mathbf{x})$ and $C'(\mathbf{x}_m)$. However, we take $C'(\mathbf{x})$ to be a monotonic function of \mathbf{x} , such that $\varphi'(\mathbf{x}_m, \Delta\mathbf{x})$ is as small as possible for $|(\Delta\mathbf{x} \cdot \mathbf{e}_i)| = \frac{1}{2}|\mathbf{e}_i|^2$. We then get for the diffraction intensity distribution from any structure:

$$\begin{aligned} I(\mathbf{s}) &= Nf^2(\mathbf{s}) \int_{-\infty}^{\infty} \exp(2\pi i \mathbf{s} \cdot \mathbf{x}) \\ &\times \sum_m \delta(\mathbf{x}_m - \mathbf{x}) d\mathbf{x} \int_{-\infty}^{\infty} C'(\mathbf{x}) \varphi'(\mathbf{x}, \Delta\mathbf{x}) \\ &\times \exp(2\pi i \mathbf{s} \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) + \{Nf^2(\mathbf{s})/v\} \\ &\times \int_{-\infty}^{\infty} \exp(2\pi i \mathbf{s} \cdot \mathbf{x}) \sum_m \delta(\mathbf{x}_m - \mathbf{x}) d\mathbf{x} \int_{-\infty}^{\infty} U(\Delta\mathbf{x}) \\ &\times \{1 - C'(\mathbf{x})\} \exp(2\pi i \mathbf{s} \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) \equiv I_a(\mathbf{s}) + I_b(\mathbf{s}). \quad (25) \end{aligned}$$

$U(\Delta\mathbf{x})$ is the form factor of one translation unit cell;

$$\begin{aligned} U(\Delta\mathbf{x}) &= 1 \text{ for } |(\Delta\mathbf{x} \cdot \mathbf{e}_i)| \leq \frac{1}{2}|\mathbf{e}_i|^2, (i=1,2 \text{ or } 3) \\ &= 0 \text{ for } |(\Delta\mathbf{x} \cdot \mathbf{e}_i)| > \frac{1}{2}|\mathbf{e}_i|^2, (i=1,2 \text{ or } 3). \quad (26) \end{aligned}$$

We consider the first term in equation (25), $I_a(\mathbf{s})$. If we put

$$A(\mathbf{s}, \mathbf{x}) = \int_{-\infty}^{\infty} C'(\mathbf{x}) \varphi'(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) \quad (27)$$

then we can write

$$\begin{aligned} I_a(\mathbf{s}) &= Nf^2(\mathbf{s}) \int_{-\infty}^{\infty} \sum_m A(\mathbf{s}, \mathbf{x}) \delta(\mathbf{x}_m - \mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \mathbf{x}) d\mathbf{x} \\ &= Nf^2(\mathbf{s}) \int_{-\infty}^{\infty} A(\mathbf{s}, \mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \mathbf{x}) d\mathbf{x} * \\ &\int_{-\infty}^{\infty} \sum_m \delta(\mathbf{x}_m - \mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \mathbf{x}) d\mathbf{x} \\ &= Nf^2(\mathbf{s}) \sum_n \delta(\mathbf{s} - \mathbf{s}_n) * \int_{-\infty}^{\infty} A(\mathbf{s}, \mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \mathbf{x}) d\mathbf{x} \\ &= Nf^2(\mathbf{s}) \sum_n \int_{-\infty}^{\infty} A(\mathbf{s}, \mathbf{x}) \exp(2\pi i \mathbf{x} \cdot \mathbf{s} - \mathbf{s}_n) d\mathbf{x}, \quad (28) \end{aligned}$$

where * means the convolution integral of the quantities at both sides of the sign. Furthermore we have to take the lattice points \mathbf{x}_m such that

$$(\mathbf{s}_m \cdot \mathbf{x}_m) = M = \text{integer}. \quad (29)$$

The above calculation of $I_a(\mathbf{s})$ is possible because $C'(\mathbf{x})\varphi'(\mathbf{x}, \Delta\mathbf{x})$ varies rapidly with $\Delta\mathbf{x}$ and consequently $A(\mathbf{s}, \mathbf{x})$ varies slowly with \mathbf{s} .

When we evaluate the second term in equation (25), $I_b(\mathbf{s})$, we find that it behaves quite differently from $I_a(\mathbf{s})$; $I_b(\mathbf{s})$ describes only a small angle effect:

$$\begin{aligned} I_b(\mathbf{s}) &= \{Nf^2(\mathbf{s})/v\} \sum_m \exp(2\pi i \mathbf{s} \cdot \mathbf{x}_m) \int_{-\infty}^{\infty} \{1 - C'(\mathbf{x}_m)\} \\ &\times U(\Delta\mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}) = \{Nf^2(\mathbf{s})/v\} \\ &\times \sum_m \int_{-\infty}^{\infty} \exp(2\pi i \mathbf{s} \cdot \mathbf{x}_m + \Delta\mathbf{x}) \{1 - C'(\mathbf{x}_m)\} U(\Delta\mathbf{x}) d(\Delta\mathbf{x}) \\ &= \{Nf^2(\mathbf{s})/v\} \int_{-\infty}^{\infty} \{1 - C'(\mathbf{x})\} \exp(2\pi i \mathbf{s} \cdot \mathbf{x}) d\mathbf{x}. \quad (30) \end{aligned}$$

It is easily shown that the small angle effect that is described by the first term in the sum for $I_a(\mathbf{s})$ in equation (28) plus $I_b(\mathbf{s})$ is a δ -function.

Let us consider further the diffraction pattern from a crystalline material. It is possible to separate the diffraction pattern into single intensity distributions $I_n(\mathbf{s} - \mathbf{s}_n)$ [equation (11)] if $I_n(\mathbf{s} - \mathbf{s}_n)$ decreases sufficiently rapidly with $|\mathbf{s} - \mathbf{s}_n|$. Following equation (28) this means that $A(\mathbf{s}, \mathbf{x})$ must vary sufficiently slowly with \mathbf{x} and hence $C'(\mathbf{x})$ and the shape of $\varphi(\mathbf{x}, \Delta\mathbf{x})$ must also change sufficiently slowly with \mathbf{x} . These are just the conditions for $\mathcal{P}(\mathbf{x})$ assumed in example (5), so the above restrictions on $\mathcal{P}(\mathbf{x})$ may be assumed to apply when the diffraction pattern consists of separated (broadened) spots.

It is important to realize that the condition (23) for $\varphi'(\mathbf{x}_m, \Delta\mathbf{x})$ holds, to a good approximation, when the diffraction spots can be measured separately; the intensity distribution around the reciprocal lattice points $\mathbf{s}_n \neq \mathbf{O}$ can then be described by

$$\begin{aligned} I_n(\mathbf{s}) &= Nf^2(\mathbf{s}) \int_{-\infty}^{\infty} \exp(2\pi i \mathbf{x} \cdot \mathbf{s} - \mathbf{s}_n) d\mathbf{x} \\ &\times \int_{-\infty}^{\infty} C(\mathbf{x}) \varphi(\mathbf{x}, \Delta\mathbf{x}) \exp(2\pi i \mathbf{s} \cdot \Delta\mathbf{x}) d(\Delta\mathbf{x}). \quad (31) \end{aligned}$$

The functions $C(\mathbf{x})$ and $\varphi(\mathbf{x}, \Delta\mathbf{x})$ are equal to $C'(\mathbf{x})$ and $\varphi'(\mathbf{x}, \Delta\mathbf{x})$ if the restrictions in example (5) apply. Equation (31) expresses the proof that the intensity distribution around the reciprocal lattice points $\mathbf{s}_n \neq \mathbf{O}$ from a distorted crystal depends on the quasiperiodic part of the average lattice function, described by $C(\mathbf{x})\varphi(\mathbf{x}, \Delta\mathbf{x})$. We may conclude that $C(\mathbf{x}_m)$ is the fraction of unit cells that are at a distance \mathbf{x} from another arbitrary unit cell in the structure, for those values of \mathbf{x} such that $|(\mathbf{x} - \mathbf{x}_m \cdot \mathbf{e}_i)| \leq \frac{1}{2}|\mathbf{e}_i|^2$, and that contribute simultaneously to scattering. The same significance can be given to the form function $V(\mathbf{x}_m)$ for a nearly perfect crystal; in this sense it gives the same information about the crystal as in the original definition in terms of the displaced ghost. Thus $C(\mathbf{x})$ can be taken to be the form function of the coherently scattering region. It is now reasonable to propose the following definition of the average coherently scattering region.

Definition of the average coherently scattering region

The average coherently scattering region in a distorted crystal is the region that corresponds to a form function $C(\mathbf{x})$.

The special value $C(\mathbf{x}_m)$ corresponds to the volume integral of $\mathcal{P}(\mathbf{x})$ under one peak around \mathbf{x}_m minus the volume integral of the monotonic part of $\mathcal{P}(\mathbf{x})$ for values of \mathbf{x} such that $|(\mathbf{x} - \mathbf{x}_m) \cdot \mathbf{e}_i| \leq \frac{1}{2}|\mathbf{e}_i|^2$. Since $V(\mathbf{x})$ and $C(\mathbf{x})$ are equivalent in the above sense, the Bertaut (1950) analysis for the particle size distribution function can be applied in the same way to both $C(\mathbf{x})$ and $V(\mathbf{x})$.

Let us now derive from equation (31) a formula that gives the intensity profile of a Debye-Scherrer line; this formula will also give the projection on to the direction of \mathbf{s}_n of a diffraction spot around \mathbf{s}_n . For this we resolve \mathbf{s} : $\mathbf{s} = \mathbf{s}_n + \mathbf{u} + \mathbf{s}_0$, where \mathbf{u} is perpendicular to \mathbf{s}_n and \mathbf{s}_0 is parallel to \mathbf{s}_n , and we take $\mathbf{s}'_0 = \mathbf{u} + \mathbf{s}_0$.

We now resolve \mathbf{x} : $\mathbf{x} = \mathbf{x}_m + \mathbf{v} + \mathbf{x}_0$, where \mathbf{v} is perpendicular to \mathbf{s}_n and \mathbf{x}_0 parallel to \mathbf{s}_n , and we also take $\Delta\mathbf{x} = \mathbf{x}_0 + \mathbf{v}$.

Let us denote $|\mathbf{x}_0|$ by L , $|\mathbf{s}_n|$ by s_n and $|\mathbf{s}_0|$ by s_0 . Then, since $(\Delta\mathbf{x}, \mathbf{s}_0)$ is small,

$$(\mathbf{s} \cdot \Delta\mathbf{x}) = s_n L. \quad (32)$$

We denote the projection of \mathbf{x} along \mathbf{s}_n by t and its modulus by t . Then $(\mathbf{u} \cdot \mathbf{t}) = 0$ and $(\mathbf{s}_0 \cdot \mathbf{x}) = s_0 t$, such that

$$(\mathbf{u} + \mathbf{s}_0 \cdot \mathbf{x}) = (\mathbf{u} \cdot \mathbf{x} - t) + s_0 t. \quad (33)$$

The projection of the intensity distribution on \mathbf{s}_n that we wish to calculate is

$$I_n(s_0) = \int_{-\infty}^{\infty} I_n(\mathbf{s}) d\mathbf{u}. \quad (34)$$

We substitute equations (31), (32) and (33) in equation (34) and if at the same time we make the substitutions

$$C(t) = \int_{-\infty}^{\infty} C(\mathbf{x}) d\mathbf{v} \quad (35)$$

and

$$\varphi(t, L) = \int_{-\infty}^{\infty} \varphi(t, L, \mathbf{v}) d\mathbf{v}, \quad (36)$$

the result is:

$$\begin{aligned} I_n(s_0) &= Nf^2(\mathbf{s}_n) \int_{-\infty}^{\infty} \exp(2\pi i \mathbf{u} \cdot \mathbf{x} - t) d\mathbf{u} \\ &\times \int_{-\infty}^{\infty} \exp(2\pi i s_0 t) d\mathbf{x} \int_{-\infty}^{\infty} C(\mathbf{x}) \exp(2\pi i s_n L) dL \\ &\times \int_{-\infty}^{\infty} \varphi(\mathbf{x}, \mathbf{v}, L) d\mathbf{v} = Nf^2(\mathbf{s}_n) \\ &\times \int_{-\infty}^{\infty} \exp(2\pi i s_0 t) dt \int_{-\infty}^{\infty} C(t) \varphi(t, L) \exp(2\pi i s_n L) dL. \end{aligned} \quad (37)$$

In analogy with equation (23) we can say that

$$\varphi(t, L) = 0 \quad \text{for } |L| \geq \frac{1}{2}d \quad (38)$$

when the diffraction lines can be measured separately. In this sense equation (37) gives the intensity distribution of a Debye-Scherrer line and at the same time it gives the projection on to the direction of \mathbf{s}_n of the intensity distribution of a diffraction spot from a single crystal around \mathbf{s}_n .

In a previous paper (La Fleur & Koopmans, 1968) equations were derived that express $\varphi(t, L)$ and $V(t)$ for the above conditions in terms of the Fourier coefficients from the line profiles of Debye-Scherrer lines, $A_n^{re}(t)$ and $A_n^{im}(t)$, by use of equation (37). [$A_n^{re}(t)$ and $A_n^{im}(t)$ are the real and imaginary parts of the Fourier coefficients from the line of the n th order.] However, in that equation $V(t)$ was put instead of $C(t)$. It is clear that here we may vary $V(t)$ with $C(t)$. The equations become:

$$\begin{aligned} \varphi(t, L) &= 1/d + \{2/[dC(t)]\} \sum_{n=1}^{\infty} [A_n^{re}(t) \cos(2\pi nL/d) \\ &\quad + A_n^{im}(t) \sin(2\pi nL/d)] \end{aligned} \quad (39)$$

and

$$C(t) = 2 \sum_{n=1}^{\infty} (-1)^{n+1} A_n^{re}(t). \quad (40)$$

The projection of the average lattice function on to the perpendicular to the reflecting planes can be determined, in principle, with the aid of equations (19), (39) and (40). The standard deviation $\langle L_t^2 \rangle$ of $\varphi(t, L)$, the average value of L , $\langle L_t \rangle$ and the average of the modulus of L , $\langle |L_t| \rangle$ can be expressed as:

$$\langle L_t^2 \rangle = d^2/12 - \{d^2/[\pi^2 C(t)]\} \sum_{n=1}^{\infty} (-1)^{n+1} A_n^{re}(t)/n^2; \quad (41)$$

$$\langle L_t \rangle = \{d/[\pi C(t)]\} \sum_{n=1}^{\infty} (-1)^{n+1} A_n^{im}(t)/n; \quad (42)$$

$$\langle |L_t| \rangle = d/4 - \{2d/[\pi^2 C(t)]\} \sum_{n=0}^{\infty} A_{2n+1}^{re}(t)/(2n+1)^2. \quad (43)$$

Discussion

We have introduced the average lattice function $\mathcal{P}(\mathbf{x})$ for a distorted crystalline material and we have given equations that express its projection, $\mathcal{P}(t)$, in terms of the Fourier coefficients of Debye-Scherrer lines, whenever the lines can be measured separately. As is shown in the paper by La Fleur & Koopmans (1968), for some hypothetical distribution functions $\varphi(t, L)$, the series in equation (40) is not always sufficiently convergent for practical application. This is especially the case when the distribution function, $\varphi(t, L)$, is a sharp function of L around the lattice points, *i.e.* nearly perfect crystals.

The average lattice function might be characterized with the aid of the Warren & Averbach (1952) method which was devised for nearly perfect crystals. We have to investigate, therefore, the relation of $C(t)$ to $V(t)^W$ obtained by the Warren & Averbach method.

The essence of this method is the insertion of distribution functions, $\varphi(t, L)^W$, in equation (37) of the form

$$\varphi(t, L)^W = \{2\pi\langle L^2(t) \rangle^W\}^{-1/2} \exp \{-L^2/2\langle L^2(t) \rangle^W\}; \quad (44)$$

$\langle L^2(t) \rangle^W$ are the strain coefficients obtained by the Warren & Averbach method. Following this method separated intensity profiles of the diffraction lines have to be measured. Therefore the substitution of functions like in equation (44) into equation (37) implies an inexactness since these functions do not satisfy the condition $\varphi(t, L) = 0$ for $|L| \geq \frac{1}{2}d$. However, for small $\langle L^2(t) \rangle^W$ values the inexactness is negligible. Let us investigate therefore to what extend functions of the form (44) are admissible. The projection of the average lattice function for the Warren & Averbach model, $\mathcal{P}(t)^W$, is

$$\begin{aligned} \mathcal{P}(t)^W &= \sum_m V(t_m)^W \{2\pi\langle L^2(t_m) \rangle^W\}^{-1/2} \\ &\times \exp \left\{ -(t - t_m)^2 / 2\langle L^2(t_m) \rangle^W \right\} + \{1 - V(t_m)^W\} (1/d). \end{aligned} \quad (45)$$

It follows from equation (31) that we can determine the quasiperiodic part of $\mathcal{P}(t)^W$ from the intensity profile of a Debye-Scherrer line; from equation (19) the area under one peak of this quasiperiodic part is equal to $C(t_m)$. The total area under $\mathcal{P}(t)^W$ between $t_m - \frac{1}{2}d < L < t_m + \frac{1}{2}d$ for the m th lattice point is unity. The contribution to that area from the monotonic part of the average lattice function is $\{1 - V(t_m)\}$ plus the area from the tails of the neighbouring gaussian distributions. Thus:

$$\begin{aligned} 1 &= C(t_m) + \{1 - V(t_m)^W\} \\ &+ \sum_{n=0}^{\infty} V(t_n)^W \{2\pi\langle L^2(t_n) \rangle^W\}^{-1/2} \\ &\times \int_{-d/2}^{d/2} \exp \left\{ -(L - t_n - t_m)^2 / 2\langle L^2(t_n) \rangle^W \right\} dL \\ &- V(t_m)^W \{2\langle L^2(t_m) \rangle^W\}^{-1/2} \\ &\times \int_{-d/2}^{d/2} \exp \left\{ -(L - t_m)^2 / 2\langle L^2(t_m) \rangle^W \right\} dL. \end{aligned} \quad (46)$$

This is illustrated in Fig. 6. When $V(t_m)^W$ and $\langle L^2(t_m) \rangle^W$ are slowly varying functions of t_m and the gaussian distributions are not too broad, equation (46) can be approximated by

$$\begin{aligned} C(t_m) &= V(t_m) \{2\langle L^2(t_m) \rangle^W\}^{-1/2} \\ &\times \int_0^{d/2} \exp \left\{ -L^2 / 2\langle L^2(t_m) \rangle^W \right\} dL. \end{aligned} \quad (47)$$

For $\langle L^2(t_m) \rangle^W \ll \frac{1}{4}d^2$ equation (47) reduces to

$$C(t_m) = V(t_m)^W, \quad (48)$$

but the deviation of $C(t_m)$ from $V(t_m)^W$ becomes more apparent as $\langle L^2(t_m) \rangle^W$ increases. A criterion could be $\langle L^2(t_m) \rangle^W < 1/36d^2$.

What are the consequences of (47) for the determination of the average lattice function, and what does (47) signify for the Warren & Averbach method? The Warren & Averbach method can be used as an independent method, as long as $\langle L^2(t_m) \rangle^W$ satisfies the above criterion.

However, it is clear from equation (47) that we have to be critical in the application of the Warren & Averbach method for large strain coefficients, even when the distribution functions are gaussian.

In the case where the gaussian curves begin to overlap each other the functions $\varphi(t, L)$ begin to look like the first period of $(1/d) \{1 + \cos(2\pi L/d)\}$. To obtain a direct criterion we note that the first period of $(1/d) \{1 + \cos(2\pi L/d)\}$ gives $\langle L^2 \rangle = 1/36d^2$; those functions with approximate form $(1/d) \{1 + \cos(2\pi L/d)\}$ can be approximated very well by the first terms of a Fourier series, as in formula (39). Therefore it is expected that an approximation of $C(t)$ by a few terms of the series in equation (40) is quite reliable in the region where the Warren & Averbach method is possibly no longer valid.

In addition, it may be inferred that the coherently scattering regions are identical with definite crystals, from the fact that, from equation (47), $C(t) = V(t)^W$ for all values of t , especially for large t .

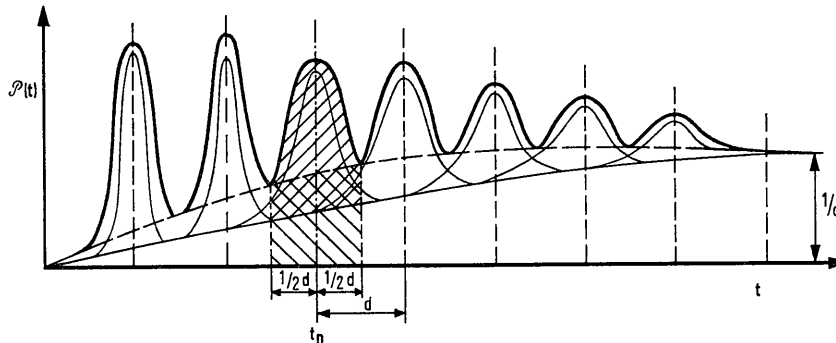


Fig. 6. The average lattice function composed of gaussian curves. The dotted line is $\{1 - C(t)\} (1/d)$; the thin continuous line is $\{1 - V(t)\} (1/d)$. The total area is 1, made up from the contributions from $C(t_n)$ (//), $\{1 - V(t_n)\}$ (\) and from the overlap of the gaussian curves (x).

Conclusions

When the intensity distribution of a diffraction pattern from a crystalline material can be measured as separate distributions around the reciprocal lattice points \mathbf{s}_n , the average lattice function $\mathcal{P}(\mathbf{x})$ (a repartition function) satisfies certain conditions. In this case $\mathcal{P}(\mathbf{x})$ is the sum of a monotonic function of \mathbf{x} and a quasi-periodic function. The quasiperiodic part of the average lattice function describes the intensity distribution of the diffraction pattern. Therefore the form function, $C(\mathbf{x}_m)$, of the coherently scattering region equals the volume integral of the peak of the average lattice function around the m th node of the average lattice, and the coherently scattering region may be defined as a region of matter corresponding to the form function $C(\mathbf{x})$. This function $C(\mathbf{x}_m)$ represents the fraction of unit cells in the structure around the m th average lattice point \mathbf{x}_m that contribute to coherent scattering. In addition, a peak of the average lattice function can be described by $C(\mathbf{x}_m)\varphi(\mathbf{x}_m, \Delta\mathbf{x})$, where $\varphi(\mathbf{x}_m, \Delta\mathbf{x}) = 0$ for $|\mathbf{e}_i \cdot \Delta\mathbf{x}| \geq \frac{1}{2}|\mathbf{e}_i|^2$.

We can determine from a powder diffraction pattern the projections on to the perpendicular to the reflecting planes $C(t)$ and $\varphi(t, L)$ of $C(\mathbf{x})$ and $\varphi(\mathbf{x}, \Delta\mathbf{x})$, if the diffraction lines can be measured separately; in this case

$\varphi(t, L)$ can be set at zero for $|L| \geq \frac{1}{2}d$. Thus equations derived in a previous paper by La Fleur & Koopmans (1968) can be used for the determination of $C(t)$ when the convergence of the series in the given expression for $C(t)$ is sufficiently rapid, that is, when the distortions are sufficiently great. The Warren & Averbach method implies a certain inexactness in this case, even when the distribution functions are gaussian. However, if the series in the given expression for $C(t)$ does not converge sufficiently rapidly, *i.e.* the distortions are sufficiently small, it is justifiable to apply the Warren & Averbach method.

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Généralisation de la Notion de Champs d'Ondes en Théorie Dynamique

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Using Takagi's theory of X-ray diffraction by a perfect crystal and the general theory of differential equations, a solution of Takagi's equations is given in the form of a linear combination of two unit vectors of the vectorial space formed by the solutions of these equations. The amplitude distribution inside the crystal is then the sum of two terms, each term being the convolution of a function depending on the amplitude distribution on the incident surface and one of the two principal solutions of Takagi's equation which are Hankel functions of the first and second kind, H_0^1 and H_0^2 . This gives an extension of the notion of wave fields since this calculation can be done for any kind of incident wave on the entrance surface. It is shown that these two 'generalized wave fields' present anomalous absorption. In the case of an incident plane wave or an incident spherical wave, these 'generalized wave fields' become identical with the usual wave fields of the dynamical theory.

1. Introduction

Les développements de la théorie dynamique des rayons X pour les cristaux parfaits ont conduit à introduire la notion de champ d'ondes. Darwin, Ewald (1917), puis Laue (1931, 1960) ont montré qu'une onde incidente plane de polarisation donnée et de vecteur
 $\vec{OM} = \mathbf{K}_0^{(\omega)}$ donnait naissance à l'intérieur du cristal à quatre ondes groupées en deux champs

d'ondes; chaque champ d'ondes est constitué par la superposition de deux ondes planes ψ_h et ψ_0 inséparables, dont les vecteurs d'onde se déduisent l'un de l'autre par translation du réseau réciproque. Les vecteurs d'onde \mathbf{K}_h et \mathbf{K}_0 menés des noeuds H et O du réseau réciproque qui se trouvent sur la sphère d'Ewald, ont donc même extrémité P ; lorsque l'écart à l'incidence de Bragg de l'onde plane incidente varie, P décrit la surface de dispersion, surface à deux nappes.