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## Diffuse Scattering in Electron Diffraction Patterns.

### I. General Theory and Computational Methods

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The solution of the  $n$ -beam dynamical theory of the diffraction of electrons by crystals is generalized to cover the case of diffraction by crystals containing defects and disorders, including thermal motion. The conditions and assumptions under which practical computer calculations of diffuse intensities can be made are explored on the basis of the slice approach of Goodman and Moodie, although matrix methods are equally applicable. It is shown that, if the range of correlation of the deviations from the perfect crystal lattice is small, the total diffuse scattering can be expressed in terms of dynamical factors which multiply the intensities calculated using the kinematical approximation. Simple expressions are derived for the absorption coefficients which must be applied to the sharp Bragg reflexions to take account of the energy lost from them into the diffuse scattering. The possibility that the intensity of diffuse scattering may show dependence on the range of correlation of the defects is discussed.

#### 1. Introduction

Especially since improved techniques have made it possible to observe single-crystal spot patterns from very small single crystals, a great many observations have been made of diffuse scattering effects in electron diffraction patterns, arising from thermal motion of the atoms and various types of defects and disorder in the crystal. In many cases these observations parallel those made on single crystals by X-ray diffraction methods,

but the relative ease of observation of the effects in electron diffraction patterns, the possibility of using extremely small crystals, and the increasing evidence for effects not directly comparable with those familiar from X-ray work are all factors which suggest that a sound basis for the interpretation of the observed intensities would be of great value.

Following the initial work of Yoshioka (1957), concerning the effects of inelastic diffuse-scattering processes, a number of authors have reported theoretical

treatments of diffraction from crystals giving various types of diffuse scattering. Takagi (1958) treated thermal diffuse scattering on the basis of the Ewald-Laue theory and this theory was later extended to other kinds of diffuse scattering by Fujimoto & Howie (1966). But, for the most part, authors have been concerned only with the consequent addition of absorption coefficients for the Bragg reflexions and, especially when results are calculated, have limited themselves almost entirely to the assumption of two-beam situations. However in the single-crystal electron diffraction patterns of interest for studies on diffuse scattering it is only rarely that there is only one strong diffracted beam, in addition to the incident beam, at any one time. Some of the most interesting patterns are obtained when the incident beam is near to a principal orientation, when many strong diffracted beams appear simultaneously for even the most perfect of crystals and within any reasonable range of crystal thickness. It is therefore necessary to make use of one of the several formulations of the  $n$ -beam scattering problem. We choose to consider, for the most part, the slice formulation of the  $n$ -beam theory due to Cowley & Moodie (1957) and the computing methods based on this, developed by Goodman & Moodie (1965), but the main arguments are independent of the choice of approach and reference will be made also to matrix formulations such as that of Fujimoto (1959) and the computational methods which derive from it, such as that described by Fisher (1967).

A formulation of the theory of diffuse scattering in the most general dynamical diffraction conditions has been made by Gjønnes (1965, 1966) and calculations based on this approach have been reported by Gjønnes & Watanabe (1966) and by Fisher (1965) who used relatively simple assumptions and dealt with small numbers of diffracted beams. The concepts of the formulation of Gjønnes form a starting point for the present considerations.

In what follows it will be assumed that the kinematical scattering problem for any system considered has been, or can be solved. We can express the kinematical intensity in terms of the Fourier transform of the generalized correlation function  $G(\mathbf{r}, t)$  of van Hove (1954). For fast electrons it is usual to make the assumption of pseudo-elastic scattering, so that we need consider only  $G(\mathbf{r}, 0)$  which is equivalent to the time average of the Patterson functions  $P(\mathbf{r})$  of the instantaneous configurations of scattering matter at time  $t$ . When the kinematical approximation is no longer valid, and dynamical effects are considered, an equivalent formulation of the scattering problem cannot, in general, be made since it is the amplitudes of scattered waves which must be added coherently. It is relevant to consider under what circumstances it may be a valid approximation to use some sort of a localized correlation function to derive diffuse scattering under conditions of dynamical diffraction. If this cannot be done it is necessary to work with an actual model of the crystal imperfections

and from that calculate amplitudes. Such a process is necessarily more difficult in practice and more subject to uncertainties arising from the particular choice of model.

## 2. $n$ -Beam calculations

In the slice formulation of  $n$ -beam theory of Cowley & Moodie (1957) the electron wave is considered to be propagated through successive slices of the crystal, cut perpendicular to the beam direction, assumed to be the  $z$  axis. Back scattering is neglected and a small angle approximation may be made if convenient. The progress of the wave through one slice, from  $z_n$  to  $z_n + \Delta z = z_{n+1}$  involves the modification of the wave by multiplication with a function  $q(x, y)$  representing the integrated effect on the amplitude of the potential distribution (which may be assumed complex) of the slice and by convolution by a propagation function, representing the effects of Fresnel diffraction on the wave. Thus

$$\psi_{n+1}(x, y) = [\psi_n(x, y) \cdot q_n(x, y)] * p_n(x, y) \quad (1)$$

where  $p_n(x, y) = \exp\{-ik(x^2 + y^2)/2\Delta z\}$  in the small-angle approximation.

It has been shown (Moodie, private communication) that in the limiting case that the slice thickness  $\Delta z$  tends to zero this procedure is completely consistent with the solution of the wave equation for electrons passing through a crystal. However, for purposes of calculation it is necessary to make the approximation of assuming a finite slice thickness,  $\Delta z$ , so the integrated effect of the crystal on the electron wave may be calculated with a finite number of iterations of the procedure represented by equation (1). It has been established by Goodman & Moodie (1965 and private communication) that no appreciable error is introduced into the calculation of intensities of 80 keV electrons diffracted from perfect single crystals if the slice thickness chosen does not exceed about 5 Å and that slice thicknesses of up to about 10 Å introduce errors of no more than a few per cent, especially for the stronger diffracted beams in the vicinity of the zero order reflexion. It seems reasonable to assume that diffuse intensities will be, if anything, less strongly dependent on the choice of slice thickness.

In calculations of diffraction from periodic or near-periodic arrays, it is usually more convenient to deal with a finite number of discrete diffracted beams, rather than the continuous functions involved in (1). If  $\Psi_n$ ,  $Q_n$  and  $P_n$  are the Fourier transforms of  $\psi_n$ ,  $q_n$  and  $p_n$  respectively, we may Fourier-transform (1) to give, for the periodic case,

$$\Psi_{n+1}(h, k) = \sum_{h' k'} \Psi_n(h', k') \cdot Q_n(h - h', k - k') \cdot P_n(h, k) \quad (2)$$

so that the computing process is reduced to the multiplication and addition of sets of complex numbers, there being one number in each set for each diffracted beam.

The extension of this computing method to deal with diffuse scattering then follows directly. If we assume that multiple diffuse scattering is unimportant, we can calculate the amplitude of the diffuse scattering due to each layer of the crystal separately and then add them with the correct phase relationship, *i.e.* either coherently or incoherently according to the statistics of the deviations from crystal perfection. For each diffusely scattering layer, the incident radiation is assumed to be the discrete set of Bragg beams with reciprocal lattice vectors  $\mathbf{h}$  calculated for transmission of the radiation through the preceding crystal (region I) with appropriate absorption coefficients. In the portion of the crystal following the diffuse scattering layer (region III) there is dynamical interaction of the diffuse amplitudes in directions given by the set of vectors  $\mathbf{h} + \mathbf{v}$  where  $\mathbf{v}$  is any vector in the first Brillouin zone. Thus for each  $\mathbf{v}$  it is necessary to sum the amplitudes for all positions of the diffuse scattering layer. Kinematically the relative phases of diffuse scattering amplitudes need never be considered and it is generally assumed that relative phases cannot be usefully defined. However it is readily shown that for kinematical diffuse scattering the relative phases of waves scattered in the set of directions  $\mathbf{h} + \mathbf{v}$  can be defined if the deviations from crystal perfection occur always at the same positions within the unit cell. This latter condition may be a serious limitation in dealing with more complicated forms of defects, but is not so for the simpler forms of defect which will concern us most.

We assume that the scattering potential can be written as

$$\varphi = \varphi_0 + \Delta\varphi = \varphi_0 + \Delta\varphi_0 * \sum_n c_n \delta(\mathbf{r} - \mathbf{a}_n),$$

where  $\varphi_0$  is periodic,  $\Delta\varphi_0$  represents the deviation from the periodic structure in one unit cell,  $c_n$  are arbitrary constants and the vectors  $\mathbf{a}_n$  represent space-lattice translations. We establish the convention that  $F'$ ,  $\Delta F'$  and  $\Delta F'_0$  represent kinematical structure factors given by Fourier transform of  $\varphi$ ,  $\Delta\varphi$  and  $\Delta\varphi_0$  respectively. Then the diffuse scattering amplitude is

$$\Delta F'(\mathbf{v}) = \Delta F'_0(\mathbf{v}) \sum_n c_n \exp\{2\pi i \mathbf{v} \cdot \mathbf{a}_n\},$$

and

$$\begin{aligned} \Delta F'(\mathbf{h} + \mathbf{v}) &= \\ \Delta F'_0(\mathbf{h} + \mathbf{v}) \sum_n c_n \exp\{2\pi i \mathbf{v} \cdot \mathbf{a}_n\} \exp\{2\pi i \mathbf{h} \cdot \mathbf{a}_n\}, \end{aligned}$$

so that

$$\frac{\Delta F'(\mathbf{h} + \mathbf{v})}{\Delta F'(\mathbf{v})} = \frac{\Delta F'_0(\mathbf{h} + \mathbf{v})}{\Delta F'_0(\mathbf{v})}, \quad (3)$$

and the phase of  $\Delta F'(\mathbf{h} + \mathbf{v})$  must be defined relative to that of  $\Delta F'(\mathbf{v})$ .

The 'perfect-crystal' calculations for both the set of beams,  $\mathbf{h}$ , in the region I, and the set of beams  $\mathbf{h} + \mathbf{v}$  in region III of the crystal, can of course be carried out by use of any valid formulation of  $n$ -beam scattering theory and Fisher (1965), following the general

scheme of Gjønnes (1965, 1966) used matrix methods for this purpose. The initial formulation in this way involved the integration of intensities from layers of infinitesimal thickness for each  $z$  value. However, since from the experience of slice-method calculations it is clear that no appreciable error is introduced by considering the scattering from layers of finite thickness, it is possible to assume also for matrix calculations that the diffuse scattering may be considered as that from layers of one or more unit cells thickness considered together. This assumption has been tested and found to be accurate and useful by Fisher (private communication).

Finally it is necessary to introduce into the calculations some equivalent of the space and time averaging which produces the observed intensity experimentally.

The general correlation function  $G(\mathbf{r}, t)$ , or the analogous function for dynamical scattering have, in practice, finite extent in all dimensions of space and time. In particular in the  $x, y$  directions perpendicular to the beam direction, assumed to be the  $z$  axis, the extent is limited by the geometric coherence of the incident beam, if by nothing else. The range of this lateral coherence is normally between 100 and 1000 Å (Cowley, 1961) so that for specimens of greater extent than this the diffraction pattern is the sum of intensities from a large number of independently scattering regions. If it can be assumed that the distribution of the crystal defects giving diffuse scattering is uniform over the specimen, these independently scattering regions can be considered equivalent states of one scattering region. Thus, even for static defects, the summation of intensities from such regions will be equivalent to a time average of intensities from a single region with a suitably weak time dependence of defect configuration. Hence for dynamical as well as kinematical scattering, time- and space-averaging may be considered interchangeable for quasi-elastic scattering processes.

### 3. General formulation of the scattering problem

Formally, we may write down the solution of the scattering problem for the configuration of scattering potential at any one time by generalizing the result obtained by Cowley & Moodie (1957) and also by Fujimoto (1959) and Fujiwara (1959) for diffraction by a perfect crystal; namely that the amplitude for a diffracted beam,  $\mathbf{h}$ , may be expressed in the form

$$\begin{aligned} \psi_i(\mathbf{h}) &= \sum_{\mathbf{h}_1} \sum_{\mathbf{h}_2} \dots \sum_{\mathbf{h}_n} \dots F_i(\mathbf{h}_1) F_2(\mathbf{h}_2) \dots \\ & F_n(\mathbf{h}_n) \dots Z(\zeta_1 \dots \zeta_n \dots, H), \end{aligned}$$

where  $F_n(\mathbf{h}_n)$  is the complex structure factor given by the Fourier transform of the transmission function for the  $n$ th layer,  $q_n(x, y) = \exp\{i\sigma\varphi_n(x, y)\}$ , where  $\sigma = 2\pi m e \lambda / h^2$ ,  $\varphi_n(x, y) = \int_{z_n}^{z_n + \Delta z} \varphi(x, y, z) dz$  and  $\varphi(xyz)$  is the potential distribution function, which may be assumed

to be complex:  $\zeta_n$  represents the set of excitation errors associated with the  $n$ th diffraction process and  $H$  is the crystal thickness, so that the function  $Z(\dots\zeta_n\dots,H)$  depends only on the geometry of the scattering processes and not on the nature or configuration of the scattering potential distribution. For a non-periodic distribution of scattering potential the  $F_n$  and  $\zeta_n$  become functions of continuous variables,  $u_n$ , and the summations may be replaced by integrals to give

$$\psi_i(\mathbf{u}) = \iiint \dots \int \dots F_n(\mathbf{u}_n) \dots Z(\dots\zeta_n\dots,H) \dots d\mathbf{u}_n \quad (4)$$

Then

$$\begin{aligned} I_{\text{obs}}(\mathbf{u}) &= \langle \psi_i(\mathbf{u}) \cdot \psi_i^*(\mathbf{u}) \rangle \\ &= \iiint \dots \int \dots \langle \dots F_n(\mathbf{u}_n) \dots F_m^*(\mathbf{u}_m) \dots \rangle \cdot \\ &\quad Z(\dots\zeta_n\dots,H) \cdot \\ &\quad Z^*(\dots\zeta_m\dots,H) \dots d\mathbf{u}_n \dots d\mathbf{u}_m \dots, \quad (5) \end{aligned}$$

where the brackets  $\langle \dots \rangle$  denote time averaging. This expression may be written in terms of the contributions by individual atoms by putting

$$F_n(\mathbf{u}_n) = \sum_i f_{ni}(\mathbf{u}_n) \cdot \exp\{2\pi i \mathbf{u}_n \cdot \mathbf{r}_{ni}\}, \quad (6)$$

so that the observed intensity is expressed in terms of the positions and scattering functions for all atoms at all times.

For example, if we consider diffuse scattering due to thermal motions of atoms, the atomic scattering functions  $f_{ni}(\mathbf{u}_n)$  may be replaced at any one time by

$$f_{ni}(\mathbf{u}_n) \cdot \exp\left\{2\pi i \mathbf{u}_n \cdot \sum_{js} \mathbf{A}_{js} \cos(\omega_{js}t - \mathbf{k}_j \cdot \mathbf{r}_{ni} - \alpha_{js})\right\}, \quad (7)$$

where  $j$  numbers the phonon wave of mode  $s$  having amplitude  $\mathbf{A}_{js}$ , wave vector  $\mathbf{k}_j$  and phase  $\alpha_{js}$ . Following Hoppe (1964), for example, we may Fourier-analyse (7) to give a product of series of Bessel functions,

$$f_{ni}(\mathbf{u}_n) \cdot \prod_{js} [J_0(2\pi \mathbf{u}_n \cdot \mathbf{A}_{js}) + \sum_p 2i^p J_p(2\pi \mathbf{u}_n \cdot \mathbf{A}_{js}) \cdot \cos\{p(\omega_{js}t - \mathbf{k}_j \cdot \mathbf{r}_{ni} - \alpha_{js})\}].$$

Putting this into (6) and substituting in (4) or (5) the total scattering can be analysed into contributions to the sharp Bragg reflexions and contributions to the diffuse scattering. Thus the amplitude (4) will contain time-independent terms in which the  $f_{ni}(\mathbf{u}_n)$  are multiplied by the temperature factors,  $\prod_{js}\{J_0(\dots)\}$ , which in the harmonic approximations are the usual Debye-Waller factors (Slater, 1958). As shown later, the Bragg reflexions will also be modified by an absorption-like term corresponding to a loss of energy to the diffuse scattering or a virtual inelastic scattering process.

The first-order diffuse scattering term, corresponding to 'single-phonon' events, will be given by all first order terms of the form

$$f_{ni}(\mathbf{u}_n) \cdot \frac{J_1(2\pi \mathbf{u}_n \cdot \mathbf{A}_{js}) \cdot 2i \cos(\omega_{js}t - \mathbf{k}_j \cdot \mathbf{r}_{ni} - \alpha_{js})}{J_0(2\pi \mathbf{u}_n \cdot \mathbf{A}_{js})},$$

which may be simplified by making the approximation  $J_1(x)/J_0(x) = x$ , which is very good for small  $x$ . Then there will be two types of 'double-phonon' term for each point in reciprocal space, which will be added coherently since they arise from the same two phonon waves. One arises from single scattering from the sum of two simultaneous phonon-wave displacements of an atom; the other corresponds to a double scattering process, or successive scatterings by the two waves.

Higher order diffuse scattering terms follow, but these are usually neglected. More detailed discussion of these various terms will be given in subsequent publications.

In making calculations of diffuse scattering it is, of course, impracticable to proceed by attempting to evaluate the infinite set of integrals (5) with the substitutions of (6) and (7). Instead, the slice or matrix methods, mentioned above, may be applied with suitable approximations.

For example, if only single diffuse scattering terms are to be considered for the thermal diffuse case, for each set of related points in the diffraction pattern the diffuse amplitude terms could be calculated separately for each of the appropriate cosine waves chosen out of the series given in (7); then these diffuse amplitudes could be combined according to the assumptions of relative phases of the various vibrational waves.

In all publications to date dealing with thermal diffuse scattering in electron diffraction the assumption has been made, explicitly or implicitly, that the individual periodic vibrational waves may be considered to be completely independent and unrelated in phase, *i.e.* that the intensities corresponding to the individual terms in the series (7) may be added together when single diffuse scattering is considered. This may be true, at least as a very good approximation, in considerations of kinematical scattering but is not necessarily true for dynamical scattering.

As is well known, the life-time and mean free path of phonons are limited by phonon-phonon and other interactions. Consequently we should consider the diffraction from phonon wave-packets of finite extent. In neutron diffraction experiments the particulate nature of the phonon shows up as a finite breadth of the peaks in the plots of intensity *versus* energy for a particular scattering angle, (see *e.g.* Brockhouse, 1964). Since for electron scattering the energy losses due to phonons may usually be considered negligible, the quasi-elastic scattering approximation is very good and such effects will not be observable. We may take into account the wave-packet nature of the phonon by considering a correlation function  $G(\mathbf{r}, 0)$ , for deviations from crystal perfection, which is of finite extent. The available evi-

dence suggests that the range of correlation involved is of the order of a hundred Å and so is of about the same order of magnitude as the 'extinction distances' common in electron diffraction. This suggests that in dynamical diffraction processes involving scattering from such phonons, the finite correlation range may be of significance.

A phonon wave packet may be described as the sum of cosine waves, having a finite range of wavelength, which are in phase at one particular point at a given time. This suggests that amplitudes rather than intensities of diffusely scattered beams should be added for groups of vibrational waves with neighbouring  $\mathbf{k}$  vectors.

Alternatively, one may assume that, for any given time, the amplitudes of diffuse scattering should be added for atoms within a finite wave packet, *i.e.* for atom displacements described by a cosine wave modulated by a finite envelope. Then the independence of separate phonons and the time averaging process are taken into account by adding intensities for all possible wave packet configurations.

The treatment of thermal diffuse scattering can then be brought into line with the treatments appropriate for diffuse scattering from short-range order in alloys or from localized lattice defects (isolated or clustered point defects) which may best be described in terms of a correlation function of limited extent. Considerations of the diffraction problem in these terms will be explored in the following sections and in subsequent papers.

The dependence of dynamical intensities on the range of correlation of deviations from the crystal lattice may perhaps be appreciated more readily by considering the analogous situation relating to correlations of the average atomic positions in crystals. For purely kinematic scattering it is well known that the integrated intensity of a reflexion is independent of the average size of the individual perfect crystal regions whereas, for dynamical scattering, the average size of the individual perfect crystal region determines the 'extinction' effects which become appreciable when this size is comparable with the 'extinction distances' for the reflexions concerned. The same extinction distances will be relevant for the phonon case since the amplitudes and phases of the diffusely scattered beams depend on those of the Bragg beams which excite them.

#### 4. Defect correlations within slices

It was pointed out in § 2 that for the usual range of electron energies, the thickness of slice which can be treated by the simple phase-object approximation without introducing appreciable errors is of the order of 5 to 10 Å for calculations of diffraction from perfect single crystals and may well be greater for calculation of diffuse scattering. There is an immediate simplification of the calculation of diffuse scattering if it can be assumed that the diffuse scattering from adjacent

slices can be considered as independent, *i.e.* if the range of correlation function  $G(\mathbf{r}, 0)$  can be assumed to be less than the slice thickness in the beam direction. This follows from consideration of equation (5).

Suppose that, for each slice, now considered to be of finite thickness, we can write

$$F_n(\mathbf{u}) = \bar{F}_n(\mathbf{u}) + \Delta F_n(\mathbf{u}),$$

where  $\bar{F}_n$  and  $\Delta F_n$  are the spatially periodic, time-averaged part and the non-periodic, time dependent parts of  $F_n(\mathbf{u})$  respectively.

Then

$$\bar{F}_n(\mathbf{u}) = \mathcal{F} \langle \exp\{i\sigma\varphi_n(x, y)\} \rangle,$$

where

$$\varphi_n(x, y) = \varphi_{0n}(x, y) + \Delta\varphi_n(x, y),$$

so that, if

$$F_{0n}(\mathbf{u}) = \mathcal{F} \exp\{i\sigma\varphi_{0n}(x, y)\},$$

then

$$\bar{F}_n(\mathbf{u}) = F_{0n}(\mathbf{u}) * [\delta(\mathbf{u}) - \frac{1}{2} \langle \Delta F'_n(\mathbf{u}) * \Delta F'_n(\mathbf{u}) \rangle + \dots], \quad (8)$$

while

$$\begin{aligned} \Delta F_n(\mathbf{u}) &= F_{0n}(\mathbf{u}) * [i\Delta F'_n(\mathbf{u}) \\ &\quad - \frac{1}{2} \langle \Delta F'_n(\mathbf{u}) * \Delta F'_n(\mathbf{u}) - \langle \Delta F'_n(\mathbf{u}) * \Delta F'_n(\mathbf{u}) \rangle \rangle - \dots] \\ &\equiv F_{0n}(\mathbf{u}) * \Delta F''_n(\mathbf{u}). \end{aligned} \quad (9)$$

As before, the  $\Delta F'_n(\mathbf{u})$  are the kinematical values given by  $\mathcal{F} \Delta\varphi_n(x, y)$ . Hence we may write for each  $F$  in the general expression (4),

$$F_n(\mathbf{u}) = \bar{F}_n(\mathbf{u}) + F_{0n}(\mathbf{u}) * \Delta F''_n(\mathbf{u}),$$

and the product of the  $F_n(\mathbf{u})$  may be written as a series of terms in increasing powers of the small factors  $\Delta F''_n(\mathbf{u})$ .

The first term of zero order in these factors contains only the product of the  $\bar{F}_n(\mathbf{u})$  which are sets of delta functions. The  $N-1$  integrals, representing convolutions for  $N$  slices, then reduce to  $N-1$  summations over indices. The corresponding time-independent part of equation (5) then gives the intensities of the sharp Bragg reflexions.

The first order terms in  $\Delta F''_n(\mathbf{u})$  vanish, since  $\langle \Delta F''_n(\mathbf{u}) \rangle = 0$  for all  $n$ . The second order terms will represent diffuse scattering for single slices. Because of the form of (9), the number of convolution integrals in (5) is increased by two and the corresponding part of the observed intensity becomes

$$\begin{aligned} I_d^2(\mathbf{u}) &= \sum_{\nu} \sum_{\mu} \int \dots \int \langle \dots \bar{F}_n(\mathbf{u}_n) \Delta F''_{\nu}(\mathbf{u}_{\nu}) \\ &\quad \dots \bar{F}_m^*(\mathbf{u}_m) \Delta F''_{\mu}^*(\mathbf{u}_{\mu}) \dots \rangle \\ &Z(\dots \zeta_n \dots, H) \cdot Z^*(\dots \zeta_m \dots, H) \dots d\mathbf{u}_n \dots d\mathbf{u}_m \\ &\quad \dots d\mathbf{u}_{\nu} d\mathbf{u}_{\mu}, \end{aligned}$$

where the replacement of  $F_{0n}$  by  $\bar{F}_n$  in one slice should create no significant difference.

The time average involved,  $\langle \Delta F''_{\nu}(\mathbf{u}_{\nu}) \cdot \Delta F''_{\mu}^*(\mathbf{u}_{\mu}) \rangle$ , will be zero except for  $\nu = \mu$  because the deviations from the average in different slices are assumed to be un-

correlated. Taking into account the discrete nature of the  $\bar{F}_n(\mathbf{u})$ , the single-slice diffuse intensity is given by a summation of the form

$$I_d^1(\mathbf{u}) = \sum_{\mathbf{g}} \sum_{\mathbf{g}'} \sum_{\mathbf{v}} \int_{2N-1} \dots \int \dots \bar{F}_n(\mathbf{u}_n) \dots \bar{F}_m^*(\mathbf{u}_m) \dots \langle \Delta F_{\mathbf{v}}''(\mathbf{u}_v - \mathbf{g}) \cdot \Delta F_{\mathbf{v}'}''^*(\mathbf{u}_v - \mathbf{g}') \rangle \cdot Z(\dots \zeta_n \dots, H) \cdot Z^*(\dots \zeta_m \dots, H) \dots d\mathbf{u}_n \dots d\mathbf{u}_m \dots d\mathbf{u}_v \quad (10)$$

where  $\mathbf{g}$  and  $\mathbf{g}'$  are two-dimensional reciprocal lattice vectors. Since the functions  $\bar{F}_n(\mathbf{u}_n)$  consist of sets of  $\delta$ -functions, all the integrals on this expression may be replaced by summations over sets of integers,  $\mathbf{h}_n$ . The time-averaged part of (10) is similar to the equivalent factor used by Gjønnes (1966), but here the  $\Delta F_n''$  need not be kinematic structure factors, and also the Bragg-beam scattering factors  $\bar{F}_n$  are modified by absorption-like terms. The precise significance of these latter terms varies, however. In the first part of the crystal ( $n < \nu$ ) they represent modification of the Bragg-beams by the diffuse scattering. In the second part ( $n > \nu$ ), where Bragg-interaction of diffuse beams occurs, they represent modification of the diffuse beams by multiple inter-slice diffuse scattering, and it is perhaps questionable whether the modified  $\bar{F}_n$  (rather than  $F_{0n}$ ) should be used in this stage of the calculation unless this multiple scattering is to be specifically determined.

In fact the next contributions to diffuse scattering in the expansion involve summations of the form

$$\sum_{\mathbf{g}} \sum_{\mathbf{g}'} \sum_{\mathbf{h}} \sum_{\mathbf{h}'} \sum_{\mathbf{v}} \sum_{\mu > \nu} \langle \Delta F_{\mathbf{v}}''(\mathbf{u}'_v - \mathbf{g}) \cdot \Delta F_{\mathbf{v}'}''^*(\mathbf{u}'_v - \mathbf{g}') \rangle \langle \Delta F_{\mu}''(\mathbf{u} - \mathbf{u}' - \mathbf{h}) \cdot \Delta F_{\mu'}''^*(\mathbf{u} - \mathbf{u}' - \mathbf{h}') \rangle,$$

representing successive diffuse scattering by two different slices. Note that 'coherent' double-diffuse scattering within the slice is contained within  $\Delta F''$ , and also that third-order processes involving real and virtual scattering are implied in the use of the  $\bar{F}_n$ .

In practice, it seems that the direct use of expressions such as (10) for the calculation of diffuse intensities would scarcely be feasible. In order to perform calculations of the diffuse scattering for the case under consideration, namely for independent diffuse scattering from individual slices, it seems more appropriate to use and extend the concept of the 'dynamical factor' in conjunction with the computing scheme outlined above. The 'dynamical factor' is that factor by which the diffuse scattering intensity for the crystal, calculated kinematically, must be multiplied to give the dynamically calculated diffuse intensity for the whole crystal. It is a function of the coordinates in the plane of the diffraction pattern, and was calculated for example by Fisher (1965) for several points in the diffraction patterns given by copper-gold alloys having short-range order.

First we consider the relatively simple case that the diffuse scattering from a single slice may be calculated

kinematically, *i.e.* (9) becomes

$$\Delta F_n(\mathbf{u}) = F_{0n}(\mathbf{u}) * i\Delta F_n'(\mathbf{u}).$$

If we are dealing with only one type of defect, occurring always at the same place in a unit cell, although possibly with different magnitudes, we may write, as in § 2, above.

$$\Delta\varphi = \Delta\varphi_0 * \sum_m c_m \delta(\mathbf{r} - \mathbf{a}_m), \quad (11)$$

where the  $c_m$  are real constants associated with the lattice translations  $\mathbf{a}_m$ . In making computations of diffuse scattering we deal with a set of points  $\mathbf{h} + \mathbf{v}$  where  $\mathbf{h}$  is the set of reciprocal lattice vectors and  $\mathbf{v}$  a vector in the first Brillouin zone. Then, as before,

$$\begin{aligned} \Delta F'(\mathbf{h} + \mathbf{v}) &= \Delta F'_0(\mathbf{h} + \mathbf{v}) \cdot \sum_m c_m \exp\{2\pi i \mathbf{v} \cdot \mathbf{a}_m\} \\ &= \Delta F'_0(\mathbf{h} + \mathbf{v}) \cdot C(\mathbf{v}). \end{aligned}$$

For the calculation of the diffuse intensity at a set of points  $\mathbf{u} = \mathbf{h} + \mathbf{v}$ , for a given  $\mathbf{v}$ , the computing involves summations over the sets of indices represented by  $\mathbf{h}$  as in (2). Hence for diffuse scattering from the  $n$ th layer we can insert the set of values  $\Delta F'_{0,n}(\mathbf{h} + \mathbf{v})$  and so calculate the corresponding set of final amplitude values  $\Psi_{\mathbf{v},n}^d(\mathbf{h})$  for the whole crystal.

Since the diffuse scattering from separate layers is assumed to be independent, the total observed intensity for the set of points  $\mathbf{h} + \mathbf{v}$  is then given by summing the intensities from all diffuse-scattering layers:

$$I_{\text{obs}}^d(\mathbf{h} + \mathbf{v}) = \sum_n |C_n(\mathbf{v})|^2 \cdot |\Psi_{\mathbf{v},n}^d(\mathbf{h})|^2.$$

If the distribution of defects is assumed to be uniform throughout the crystal, all functions  $|C_n(\mathbf{v})|^2$  will be equal, and

$$I_{\text{obs}}^d(\mathbf{h} + \mathbf{v}) = |C(\mathbf{v})|^2 \cdot \sum_{n=1}^N |\Psi_{\mathbf{v},n}^d(\mathbf{h})|^2. \quad (12)$$

This may be compared to the kinematic scattering intensity for the whole crystal,

$$\begin{aligned} I_{\text{kin}}^d(\mathbf{h} + \mathbf{v}) &= \sum_n |C_n(\mathbf{v})|^2 \cdot |\Delta F'_0(\mathbf{h} + \mathbf{v})|^2 \\ &= N \cdot |C(\mathbf{v})|^2 \cdot |\Delta F'_0(\mathbf{h} + \mathbf{v})|^2. \end{aligned} \quad (13)$$

The dynamical factor  $D(\mathbf{u})$  is thus given as the ratio of the two quantities (12) and (13) for each  $\mathbf{v}$  so that (12) becomes

$$I_{\text{obs}}^d(\mathbf{u}) = N |C(\mathbf{v})|^2 \cdot |\Delta F'_0(\mathbf{u})|^2 \cdot D(\mathbf{u}).$$

Then for each new model of the crystal defect configurations, involving the same type of defect, the intensity of diffuse scattering is given merely by inserting the appropriate function  $|C(\mathbf{v})|^2$ . It may be noted, of course, that  $|C(\mathbf{v})|^2 \cdot |\Delta F'_0(\mathbf{u})|^2$  is the Fourier transform of the correlation functions  $G(\mathbf{r}, 0)$ , or the difference Patterson function, relating to the deviations from the average lattice.

When it is not possible to make a kinematic approximation for the diffuse scattering from a single slice, or when several types of crystal defects occur, the

situation is more complicated but simplifying approximations can usually be made. For example, when we must use the phase-grating form of (11),

$$\exp\{i\sigma\Delta\varphi\} = \exp[i\sigma\Delta\varphi_0 * \sum_m c_m \delta(\mathbf{r} - \mathbf{a}_m)],$$

it may often be a good approximation to write

$$\exp\{i\sigma\Delta\varphi\} - 1 = \sum_p [\exp\{ic_p\sigma\Delta\varphi_0\} - 1] * \sum_m \delta(\mathbf{r} - \mathbf{a}_{mp}), \quad (14)$$

where  $\mathbf{a}_{mp}$  represents a vector to a peak containing  $c_p$ . In this case the diffuse scattering function can be written in terms of general deviation structure factors  $H_p$ , replacing  $\mathcal{F}[\exp\{ic_p\sigma\Delta\varphi_0\} - 1]$  in (14), thus

$$H(\mathbf{v}) = \sum_p H_p(\mathbf{v}) \cdot C_p(\mathbf{v}),$$

where

$$C_p(\mathbf{v}) = \sum_m \exp\{2\pi i \mathbf{v} \cdot \mathbf{a}_{mp}\}.$$

Then the intensity of diffuse scattering from all slices is

$$\begin{aligned} I_{\text{obs}}^d(\mathbf{h} + \mathbf{v}) &= \sum_n \sum_p | \sum C_{p,n}(\mathbf{v}) \cdot \Psi_{np\mathbf{v}}(\mathbf{h}) |^2 \\ &= \sum_n \sum_q \sum_p C_{qn} C_{pn}^* \Psi_{nq\mathbf{v}}(\mathbf{h}) \cdot \Psi_{np\mathbf{v}}^*(\mathbf{h}), \end{aligned}$$

or, if we assume uniformity in the distribution of defects,

$$I_{\text{obs}}^d(\mathbf{h} + \mathbf{v}) = \sum_q \sum_p C_q C_p^* \sum_n \Psi_{nq\mathbf{v}}(\mathbf{h}) \cdot \Psi_{np\mathbf{v}}^*(\mathbf{h}). \quad (15)$$

In this, we may note that we can write

$$C_q C_p^* = \sum_n \sum_m \exp\{2\pi i \mathbf{u} \cdot (\mathbf{a}_{nq} - \mathbf{a}_{mp})\},$$

and this, plus its complex conjugate, represents the Fourier transform of the cross-correlation function for the two sets of defects,  $q$  and  $p$ , which determines the corresponding contribution to the intensity of the diffuse scattering from a single slice. A detailed discussion of (15) for the case of diffuse scattering from alloys containing short-range order will be contained in a future publication.

For the kinematical case with several different types of defect, it is possible to set-up an equivalent formulation by defining the appropriate set of deviation structure factors,  $H_p$ .

If the correlation range for the deviations from the average lattice in the beam direction extends beyond the distance which can conveniently be used for a single slice thickness, the simplifying assumptions of this section can no longer be made. It is, in general, necessary to define the relative phases of diffuse scattering from successive slices so that amplitudes from the various successions of slices may be summed. This is not possible purely on the basis of a known or assumed correlation function. What is required is a detailed model of the defects, as in the case of the phonon wave packet model for thermal vibrations, mentioned above.

## 5. Absorption coefficients for Bragg reflexions

Any diffraction process resulting in the diffuse scattering of some energy into the background of an electron diffraction pattern necessarily involves a loss of energy by the sharp, Bragg reflexions arising from the averaged periodic component of the distribution of scattering potential. This may be interpreted in terms of a periodic absorbing function which will give an out-of-phase addition to the effective scattering factor.

If we assume the diffuse scattering from successive crystal slices to be independent, this absorption effect can be derived by considering individual slices separately. For one slice the Bragg reflexions are given by

$$\mathcal{F}\langle \exp\{i\sigma\varphi(x, y)\} \rangle$$

and the effective absorption function  $\chi(x, y)$  is introduced by equating this to

$$\bar{F}(\mathbf{u}) = \mathcal{F} \exp\{i\sigma\varphi_0(x, y) - \chi(x, y)\}, \quad (16)$$

where

$$\varphi(x, y) = \varphi_0(x, y) + \Delta\varphi(x, y)$$

and  $\varphi_0(x, y)$  is the time-independent, periodic, averaged structure.

Then

$$\begin{aligned} \langle \exp\{i\sigma\varphi(x, y)\} \rangle &= \\ \langle 1 + i\sigma\Delta\varphi(x, y) - \frac{1}{2}\sigma^2\Delta\varphi^2(x, y) + \dots \rangle \cdot \exp\{i\sigma\varphi_0(x, y)\} \\ &= \exp\{i\sigma\varphi_0(x, y) - \frac{1}{2}\sigma^2\langle \Delta\varphi^2(x, y) \rangle + \dots\}, \quad (17) \end{aligned}$$

so that as a first approximation the absorption function is given by

$$\chi(x, y) = \frac{1}{2}\sigma^2\langle \Delta\varphi^2(x, y) \rangle,$$

where  $\chi(x, y)$  may be considered as the projection of a slice of the three-dimensional absorption function  $\chi(x, y, z)$ . But in general  $\chi(x, y)$  will have both real and imaginary parts and the imaginary parts may be considered as a modification of  $\varphi_0(x, y)$ . The complex structure factors  $\bar{F}_n(\mathbf{u}_n)$  as defined by (16) may then be used in calculations based on the general equation (4), such as the slice method calculation (2), or the matrix method.

It may be noted that  $\varphi_0(x, y)$ , being the time-averaged potential distribution, corresponds to atoms spread out by the thermal motion, so that the Debye-Waller factor is already contained in  $\mathcal{F} \exp\{i\sigma\varphi_0(x, y)\}$  and is separate from the absorption factor here considered.

For kinematical scattering it can be shown that to a good approximation the Debye-Waller factor is independent of the degree or extent of correlation of the atomic motions. From the above considerations it is clear that this is true also in the dynamical case. Also it can be shown that, to the degree of approximation which may be considered sufficient for many purposes, the absorption factor derived above is independent of the correlation of atomic motions or displacements.

For the case where correlation is confined within individual crystal slices, this follows from the form of equation (17). When there is correlation between slices

we may evaluate the approximation by considering transmission through two slices with transmission functions  $q_n(x, y)$  and  $q_m(x, y)$  where  $q_n(x, y) = \exp\{i\sigma\varphi_{0n}(x, y) + i\sigma\Delta\varphi_n(x, y)\}$ . Using the formulation of equation (1), the equivalent of equation (17) is

$$\begin{aligned} & \langle \{q_n(x, y) * p(x, y)\} \cdot q_m(xy) \rangle = \\ & \quad [\exp\{i\sigma\varphi_{0n}\} * p(xy)] \cdot \exp\{i\sigma\varphi_{0m}\} \\ & - \frac{\sigma^2}{2} [(\exp\{i\sigma\varphi_{0n}\} \cdot \langle \Delta\varphi_n^2 \rangle * p(xy)) \cdot \exp\{i\sigma\varphi_{0m}\} \\ & + (\exp\{i\sigma\varphi_{0n}\} * p(xy)) \cdot \exp\{i\sigma\varphi_{0m}\} \cdot \langle \Delta\varphi_m^2 \rangle] \\ & + \dots \\ & + \frac{\sigma^4}{2} \langle [\exp\{i\sigma\varphi_{0n}\} \cdot \Delta\varphi_n^2 * p(xy)] \exp\{i\sigma\varphi_{0m}\} \cdot \Delta\varphi_m^2 \rangle + \dots \end{aligned} \quad (18)$$

Since, in general,  $\langle \Delta\varphi_n^2 \rangle = \langle \Delta\varphi_m^2 \rangle$ , it is only in the final cross product term of this expression and similar terms of higher order that there will be any dependence on correlations between the functions  $\Delta\varphi_n$  and  $\Delta\varphi_m$ . Such terms are of the fourth and higher orders of the small quantities  $\sigma\Delta\varphi$  and so may often be neglected. Since the calculation of the diffuse intensity for the whole crystal follows from a repetition of such two-slice calculations, this argument can be extended to suggest validity of the result for complete  $n$ -beam calculations. Then it can be concluded that, to a good approximation, absorption terms calculated from the phase grating approximation for a single slice may be used to modify the structure factors, or atomic scattering factors, used for any formulation of, or approximation to, dynamical scattering of electrons by crystals. In particular it should be identical with the absorption terms calculated by various authors using a two-beam approximation to scattering theory.

## 6. Conclusion

In subsequent publications, the principles outlined here for the calculation of intensities of diffuse scattering will be applied to the detailed consideration of thermal diffuse scattering, and the diffuse scattering due to short range order and other localized crystal imperfections, and the results of calculations will be compared with experimental observations.

However, it is worth pointing out here one general conclusion which may be drawn. Deviations from the kinematical form of the diffuse scattering will naturally result from the dynamical interactions of diffracted beams. More fundamental differences from the kinematical result arise because the dynamical scattering is not completely determined by the correlation func-

tion,  $G(\mathbf{r}, 0)$  relating to deviations from the average lattice. These differences will presumably be appreciable when the range of the correlations of these deviations is comparable with the thicknesses of crystal which give appreciable dynamical effects, *i.e.* of the order of 10 to 100 Å, depending on the atomic numbers of elements present. For such cases, it is necessary to postulate actual models of the deviations from the average lattice.

While this complicates the calculation of diffuse intensities, it also introduces the possibility that dynamical scattering effects may allow an increase in the information obtainable from diffuse scattering observations. For example from thermal diffuse scattering it may be possible to make deductions regarding the 'size' and 'shape' of phonons and so gain information on phonon interactions; and for short-range order diffuse scattering it may be possible to make some deductions regarding the vexed question of the nature of short-range order; for example, on the validity of the model of an alloy with short-range order which supposes it to consist of arrays of very small out-of-phase domains (see *e.g.* Moss, 1964). The assessment and implications of these possibilities will be reported later.

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