# Diffuse Scattering in Electron Diffraction Patterns. II. Short-Range Order Scattering

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The general method of computing the intensities of diffuse scattering in electron diffraction patterns, outlined by Cowley & Pogany in Part I, has been applied to the case of diffuse scattering given by the short-range ordering in binary solid solutions. If the diffuse scattering from individual crystal slices, of thickness greater than the effective range of ordering, can be assumed to be kinematical, the total diffuse scattering can be expressed in terms of the usual short-range order parameters, $\alpha_i$, and 'dynamical factors'. When the diffuse scattering from a slice cannot be assumed to be kinematical, as in the case of copper–gold alloys, a new type of order parameter, involving some higher-order correlations, must be introduced. Expressions are derived for the absorption coefficients which must be applied to the Bragg reflexions. The intensity of diffuse scattering from a single slice of crystal is calculated for a simple domain model of short-range order to evaluate the order of magnitude of departures from kinematical scattering and the possible sensitivity of the diffuse intensity to higher-order correlations. The methods are outlined by which diffuse intensity could be calculated for the whole crystal by a modification of the $n$-beam dynamical multi-slice procedure and a procedure for the approximate calculation of multiple-diffuse scattering is suggested.

## Introduction

The first paper of this series (Cowley & Pogany, 1968), hereafter referred to as I, contained a general account of the theory and computational methods for the calculation of diffuse scattering in electron diffraction patterns using $n$-beam dynamical theory. In the present paper we take up the case of the diffuse scattering due to short-range ordering of atoms in a crystal, such as is given by binary alloy solid solutions in the temperature range above the critical temperature at which long-range order disappears. Previously it was assumed that for such alloys the range over which there is appreciable correlation of atomic positions is only a few unit cells. Recently evidence has accumulated that in many cases, for temperatures not too much greater than the critical temperature, there may be some degree of correlation over distances of 30 or 40 Å or more (see, for example, Watanabe & Fisher, 1965). However if we confine our attention to systems where this does not occur, or make the assumption, as a first approximation, that these relatively long-range correlations are small compared with correlations between near neighbours, we can assume that the correlation range to be considered is of about the same magnitude as the thickness of slice which may be used in $n$-beam calculations without introducing appreciable error. Under these circumstances it is a reasonable assumption that for computational purposes the crystal may be divided into slices between which no correlation exists in the deviations from the average lattice. Then, as pointed out in part I, the total diffuse intensity can be expressed as the sum of the intensities of diffuse scattering originating in each of the slices considered separately, and 'dynamical factors' may be used.

It was suggested in part I that in the case that the diffuse scattering from an individual slice cannot be closely approximated by kinematical scattering theory, the usual short-range order parameters used in, and derivable from, X-ray diffraction observations may not be sufficient to define the diffuse scattering observed. It is then necessary to introduce higher-order correlation coefficients in order to calculate intensities, and, correspondingly, from the observed intensities it may be possible to derive some information beyond that which may be deduced from kinematical scattering experiments. The purpose of this paper will be, in part, to provide a basis for the exploration of these possibilities.

Our arguments will be phrased in terms of the slice method of $n$-beam calculations (Goodman & Moodie, 1965) but it is clear that they will apply equally well if matrix methods such as described by Fisher (1968) are used to treat the $n$-beam interactions, and the reasonable assumption is made that the diffuse scattering from any infinitesimally thick crystal layer may be taken to be the same as for a slice of thickness exceeding the range of correlation of atomic positions.

## Kinematical diffuse scattering by slices

Kinematically, the distribution of diffuse scattering power in reciprocal space, for a binary AB alloy with fractions $m_A$ and $m_B$ of A and B atoms, is given by

$$|\Delta F'(\mathbf{u})|^2 = M m_A m_B |f_A - f_B|^2 \sum_{lmn} \alpha_{lmn} \exp\{2\pi i \mathbf{u} \cdot \mathbf{r}_i\},$$

where $M$ is the total number of atoms, the vectors $\mathbf{r}_i$ denote the interatomic vectors and the $\alpha_{lmn}$ are the Warren short-range order parameters (Cowley, 1950)

defined in terms of the probability $P_{AB,i}$ that a B atom should be separated from an A atom by the vector $\mathbf{r}_i$ (coordinates $l\mathbf{a}, m\mathbf{b}, n\mathbf{c}$); thus

$$P_{AB,i} = m_B(1 - \alpha_{lmn}) . \quad (1)$$

When we deal with the projection of a thin slice of a crystal, the distribution of scattering power for the corresponding section of reciprocal space is

$$|\Delta F'(uv)|^2 = Mm_Am_B \sum_l \sum_m (\sum_n \alpha_{lmn}) \exp\{2\pi i(ul + mv)\} , \quad (2)$$

where $u, v, w$ are the coordinates in reciprocal space.

In setting up $n$-beam dynamical calculations, we must consider the scattering from each slice in terms of the phase-grating approximation. The transmission function for the slice is

$$\exp\{i\sigma\varphi(xy)\} = \exp\{i\sigma[\varphi_0(xy) + \Delta\varphi(xy)]\} ,$$

where $\varphi_0(xy)$ is periodic, being the projection of the average potential distribution, and $\sigma = 2\pi me\lambda/h^2$. Fourier transformation of this gives

$$F(uv) = \mathscr{F} \exp\{i\sigma\varphi_0(xy)\} * \mathscr{F} \exp\{i\sigma\Delta\varphi(xy)\} .$$

If the deviations from the average projection are small we may expand the corresponding exponential and write

$$F(\mathbf{u}) = \bar{F}(\mathbf{u}) + \Delta F(\mathbf{u})$$
$$= \mathscr{F} \exp\{i\sigma\varphi_0(xy)\} * [\delta(uv) + i\Delta F'(uv) - \ldots]$$
$$\simeq F_0(\mathbf{u}) + F_0(\mathbf{u}) * i\Delta F'(\mathbf{u}) , \quad (3)$$

where here, as in what follows, the vector $\mathbf{u}$ is redefined to refer to the two-dimensional section of reciprocal space (coordinates $u, v$) involved with $n$-beam calculations.

$\bar{F}(\mathbf{u})$ is the Fourier transform of the averaged value of $\exp\{i\sigma\varphi(xy)\}$ and so represents the contributions of the slice to the amplitudes of the sharp 'Bragg' reflexions. It may be equated to $F_0(\mathbf{u}) = \mathscr{F} \exp\{i\sigma\varphi_0(x,y)\}$ if the higher-order (absorption) terms in the expansion of $\mathscr{F} \exp\{i\sigma\Delta\varphi\}$ are neglected. The term $\Delta F(\mathbf{u}) \simeq F_0(\mathbf{u}) * i\Delta F'(\mathbf{u})$ represents the diffuse scattering.

It was shown in part I that, assuming the kinematical approximation for such a case of diffuse scattering, the total diffuse scattering for the whole crystal may be expressed in the form

$$I_{obs}^d(\mathbf{u}) = N|\Delta F'(\mathbf{u})|^2 . D(\mathbf{u}) , \quad (4)$$

where $|\Delta F'(\mathbf{u})|^2$ is given by (2) and $D(\mathbf{u})$ is the dynamical factor which may be calculated for each set of coordinates $\mathbf{u} = \mathbf{h} + \mathbf{v}$, for the set of reciprocal lattice vectors $\mathbf{h}$, where $\mathbf{v}$ is a vector in the first Brillouin zone. This holds if the deviation from the average lattice can be expressed in the form $\Delta\varphi = \Delta\varphi_0 * \sum_n c_n\delta(\mathbf{r} - \mathbf{a}_n)$ where the $c_n$ are real numbers. In the present case we put $\Delta\varphi_0$ equal to $(\varphi_A - \varphi_B)$ and $c_n = \pm 1$ so that to calculate

$D(\mathbf{u})$ we insert $(f_A - f_B)$ as a diffuse scattering amplitude into the $n$-beam dynamical diffuse scattering calculations, performed either by the slice method or by the matrix method. This dynamical factor has been calculated by Fisher (1965), using matrix methods, for several points in reciprocal space for copper–gold alloys.

Once this dynamical factor has been calculated for a given system, the kinematical intensity function $|\Delta F'(\mathbf{u})|^2$ can be derived, and the short-range order coefficients contained in equation (2) can therefore be deduced by a Fourier transform operation.

## Phase grating approximation for diffuse scattering

In the projection of the potential of a slice which may be several unit cells in thickness, the deviations from the average value of projected potential may be several times $(\varphi_A - \varphi_B)$. In the case of copper–gold alloys, for example, these deviations may represent several times the scattering potential of a moderately heavy atom. Hence the assumption made in equation (3), that $\sigma\Delta\varphi(xy) \ll 1$, may not be a good approximation and consequently there may be appreciable deviations from the predictions based on kinematical diffuse scattering.

The deviations from kinematical conditions will be greatest when the electron beam is close to a principle axis of the crystal. Then the projection, $\varphi(xy)$, will consist of a number of clearly defined peaks of projected potential. The validity of the kinematical formula (2) depends on the assumption of a linear relationship between the heights of these peaks and their scattering factors. Since in the phase grating approximation the scattering factors are given by

$$\mathscr{F}[\exp\{i\sigma\varphi_p(xy)\} - 1] , \quad (5)$$

the relationship is not linear unless the projected potentials of the peaks, $\varphi_p(xy)$, are very small. We must therefore reformulate the scattering function in terms of the complex scattering factors (5).

Consider an AB alloy with $N$ layers of atoms per slice. The projection of the slice in the direction near to that of a principal axis will contain potential peaks of $(N+1)$ different kinds, namely,

$$N\varphi_A, (N-1)\varphi_A + \varphi_B, (N-2)\varphi_A + 2\varphi_B, \ldots,$$
$$\varphi_A + (N-1)\varphi_B \text{ and } N\varphi_B .$$

If we make the assumption that there is no appreciable overlapping of the projected peaks, the scattering factors associated with these peaks are

$$f_n = \mathscr{F}[\exp\{i\sigma[n\varphi_A + (N-n)\varphi_B]\} - 1] . \quad (6)$$

Then the total scattering amplitude of the layer is given by

$$F(\mathbf{u}) = \delta(\mathbf{u}) + \sum_i \sum_n f_n \exp\{2\pi i\mathbf{u} . \mathbf{r}_{ni}\} ,$$

where the vectors $\mathbf{r}_{ni}$ (components $x_i, y_i, 0$) specify the positions of peaks with scattering factors $f_n$. We can

then calculate the intensity of diffuse scattering which would be given by an isolated slice as

$$I_s(\mathbf{u}) = \sum_i \sum_j \sum_n \sum_m f_n f_m^* \exp\{2\pi i \mathbf{u} \cdot (\mathbf{r}_{ni} - \mathbf{r}_{mj})\}.$$

Let $P_{nmi}$ be the probability that a peak with scattering factor $f_m$ should be at a position given by vector $\mathbf{r}_i$ from a $f_n$ peak, so that $\mathbf{r}_{ni} - \mathbf{r}_{mj} = \mathbf{r}_i$, and let $M_n$ be the fraction of $f_n$-type peaks, where the total number of peaks is $P$.

Then

$$I_s(\mathbf{u}) = P \sum_n \sum_m \sum_i M_n f_n f_m^* P_{nmi} \exp\{2\pi i \mathbf{u} \cdot \mathbf{r}_i\}. \quad (7)$$

We then introduce order parameters $\gamma_{nmi}$ defined by the relation

$$P_{nmi} = M_m(1 + \gamma_{nmi}/M_n M_m) \quad (8)$$

and (7) becomes

$$I_s(\mathbf{u}) = P \sum_n \sum_m M_n M_m f_n f_m^* \sum_i \exp\{2\pi i \mathbf{u} \cdot \mathbf{r}_i\}$$
$$+ P \sum_n \sum_m f_n f_m^* \sum_i \gamma_{nmi} \exp\{2\pi i \mathbf{u} \cdot \mathbf{r}_i\}. \quad (9)$$

In this expression the first term is independent of the order parameters $\gamma_{nmi}$ and represents the sharp, Bragg reflexions due to the average, periodic part of the exponential of the projected potential. This term is not, however, independent of the state of order, as in the kinematical case, since the relative proportions $M_n$ of the different types of peaks will depend on the state of order and the relation between the complex $f_n$ is not linear.

The second term gives the diffuse scattering. This may be compared with equation (2). The following relationships between the parameters involved may be readily derived:

$$M = NP,$$
$$m_A = \sum_{p=1}^{N} p \cdot M_p,$$

and

$$\sum_n \alpha_{lmn} = \frac{1}{Nm_A m_B} \sum_p \sum_q p \cdot q \cdot \gamma_{pqi}.$$

The last equation follows from the relationship between probabilities of atom pairs and probabilities of column pairs,

$$Nm_A \sum_n P_{AA, lmn} = \sum_p \sum_q p \cdot q \cdot P_{pqi} M_p.$$

Hence values for the $\alpha$ parameters can be deduced from the $\gamma$ values. But the reverse is not the case. For example, given a line of $n$ A atoms and $(N-n)$ B atoms, we can derive from a knowledge of $\alpha_{lmn}$ values the average number of A atoms in a neighbouring line but not the probability that a given number, $m$, of A atoms will occur in the second line. The parameters $\alpha_{lmn}$ describe only pair-wise correlations of atomic site occupancies. The parameters $M_n$ and $\gamma_{nmi}$ depend on the

correlations of occupancies of three or more atomic sites and so may be referred to as higher-order correlation coefficients, although not perhaps belonging to the most general class of such coefficients which could be defined.

For a layer of thickness $N$ atoms there will be a maximum of $(N+1)^2$ parameters $\gamma_{nmi}$ for each vector $\mathbf{r}_i$. These will not all be independent. From elementary considerations it is possible to deduce relations between them: for example

(a) $\gamma_{nmi} = \gamma_{mni}$ since $M_n P_{nmi} = M_m P_{mni}$.

(b) $\sum_m \gamma_{nmi} = \sum_m \gamma_{mni} = 0$ since $\sum_m P_{nmi} = 1$.

(c) $\sum_i \gamma_{nmi} = 0$ since $\sum_i P_{nmi} = PM_m$.

(d) For zero order, $\gamma_{nm0} = -M_n M_m$, except that $\gamma_{nn0} = M_n - M_n^2$.

## Absorption coefficients for Bragg reflexions

From the first part of the expression (9) which gives the intensities of sharp, Bragg reflexions, we see that the intensity for the $h, k$ reflexion can be written

$$I_{hk}/P = \bar{F}(hk) \cdot \bar{F}^*(hk),$$

where

$$\bar{F}(hk) = \sum_n M_n f_n(hk). \quad (10)$$

In order to express this in terms of an absorption coefficient, as normally defined, we define a complex 'potential' such that

$$\bar{F}(\mathbf{u}) = \mathscr{F} \exp\{i[\sigma\varphi_0(\mathbf{r}) + i\chi(\mathbf{r})]\}, \quad (11)$$

i.e. the kinematic structure factor is replaced by

$$F'(\mathbf{u}) = \mathscr{F}\{\sigma\varphi_0(\mathbf{r}) + i\chi(\mathbf{r})\} = F_r'(\mathbf{u}) + iF_i'(\mathbf{u}).$$

Putting $\varphi_0(\mathbf{r})$ equal to the average structure,

$$\varphi_0(\mathbf{r}) = Nm_A\varphi_A(\mathbf{r}) + Mm_B\varphi_B(\mathbf{r}),$$

we have

$$\bar{F}(\mathbf{u}) = \mathscr{F}[\sum_{n=0}^{N} M_n \exp\{i\sigma N(m_A\varphi_A + m_B\varphi_B)\} \cdot$$
$$\exp\{i\sigma(n - Nm_A)(\varphi_A - \varphi_B)\}],$$

and substituting $\varphi_d = \varphi_A - \varphi_B$ and $p = n - Nm_A$,

$$\bar{F}(\mathbf{u}) = \mathscr{F}[\exp\{i\sigma\varphi_0(\mathbf{r})\} \sum_{p=-Nm_A}^{Nm_B} M_p \exp\{i\sigma p\varphi_d\}]. \quad (12)$$

The summation may be written

$$\sum_{p=-Nm_A}^{Nm_B} M_p[1 + i\sigma p\varphi_d - \tfrac{1}{2}(\sigma\varphi_d)^2 p^2 - \ldots].$$

For the first term $\sum_p M_p = 1$ by definition. In the second term $\sum_p M_p p = 0$ since the summation from $-Nm_A$ to $0$ represents the number of A atoms in defect

of the average and the summation 0 to $Nm_B$ represents the number of A atoms in excess of the average. Hence (12) becomes

$$F(\mathbf{u}) = \mathscr{F}[\exp\{i\sigma\varphi_0(\mathbf{r})\}] .$$

$$(1 - \tfrac{1}{2}(\sigma\varphi_d)^2 \sum_{p=-Nm_A}^{Nm_B} M_p p^2 - \frac{1}{3!}(\sigma\varphi_d)^3 \sum_{p=-Nm_A}^{Nm_B}$$

$$M_p . p^3 + \dots)] .$$

For the series in the bracket [. . .] we make the approximation $[1 - x_1 - x_2 \dots] \simeq \exp(-x_1)\exp(-x_2) \dots$
Then

$$F(\mathbf{u}) \simeq \mathscr{F}[\exp(i\{\sigma\varphi_0(\mathbf{r}) - \frac{1}{3!}(\sigma\varphi_d)^3 \sum_p M_p . p^3\}$$

$$- \{\tfrac{1}{2}(\sigma\varphi_d)^2 \sum_p M_p . p^2\})] . \quad (13)$$

Hence the real, average potential is modified by the addition of third and higher odd-order terms, while an imaginary part is added consisting of second and higher even-order terms. For most cases of interest it will probably be sufficient to add only the second order imaginary term

$$\chi_2(r) = \tfrac{1}{2}(\sigma\varphi_d)^2 \sum_{p=-Nm_A}^{Nm_B} M_p . p^2 ,$$

or to modify the structure factor by the addition of

$$iF_i(\mathbf{u}) = \frac{i\sigma^2}{2} [(f_A - f_B)*(f_A - f_B)] \sum_p M_p . p^2 . \quad (14)$$

The modification $\Delta F_r(\mathbf{u})$ of the real part of the structure factor will come mostly from the Fourier transform of the third-order term, $\chi_3(\mathbf{r})$.

Calculation of these absorption terms for any specific case requires a knowledge of the $M_p$ values. As previously indicated, these cannot be derived from the short-range order coefficients or from any existing theory of ordering. The only approach which appears possible at the moment is to derive the values for the $M_p$ appropriate to a postulated model of atomic arrangement. To serve as examples for the derivation of $M_p$ values and to provide estimates of the order of magnitude of the absorption effects to be expected, three limiting cases will be considered.

(a) *Zero short-range order*

For a completely random arrangement of A and B atoms, if we consider a row of $N$ atoms in the beam direction, the probability of $n$ A atoms and $N-n$ B atoms will be given by

$$M_n = C_n^N m_A^n m_B^{N-n}$$

if $n$ varies from 0 to $N$; then

$$\sum_{p=-Nm_A}^{Nm_B} M_p . p^2 = \sum_{n=0}^{N} C_n^N (n - Nm_A)^2 . m_A^n m_B^{N-n}$$

$$= \sum_{n=0}^{N} C_n^N m_A^n m_B^{N-n}[n(n-N)]$$

$$- Nm_A(n - Nm_A) + Nnm_B] = Nm_A m_B .$$

Similarly

$$\sum_{p=-Nm_A}^{Nm_B} M_p . p^3 = Nm_A m_B(m_B - m_A) .$$

Thus

$$F_i(\mathbf{u}) = \frac{\sigma^2}{2} [(f_A - f_B)*(f_A - f_B)]Nm_A m_B . \quad (15)$$

It follows that, as might be expected in the absence of correlation, the absorption factor for $N$ layers of atoms is $N$ times that for a single layer of atoms, for which

$$\chi_2(\mathbf{r}) = \tfrac{1}{2}m_A m_B(\sigma\varphi_d)^2 .$$

This is the same result as is obtained directly from the considerations of part I. There it was shown that the absorption factor could be written as $\chi(\mathbf{r}) = \tfrac{1}{2}\sigma^2\langle\Delta\varphi^2(\mathbf{r})\rangle$, where $\Delta\varphi(\mathbf{r})$ is the deviation from the average potential. Since $\Delta\varphi^2 = m_B^2(\varphi_A - \varphi_B)^2$ when there is an A atom, *i.e.* with relative probability $m_A$, and $\Delta\varphi^2 = m_A^2(\varphi_A - \varphi_B)^2$ when there is a B atom, we get $\tfrac{1}{2}\sigma^2\langle\Delta\varphi^2\rangle = \tfrac{1}{2}\sigma^2 m_A m_B \varphi_d^2$, as before.

(b) *Perfect order within a slice*

We assume that perfect ordering exists within a slice, but there is no correlation between slices. This assumption corresponds to the case of a random sequence of out-of-phase domains, with perfect ordering within each domain.

For some particular directions of the incident beam, a fraction $m_A$ of the projected peaks will correspond to $N$ A atoms, and a fraction $m_B$ will correspond to $N$ B atoms. This case represents the most extreme deviation from the average projection for the zero short-range order case.
Then

$$\sum_p M_p . p^2 = m_B(Nm_A)^2 + m_A(Nm_B)^2$$

$$= N^2 m_A m_B ,$$

and

$$\chi_2(\mathbf{r}) = N^2 m_A m_B . \tfrac{1}{2}\sigma^2\varphi_d^2 .$$

Thus, for these beam directions, the absorption term is greater than that for complete disorder, given by (15), by a factor $N$. It may be noted that for this case the higher-order terms will not be negligible unless $N\sigma\varphi_d$ is small since, for example,

$$\sum_p M_p . p^3 = N^3 m_A m_B(m_B - m_A) ,$$

$$\sum_p M_p . p^4 = N^4 m_A m_B(1 - 3m_A m_B) .$$

(c) *Perfect order in domains within a slice*

Detailed considerations and calculations for specific cases have indicated that, irrespective of the choice of

slice thickness ($N$ atoms in a column) the presence of ordered domains with $R$ atoms in a column ($R < N$) will lead to

$$\sum_p M_p p^2 = NRm_Am_B ,$$

$$\sum_p M_p p^3 = NR^2m_Am_B(m_B - m_A) .$$

These relations are exact for $N$ divisible by $R$ and very nearly correct for any $R < N$ or for $R$ an average value for variable domain size. The absorption functions to be applied in multislice calculations are then

$$\chi(\mathbf{r}) = \tfrac{1}{2}Rm_Am_B\sigma^2\langle\Delta\varphi^2(\mathbf{r})\rangle$$

for a single layer of atoms. This result is independent of the slice thickness chosen and also of any consideration of the coincidence, or otherwise, of slice and domain boundaries.

The form and order of magnitude of the second and third order terms of (13) have been determined for the case of copper–gold alloys of $A_3B$ composition by performing the self convolutions of the function ($f_A - f_B$). The atomic scattering curves were modified by a temperature factor of $B = 0.7$ Å$^2$ assumed to be appropriate to a temperature of about 200 °C. The results are shown in Fig. 1. The imaginary part of the scattering factor, given by the second order term is seen to fall off more slowly than the real part with scattering angle. The fall-off is comparable with that of the imaginary part due to thermal motion of the atoms (Hall & Hirsch, 1965).

Also the magnitude of the absorption term is of the same order as for that due to thermal motion. Thus
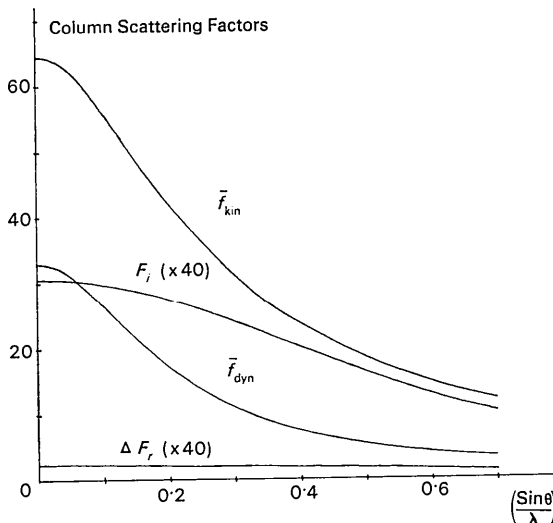


Fig. 1. The values of the average peak scattering factor for a column of 6 atoms calculated (a) kinematically, i.e. $f_{kin} = 6(\tfrac{3}{4}f_{Au} + \tfrac{1}{4}f_{Cu})$, and (b) dynamically, i.e. $f_{dyn} = |\bar{F}(u)| = |\tfrac{1}{2}f_0 + \tfrac{1}{2}f_3|$. Also shown are the second and third order absorption terms $F_i(u)$ and $\Delta F_r(u)$ (both scaled ×40) for a CuAu$_3$ crystal assumed to have a domain size of 3 unit cells.

for the (111) reflexion, $F_i(\mathbf{h})/F_r(\mathbf{h}) = 0.04$, per layer of atoms, for perfect order within layers for which the domain size $R = 3$. This value may be compared with those due to thermal motion, namely 0.124 for gold and 0.045 for copper at 300 °K (Hall & Hirsch, 1965; P. S. Turner, private communication). The third-order term modifying $F_r(\mathbf{h})$ was also calculated for the case of ordered domains with $R = 3$. The value was found to be relatively small; approximately 0.003 of $F_r(\mathbf{h})$. Thus the differences in the absorption coefficients which result from assuming different models for the state of short-range order are of such a magnitude that they should lead to experimentally observable intensity differences, given suitable specimens of copper-gold alloys. These conclusions will be tested by further calculation and by experimental observations, when possible.

## Diffuse intensity from a single slice

It was shown in part I that the intensity for diffuse scattering from the whole crystal could be expressed in terms of amplitudes calculated for single slices if, as in the case under consideration, the correlation in the deviations from the average lattice does not extend over greater distances than the slice thickness. The actual calculation of the diffuse scattering for the whole crystal involves the extension to the dynamical factor concept which was outlined in part I and will be treated in more detail in a later section. However it seems likely that the diffuse scattering intensity for the whole crystal will differ appreciably from that calculated for kinematical diffuse scattering from each slice, only if the intensity calculated for the diffuse scattering from a slice considered separately, as in equation (9), is appreciably different from the kinematical value. Hence, in order to evaluate the likely magnitude of the effects on diffuse scattering of deviations from kinematical scattering without the extreme labour of whole-crystal calculations, equation (9) was used to calculate the diffuse scattering intensity given by a single slice containing a high degree of local order in the form of idealized simple domain configurations.

The single slice was assumed to be of CuAu$_3$, six unit cells thick in the beam direction, which was parallel to [001]. In the $x$ and $y$ directions it was assumed that out-of-phase domain boundaries, with random interdomain shifts, occurred regularly every three unit cells. In the $z$ direction a domain boundary was assumed to occur perpendicular to the $z$ axis, half-way through the slice, separating two perfectly ordered domains of three unit cell thickness each. The four forms which such a domain boundary could take are, (1) no relative displacement of the columns of copper atoms, i.e. no anti-phase boundary; (2) a relative translation of columns of copper atoms by ($a/2, a/2, 0$), i.e. a 'good' type; (3) and (4), 'bad' type boundaries with translations, ($a/2, 0, a/2$) and ($0, a/2, a/2$), not in the $x - y$ plane.

Such domain sizes are of the same order of magnitude as the average domain size which must be postu-

lated in order to give short-range order coefficients approximately in agreement with experimental results on Cu₃Au not far above the critical temperature (Moss, 1965). The slice thickness involved is probably too great for accuracy in $n$-beam calculations, but may be assumed to give at least a rough indication of the magnitudes of dynamical effects to be expected.

The special shape assumed for the domains simplified the calculation of diffuse intensities considerably, since the only peaks which could occur from the projection of the columns of atoms in the slice were $f_0$, $f_3$ and $f_6$ and also intensities from domains separated in the $x$ and $y$ directions were additive.

The two cases of particular interest for assessing the differences of dynamical and kinematical scattering behaviour are the case (1) above with no copper translations, and the case of random phasing across the domain boundary in the $z$ direction. For kinematical scattering the diffuse intensity is proportional to the thickness of the domain in the beam direction so that the diffuse intensity should be twice as great for the first of these cases as for the second. This may be approximately so for dynamical scattering but it is to be expected that differences in principle between dynamical and kinematical scattering would show up because the complex $f_n$ do not vary linearly with $n$, so that $f_3 \neq \frac{1}{2}(f_0 + f_6)$.

The values of the complex peak scattering factors, $f_n$, were evaluated using a computer program developed by P.A.Doyle for evaluating complex scattering factors for individual atoms. Computer programs were developed to calculate diffuse intensities and used to give intensity values along the lines $(1,v,0)$ and $(3,v,0)$ in reciprocal space for small intervals of the coordinate, $v$.

Because the magnitudes and angular variation of the complex peak scattering factors, $f_n$, are markedly different from the kinematical scattering factors, it is convenient to calculate diffuse scattering intensities by using a sort of pseudo-kinematical expression involving the $f_n$, thus

$$I' = P(f_0 - f_n)(f_0^* - f_n^*) \sum_{lm} \left\{ \sum_{n=-N}^{N} \alpha_{lmn}/N \right\} \exp \left\{ 2\pi i (ul + vm) \right\} = \frac{|f_0 - f_n|^2}{N^2 |f_{Au} - f_{Cu}|^2} \cdot I_{kin}. \quad (16)$$

For the case of no domain boundary within the slice, this expression with $f_n = f_6$ is identical with the dynamical intensity, $I_{dyn}$, given by equation (9). The angular variation of the ratio $I_{dyn}/I_{kin}$ for this case is shown in Fig.2.

The absolute magnitude of the diffuse intensity calculated dynamically is roughly an order of magnitude less than the kinematic value. This follows because the peak scattering factors, $f_n$, are smaller in magnitude and vary less rapidly with the atomic number of the contributing atoms than the kinematic scattering factors for the same number of atoms. The ratio of dynamical and kinematical values varies strongly with scat-

tering angle in a manner reminiscent of the modulation of intensities of gas diffraction patterns resulting from the varying phase differences of the complex atomic scattering factors of unequal atoms.

For the other cases considered, involving good, bad or random phasing at the domain boundary, the large differences between the complex peak scattering factors, $f_n$, and the kinematical scattering factors are similarly important and account for the major part of the difference between dynamical and kinematical intensities. The remaining part of the difference is expressed by the value of the ratio $I_{dyn}/I'$.

In the vicinity of the (100) reciprocal lattice point this ratio is 0·84 for the case of a good domain boundary and also for both cases of bad domain boundaries. For random phasing the ratio is 0·91. In each case the value is only weakly dependent on the scattering angle, and does not vary by more than five per cent for $(\sin \theta)/\lambda$ values out to 0·7.

The positions of maxima and minima and the general shape of the diffuse scattering distributions in reciprocal space are very nearly independent of the model chosen and are close to the kinematical predictions. This is to be expected since these are determined almost entirely by the domain shapes and sizes in the $x$ and $y$ directions which were assumed to be the same in all cases.

On the other hand, some deviations from the form of the kinematical diffuse scattering can occur under the special circumstances created by zeros in the contributions from particular models. For example, if the domain boundary in the $z$ direction is good there will be zero intensity at the points $(1,0,0)$ and $(0,1,0)$ but for no domain boundary these is a maximum at each of these points. The differences in peak scattering fac-
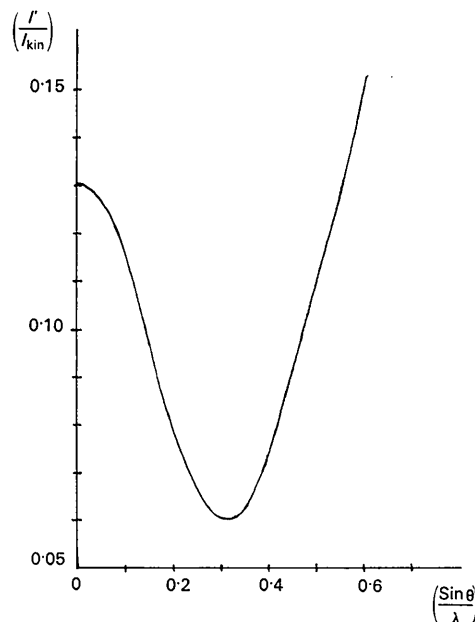


Fig.2. The variation of the factor $I'/I_{kin} = |f_0 - f_6|^2/(f_A - f_B)^2$, which modulates the dynamical intensities, with $(\sin \theta)/\lambda$.

tors for these two cases lead to the result that for equal probabilities of no mistakes and good mistakes, the ratio $I_{dyn}/I'$ differs by about ten per cent for the (100) and (110) peaks as shown in Fig. 3.

Although it has been shown that, for the special models considered, there are differences in diffuse intensities other than those directly attributable to the differences between the kinematical and complex peak scattering factors, the above results suggest that the derivation of information from diffuse scattering, other than that provided by kinematical diffraction experiments, may depend on the detection of relatively small variations in intensities. It remains to be seen whether the $n$-beam dynamical interactions occurring in crystals of greater thickness will enhance or reduce these variations.

## Diffuse intensity from a crystal

In order to calculate the effects of $n$-beam dynamical interactions on the diffuse scattering, and so get the diffuse scattering from the whole crystal, we make use of the generalization of the dynamical factor idea, as outlined in part I. We consider first the relatively simple case that the diffusely scattered radiation from any slice suffers multiple scattering by Bragg reflexions but is not again diffusely scattered, *i.e.* we ignore multiple inter-slice diffuse scattering.

As before we write the scattering from a slice, for $u \neq 0$,

$$F(u) = \sum_m \sum_i f_m \exp \{2\pi i u \cdot r_{mi}\}$$

$$= \sum_m f_m C_m(u) ,$$

where $f_m$ is given by (6) and the vectors $r_{mi}$ specify the sites of the peaks with scattering factors $f_m$. If we assume an amplitude of scattering $f_m(u_n)$ for the $n$th slice of the crystal, the diffuse scattering produced outside the crystal, calculated by applying $n$-beam dynamical theory separately for each $v$ vector, where $u = h + v$, as in part I, is written $\Psi_{mn}(u)$. This calculation does not allow for multiple diffuse scattering. Adding the



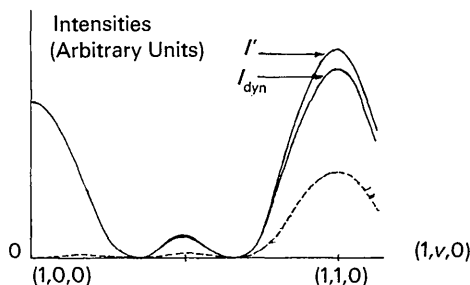Fig. 3. The variation of $I_{dyn}$ and $I'$ along the line from the (1,0,0) to the (1,1,0) reciprocal lattice point, resulting from the non-linearity of the complex peak scattering factors, $f_n$, in the case of fifty per cent 'good' type horizontal domain boundaries. $I'$ is calculated with the use of the approximation $f_3 = \frac{1}{2}(f_0 + f_6)$. The dotted curve shows the contribution from the domains with a 'good' boundary.

amplitudes for all slices, the total diffuse scattering amplitude for the crystal is then

$$\Psi(u) = \sum_m \sum_n C_{mn}(u) \Psi_{mn}(u) ,$$

and the intensity distribution is

$$I(u) = \sum_m \sum_n \sum_p \sum_q C_{mn}(u) C^*_{pq}(u) \Psi_{mn}(u) \Psi^*_{pq}(u) .$$

But

$$C_{mn} C^*_{pq} = \sum_i \exp \{2\pi i u \cdot r_{mni}\} \cdot \sum_j \exp \{-2\pi i u \cdot r_{pqj}\}$$

$$= P \sum_i P(mn,pq,i) \exp \{2\pi i u \cdot r_i\} ,$$

where $P(mn,pq,i)$ is the probability that the peak of scattering power $f_p$ in the $q$ slice will be displaced laterally by a vector $r_i$ from a peak of scattering power $f_m$ in the $n$ slice.

Putting

$$P(mn,pq,i) = M_p[1 + \gamma(mn,pq,i)/M_m M_p] ,$$

the intensity expression then becomes

$$I(u) = P \sum_m \sum_n \sum_p \sum_q M_m M_p \Psi_{mn}(u) \Psi^*_{pq}(u)$$

$$\sum_i \exp \{2\pi i u \cdot r_i\}$$

$$+ P \sum_m \sum_n \sum_p \sum_q \Psi_{mn}(u) \Psi^*_{pq}(u) \sum_i \gamma(mn,pq,i)$$

$$\exp \{2\pi i u \cdot r_i\} , \quad (18)$$

where the first term represents the Bragg peaks which may be calculated by the usual $n$-beam dynamical, perfect-crystal technique, with structure factors modified by absorption, and the second term represents the diffuse scattering in which we are now interested. Since we assume that there is no correlation of the deviations from the average lattice between slices, it follows that $\gamma(mn,pq,i) = 0$ unless $n = q$. Also we may assume the correlation parameters to be the same in all layers, so we may put $\gamma(mn,pn,i) = \gamma_{mpi}$, and the diffuse intensity term becomes

$$I_d(u) = P \sum_m \sum_p \sum_n \Psi_{mn}(u) \Psi^*_{pn}(u) \sum_i \gamma_{mpi} \exp \{2\pi i u \cdot r_i\} ,$$

$$(19)$$

$$= P \sum_m \sum_p f_m f^*_p D_{mp}(u) \sum_i \gamma_{mpi} \exp \{2\pi i u \cdot r_i\} . \quad (20)$$

This is then identical with the expression in (9) for the diffuse intensity for a single layer except for the insertion of the dynamical factors

$$D_{mp}(u) = \sum_n \Psi_{mn}(u) \Psi^*_{pn}(u)/f_m(u) f^*_p(u) .$$

In order to calculate the diffuse intensity it is thus necessary to calculate separately the dynamical factors or, more directly, the sets of functions $\Psi_{mn}(u)$. This of course involves a great deal of computation, but once it has been accomplished the diffuse intensity corresponding to different sets of order parameters $\gamma_{mpi}$ can be evaluated readily.

## Multiple inter-slice diffuse scattering

The deviation from kinematical diffuse scattering within a slice implies that multiple coherent diffuse scattering terms are appreciable within the range of atomic correlations. Under these circumstances it seems possible that the multiple incoherent diffuse scattering terms representing repeated scattering between uncorrelated regions of the crystal may also be appreciable. Such terms have been considered briefly in part I.

The calculation of such multiple inter-slice diffuse scattering would appear to be very complicated and prohibitively lengthy unless some severe approximations are made.

One possible basis for approximation is the assumption that the dynamical factors, $D_{mp}(\mathbf{u})$, are independent of crystal thickness. It has been shown by Fisher (1965, and private communication), for the case of kinematical scattering within a slice, that for a given $\mathbf{u}$, the dynamical factor $D(\mathbf{u})$ usually changes rapidly at first with increasing thickness and then oscillates about some limiting value. For copper–gold alloys the oscillations have a periodicity of about 100 Å or less. Hence if we deal with relatively thick crystals it is a good assumption in this case to take $D(\mathbf{u})$ as a constant when considering higher-order terms.

On this basis we may write the intensity for single diffuse scattering, given by (20), as

$$I_d^{(1)}(\mathbf{u}) = N I_d^0(\mathbf{u}) = \sum_{n=1}^{N} I_d^0(\mathbf{u}) ,$$

*i.e.* we assume that each slice, from 1 to $N$, gives the same contribution, $I_d^0(\mathbf{u})$, to the final diffuse scattering.

Then the second order term, corresponding to double diffuse scattering is

$$I_d^{(2)}(\mathbf{u}) = \int \sum_{n=1}^{N} I_d^0(\mathbf{u}_1) \sum_{r=n}^{N} I_d^0(\mathbf{u}-\mathbf{u}_1)d\mathbf{u}_1$$

$$\simeq \tfrac{1}{2}N^2 I_d^0(\mathbf{u}) * I_d^0(\mathbf{u}) ,$$

and the total diffuse scattering will be

$$I_d(\mathbf{u}) = \sum_{m} I_d^{(m)}(\mathbf{u})$$

$$\simeq \mathscr{F}[\exp\{\mathscr{F}^{-1}I_d^0(\mathbf{u})\}-1] . \qquad (21)$$

On this basis the total effects of multiple inter-slice diffuse scattering could be calculated without a great deal of additional computation.

### References

COWLEY, J. M. (1950). *J. Appl. Phys.* **21**, 24.
COWLEY, J. M. & POGANY, A. P. (1968). *Acta Cryst.* A **24**, 109.
FISHER, P. M. J. (1968). In the press.
FISHER, P. M. J. (1965). *Proc. Intern. Conf. Electron Diffraction and Defects in Crystals*, Melbourne.
GOODMAN, P. & MOODIE, A. F. (1965). *Proc. Intern. Conf. Electron Diffraction and Defects in Crystals*, Melbourne.
HALL, C. R. & HIRSCH, P. B. (1965). *Proc. Roy. Soc.* A **286**, 158.
MOSS, S. C. (1965). *Metallurg. Soc. Conf.* **36**, 95.
WATANABE, D. & FISHER, P. M. J. (1965). *J. Phys. Soc. Japan*, **20**, 2170.

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# Correction for Second-Order Diffuse X-ray Scattering in the Determination of the Elastic Constants of Crystals

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A new and improved method of allowing for second-order thermal diffuse X-ray scattering, close to a reciprocal-lattice point, is proposed; an appropriate equation for first- and second-order contributions is matched, by the method of least-squares, to the experimentally measured scattering data. A program was written for the I.C.T. 1905 computer and some $K[ABC]_{hkl}$ values for KCl were compared with those previously reported.

## Introduction

Several investigators have shown that measurement of the thermal diffuse scattering of X-rays close to a reciprocal-lattice point provides values for elastic constants, which are – at least for cubic crystals – comparable to those found by other methods (Wooster, 1962). The diffuse intensity, due to the thermal motion of atoms within the crystals, may be considered as a sum of contributions from multiple photon–phonon