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Structure Information from Anomalous Absorption Effects in Diffuse Scattering of Electrons

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The theory of diffuse scattering of electrons in the presence of Bragg scattering is examined with particular emphasis on the structure information which can be obtained from diffuse scattering under such conditions. The maximum information which can be extracted from intensity distributions is shown to be included in a scattering function $\langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h})\rangle$ of three continuous and three discrete variables in reciprocal space. The Fourier transform into direct space of this function renders a six-dimensional distribution which is shown to describe position as well as correlation for fluctuations responsible for diffuse scattering. This function in direct space is termed a distribution-correlation function. The Patterson function and the imaginary potential associated with anomalous absorption are shown to be included as special cases, *viz.* a three-dimensional section and a three-dimensional projection, respectively. The additional structure information which can be obtained from the distribution-correlation function as compared with the ordinary Patterson function, is discussed for different types of diffuse scattering. As an example anomalous absorption effects in many beam cases are discussed with particular reference to characteristic X-ray emission. Numerical calculations indicate that such effects can be exploited for determination of sites of dissolved atoms.

1. Introduction

Whereas diffuse scattering of X-rays and neutrons have been used extensively in order to obtain information about defects and excitations in crystals, the utilization of diffuse scattering in electron diffraction patterns for such purposes has been more limited.

One important reason for this has been the lack of an adequate theoretical basis for quantitative interpretation of diffuse scattering of electrons. Such a theory must necessarily take into account the simultaneous Bragg scattering. However, starting with Kainuma's (1955) work on Kikuchi lines, a number of authors have contributed to a theory which takes into account Bragg scattering of the incident beam as well as the Bragg scattering between diffuse beams. A quite general theory, based on a slice approach, was developed in a previous paper (Gjønnes, 1966).* There it was shown that the Bragg scattering effects in the distribution of diffuse scattering can be described partly as a redistribution of intensity between diffuse scattering in directions $\mathbf{k}_0+\mathbf{s}+\mathbf{h}$ coupled through Bragg reflexions, partly as an enhancement or reduction of the sum of intensities, $\sum_h I_{\mathbf{s}+\mathbf{h}}$, over all these directions. The latter effect is closely connected with anomalous absorption and depends on certain phase relationships in the diffuse scattering. Hence it will appear that this effect may contain structure information of a kind which can not be obtained from a scattering experiment under kinematic conditions. Actually, the use of such anomalous effects in the diffuse scattering has been suggested by some authors (Cowley, 1965; Gjønnes, 1965).

From such considerations it seems desirable to perform a general investigation, based on recent theories, into the information which may be contained in the distribution of diffuse scattering, especially under many beam conditions.

The purpose of this paper is to present some results from such an investigation, in particular to discuss the representation of this structure information in terms of a distribution function. The connexion with anomalous absorption in the discrete beams is also discussed.

2. The theory of Bragg diffraction effects in diffuse scattering

The theory of Bragg diffraction effects in the diffuse scattering of electrons has been developed by several authors (Kainuma, 1955; Takagi, 1958; Fujimoto & Kainuma, 1963; Fukuhara, 1963; Gjønnes, 1966 (I); Fujimoto & Howie, 1966; Cowley & Pogany, 1968). Here we shall use the formulation given in I. Let us sketch briefly the basic ideas and general results.

Diffuse scattering originates from the non-periodic part, U_d, of the Coulomb interaction, $U(\mathbf{r},\mathbf{r}_j)$ between the incident electron, $\mathbf{r}$, and the particles, $\mathbf{r}_j$, of the object:

$$\sum \frac{2}{a_H} \frac{Z_j}{|\mathbf{r}-\mathbf{r}_j|} = U(\mathbf{r},\mathbf{r}_j) = \sum_h U_h \exp\,[i\mathbf{h}\mathbf{r}] + U_d(\mathbf{r},\mathbf{r}_j) \equiv U_p + U_d$$

$$U_d(\mathbf{r},\mathbf{r}_j) = \int f(\mathbf{s},\mathbf{r}_j) \exp\,[i\mathbf{s}\mathbf{r}]d\mathbf{s}\,. \qquad (1)$$

Here Z_j is the charge of the jth particle, $\mathbf{h}$ are the reciprocal-lattice vectors, $\mathbf{s}$ is a vector in reciprocal space and a_H is the first Bohr radius.

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* Referred to later as I

Inelastic scattering arise through time dependence of the coordinates $\mathbf{r}_j$, which in the most general case should be treated as operators. It is found, however, that diffraction effects at high or moderate energies are not significantly influenced by this time dependence, that is by the energy transfer. Hence, the $\mathbf{r}_j$'s can, for our purpose, be treated as parameters and be suppressed during the scattering calculations. The energy transfer in elastic scattering may then be introduced at the end of the calculations as energy dependence in the scattering function $\langle f(\mathbf{s}+\mathbf{g})f^*(\mathbf{s}+\mathbf{g}')\rangle$ to be defined below.

When the scattering from U_d is considered in first order only, and independently of the periodic part U_p, a kinematical theory of diffuse scattering is obtained. As is well known from experimental and theoretical studies, such an approximation is insufficient and may lead to incorrect interpretation of experimental patterns. Bragg scattering of the incident beam, as well as of the continuous distribution of diffuse scattered beams must be included. A formal expression can be obtained from the Born series of scattering. To the first order in the non-periodic potential, U_d, the amplitude, Ψ, of diffuse scattering can be written formally,

$$\Psi=\{1+GU_p+(GU_p)^2+\ldots\}GU_d\{1+GU_p+\ldots\}\Psi^0$$

where $G=G(\mathbf{r},\mathbf{r}')=\exp(ik|\mathbf{r}-\mathbf{r}'|)/4\pi|\mathbf{r}-\mathbf{r}'|$ is the Greens function for the incident electron.*

The operators acting on the incident wave Ψ^0 represent, from right to left: Bragg scattering of the incident beam into a set of discrete beams; diffuse scattering of these discrete beams into a continuous distribution of diffuse beams; Bragg scattering between those diffuse beams which differ by reciprocal-lattice vectors, $\mathbf{h}$.

A more convenient expression is obtained when the Bragg scattering is represented by scattering matrices (see *e.g.* Hirsch, Howie, Nicholson, Pashley & Welan, 1965), and the non-periodic potential by its Fourier components, $f(\mathbf{s})$. On neglecting back scattering and taking the z axis near the incident beam direction and near the surface normal, one obtains for a crystal slab of thickness z and infinite lateral dimensions the amplitude expression

$$\Psi(\mathbf{s}+\mathbf{h})=\sum_g\sum_f\int_0^z S_{hg}(\mathbf{k}_0+\mathbf{s},z-z_1)f(\mathbf{s}+\mathbf{g}-\mathbf{f})S_{f0}(\mathbf{k}_0,z_1)\mathrm{d}z_1 \quad (2)$$

where the arguments, *e.g.* $(\mathbf{k}_0,z_1)$, of the scattering matrix define the zero beam direction and crystal thickness. We shall be concerned mainly with Bragg scattering through reflexions, $\mathbf{h}$, lying in a section, normal or near normal to the z axis, through the origin of reciprocal space. Similarly $\mathbf{s}$ is taken to be a vector in that section, reduced to the first Brillouin zone through the subtraction of $\mathbf{g}-\mathbf{f}$.

According to equation (2), the amplitude of diffuse scattering in the direction $\mathbf{k}_0+\mathbf{s}+\mathbf{h}$ is made up of diffuse scattering contributions from each infinitesimal slice $\mathrm{d}z_1$ within the crystal: The discrete beams f which arise through Bragg scattering in the crystal slab (1) above the level z_1 are scattered in the slice $\mathrm{d}z_1$ into diffuse beams $\mathbf{k}_0+\mathbf{s}+\mathbf{g}$ which on passing through the lower part (2) of the crystal are Bragg scattered into $\mathbf{k}_0+\mathbf{s}+\mathbf{h}$. The different terms in the double sum over intermediate beams f and $\mathbf{k}_0+\mathbf{s}+\mathbf{g}$ can be represented by diagrams as shown in (I).

If correlations in the non-periodic potential in the z direction are neglected (I; Cowley & Murray, 1968), the intensity expression will involve only a single integration over thickness:

$$I(\mathbf{s}+\mathbf{h})=\sum_g\sum_{g'}\sum_f\sum_{f'}\int_0^z S_{hg}(2)S^*_{hg'}(2)\langle f(\mathbf{s}+\mathbf{g}-\mathbf{f}) \times f^*(\mathbf{s}+\mathbf{g}'-\mathbf{f}')\rangle S_{f0}(1)S^*_{f'0}(1)\mathrm{d}z_1 \quad (3)$$

where the abbreviated arguments (2) and (1) have been introduced instead of $(\mathbf{k}_0+\mathbf{s},z-z_1)$ and $(\mathbf{k}_0,z_1)$ respectively. The intensity expression (3) can be divided in a thickness-independent part and terms which oscillate with the crystal thickness, z. The latter type of terms are important in the interpretation of electron microscope contrast from inelastic scattering (see *e.g.* Fukuhara, 1963) and of certain effects in the diffuse scattering from very flat and perfect crystals (Gjønnes & Watanabe, 1966). They are negligible, however, in diffraction patterns from crystals with small thickness or orientation variations.

The approximations implied in the intensity expression (3), which forms the basis for the following treatment were discussed in I (see also Cowley & Murray, 1968). The most important one is connected with the use of two-dimensional distributions to describe the diffuse scattering in reciprocal space. In order that this shall be valid, the diffuse scattering functions must vary slowly in the z direction; that is to say that the range of correlations in the non-periodic potential in this direction must be short relative to typical extinction distances.

For numerical calculations it is often convenient to expand the Bragg scattering matrix elements in terms of the normalized Bloch waves

$$\exp[i\mathbf{k}_0\mathbf{r}]\exp[i\xi^jz]\sum_f C^j_f\exp[i\mathbf{f}\mathbf{r}]$$

and

$$\exp[i(\mathbf{k}_0+\mathbf{s})\mathbf{r}]\exp[i\eta^lz]\sum_g B^l_g\exp[i\mathbf{g}\mathbf{r}]$$

corresponding to the incident and the scattered waves. With such a notation one has, *e.g.*

$$S_{hg}(z-z_1)=\sum_i B^l_hB^l_g\exp[i\eta^l(z-z_1)]\,.$$

On introducing these expansions in (3), one obtains a summation over band indices in the intensity expres-

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* The use of the Green's function operator in electron diffraction problems has been discussed by Fujiwara (1959), Gjønnes (1962*a*) and in (I).

sion. Within the present approximations, the z dependence of this expression will be contained in a product of the form

$$\int \exp\,[i\eta^i(z-z_1)]\,\exp\,[i\xi^j z_1] \times \exp\,[-i\eta^{i'}(z-z_1)]\,\exp\,[-i\xi^{j'}z_1]\mathrm{d}z_1$$

from which it is seen that the thickness independent terms are those for which $i=i'$ and $j=j'$. Restricting the attention to these terms only, one obtains then an expression for the non-oscillating part of the intensity:

$$I(\mathbf{s}+\mathbf{h})_{\text{non-osc}}=\sum_i\sum_j|B^i_hC^j_o|^2|\sum_g\sum_f B^i_gC^j_f f(\mathbf{s}+\mathbf{g}-\mathbf{f})|^2$$

where $i=j$ and $i\neq j$ corresponds to intra- and inter-band transitions, respectively.

The terms in the fourfold summation over g, g', f and f' in equation (3) contain factors of the type $\langle f(\mathbf{s}+\mathbf{h})f^*(\mathbf{s}+\mathbf{h}')\rangle$. Those with $h=h'$ are included also in a kinematical expression, *i.e.*

$$I_{\text{kin}}(\mathbf{s}+\mathbf{h})\propto\langle|f(\mathbf{s}+\mathbf{h}|^2\rangle$$

However, due to the Bragg scattering prefactors in equation (3), one gets a redistribution of the kinematical scattering between the directions $\mathbf{k}_0+\mathbf{s}+\mathbf{h}$ which are coupled through Bragg reflexions. The results are regions of excess and deficient diffuse scattering, that is to say, the Kikuchi pattern.

The remaining terms are those with $\mathbf{h}\neq\mathbf{h}'$ in $\langle f(\mathbf{s}+\mathbf{h})f^*(\mathbf{s}+\mathbf{h}')\rangle$. They do not occur in kinematic scattering and are peculiar to Bragg scattering effects. In the next section we shall discuss the nature of the structure information contained in these terms.

3. Distribution-correlation function for diffuse scattering

When kinematic scattering conditions apply, the structure information in diffuse scattering can be represented by a correlation function, the Patterson function,

$$P(\mathbf{r})=F\{\langle|f(\mathbf{s})|^2\rangle\} \tag{4}$$

where $\langle|f(\mathbf{s})|^2\rangle$ can be obtained from measurements. $F\{\}$ means Fourier transformation; the scattering vector $\mathbf{s}$ is here not restricted to the first Brillouin zone.

The intensity expression (3) under dynamic Bragg scattering conditions cannot be directly related to a similar distribution. However, in this expression the non-periodic potential enters through the scattering function which can be written $\langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h})\rangle$ when $\mathbf{s}$ is not restricted to the first Brillouin zone. It may be doubtful whether this function can be determined unequivocally from experimental distributions of diffuse scattering in the presence of Bragg scattering. However, it expresses the maximum amount of structure information which can be extracted from such measurements. Conversely, knowledge of this function will permit calculation of the expected experimental intensity. Hence, we shall in this paragraph, discuss the relation of this function to *structure*, and in particular derive a more general relation which include equation (4) as a special case.

Let us now specify $f(\mathbf{s})$, *viz*

$$f(\mathbf{s})=(1/s^2)\,(\sum_j Z_j(\exp\,[i\mathbf{s}\mathbf{r}_j]-\langle\exp\,[i\mathbf{s}\mathbf{r}_j]\rangle))$$

where $\mathbf{r}_j$ is the coordinate, Z_j the charge of the jth particle in the object. The second term in the parenthesis is subtracted in order to exclude the contributions to the periodic part of the potential, when summed over j, this term adds up to zero for $\mathbf{s}$ different from a reciprocal lattice vector. The bracket denotes the expectation value, *e.g.*

$$\langle\exp\,[i\mathbf{s}\mathbf{r}_j]\rangle=\int\cdots\int\Phi_0(\mathbf{r}_1\cdots\mathbf{r}_j\,\ldots)\,\exp\,[i\mathbf{s}\mathbf{r}_j]\Phi_0^*(\mathbf{r}_1\cdots\mathbf{r}_j\,\ldots)\mathrm{d}\mathbf{r}_1\cdots\mathrm{d}\mathbf{r}_j\,\ldots$$

if the object is taken to be in its ground state, Φ_0. As defined, $f(\mathbf{s})$ are the Fourier components of the potential fluctuations in the object. It will simplify the discussion if the charge fluctuations are treated instead. This is accomplished by removing the Coulomb denominators s^2 and $(\mathbf{s}+\mathbf{h})^2$ from $\langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h})\rangle$; let us define

$$\begin{aligned}Q(\mathbf{s},\mathbf{h})&=\langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h})\rangle s^2(\mathbf{s}+\mathbf{h})^2\\&=\sum_j\sum_{j'}Z_jZ_{j'}\{\langle\exp\,[i\mathbf{s}\mathbf{r}_j]\,\exp\,[-i(\mathbf{s}+\mathbf{h})\mathbf{r}_{j'}]\rangle\\&\quad-\langle\exp\,[i\mathbf{s}\mathbf{r}_j]\rangle\langle\exp\,[-i(\mathbf{s}+\mathbf{h})\mathbf{r}_{j'}]\rangle\}\end{aligned} \tag{5}$$

and discuss this function of six variables in reciprocal space.

The corresponding function in direct space is obtained on taking the six-dimensional Fourier transform $R(\mathbf{q},\mathbf{r})$ of $Q(\mathbf{s},\mathbf{h})$:

$$\begin{aligned}R(\mathbf{q},\mathbf{r})&=\left(\frac{1}{2\pi}\right)^3\int\exp\,[i\mathbf{s}\mathbf{r}]\sum_h\exp\,[i\mathbf{q}\mathbf{h}]Q(\mathbf{s},\mathbf{h})\mathrm{d}\mathbf{s}\\&=\sum_j\sum_{j'}Z_jZ_{j'}\{\langle\delta(\mathbf{r}-\mathbf{r}_{jj'})\delta(\mathbf{q}-\mathbf{r}_{j'})\rangle-\langle\delta(\mathbf{r}-\mathbf{q}-\mathbf{r}_j)\rangle\\&\quad\langle\delta(\mathbf{q}-\mathbf{r}_{j'})\rangle\}\end{aligned} \tag{6}$$

where $\mathbf{r}_{jj'}$ is the interparticle vector $\mathbf{r}_j-\mathbf{r}_{j'}$.

It may be evident that this function in some way describes location as well as correlations in the charge fluctuations. It should also be noted that $Q(\mathbf{s},\mathbf{h})$ varies continuously with $\mathbf{s}$ but is defined only for discrete $\mathbf{h}$. Hence $R(\mathbf{q},\mathbf{r})$ must be periodic in $\mathbf{q}$, and non-periodic in $\mathbf{r}$. Inspection of equation (6) reveals that the first term in $R(\mathbf{q},\mathbf{r})$ expresses the probability of having a charge at $\mathbf{q}$ and another charge at a distance $\mathbf{r}$ from the former, *i.e.* at $\mathbf{q}+\mathbf{r}$. After subtraction of the second term the fluctuations in that probability are retained. It may also be noticed that $R(\mathbf{q},\mathbf{r})$ equals the integrand in the usual definition of a Patterson function for charge fluctuations.

We must now discuss what sort of information will be contained in such a function $R(\mathbf{q},\mathbf{r})$ for various types of fluctuations and to what extent this information can be attained by measurements which depend on the magnitudes $\langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h})\rangle$.

However, two important special cases of the relation (6) between Q and R should at once be pointed out: The section $\mathbf{h}=0$, through the scattering function Q corresponds to the kinematic intensity; its Fourier transform

$$\int \exp\,[i\mathbf{sr}]Q(\mathbf{s},0)\mathrm{d}\mathbf{s} = \int R(\mathbf{q},\mathbf{r})\mathrm{d}\mathbf{q} = P(\mathbf{r}) \qquad (7)$$

is, of course, the Patterson function.

The 'projection' $\int Q\mathrm{d}\mathbf{s}$ of the scattering function is related to a section through $R(\mathbf{q},\mathbf{r})$, *i.e.*

$$\int Q(\mathbf{s},\mathbf{h})\mathrm{d}\mathbf{s} = \int \exp\,[i\mathbf{hq}]R(\mathbf{q},0)\mathrm{d}\mathbf{q}\,. \qquad (8a)$$

From equation (6) it is seen that this section describes the charge fluctuations in the unit cell:

$$R(\mathbf{q},0) = \langle \varrho^2\rangle - \langle \varrho\rangle^2 \quad \text{where} \quad \varrho = \sum_j Z_j\delta(\mathbf{q}-\mathbf{r}_j)\,. \qquad (8b)$$

The same function is obtained when one includes only the contribution from $j=j'$ in equation (6), that is when inter-particle correlations are neglected.* It will be shown below that the Fourier components $\Phi_h = \int\langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h})\rangle\mathrm{d}\mathbf{s}$ may be susceptible to measurement. By the same argument as above this magnitude is related by a Fourier transformation to *potential* fluctuations in the unit cell. Broadly speaking, the variation of $R(\mathbf{q},\mathbf{r})$ with $\mathbf{r}$ describes correlations in the particle fluctuations responsible for diffuse scattering, whereas the $\mathbf{q}$ variation describes the location of the fluctuations within the framework defined by the average unit cell. From the present point of view the $\mathbf{q}$ dependence may be considered to be the more interesting, since this represents the new feature in $R(\mathbf{q},\mathbf{r})$ as compared with the Patterson function. Let us therefore discuss this part of the correlation distribution in particular.

For substitutional short range order in a structure with one lattice site *e.g.* disordered Cu_3Au – the $\mathbf{r}$ variation contains all the interesting structure information. The $\mathbf{q}$-variation is here trivial and only expresses the known fact that the deviation from the periodic structure is located at the atomic site. The situation is clearly different when more than one lattice site is involved in the ordering, for instance in a structure with two interpenetrating lattices. Then knowledge of the $\mathbf{q}$-dependence will enable one to discriminate between ordering on the two lattices. Also when size-effects accompany the ordering one will expect the $\mathbf{q}$-dependence to provide useful information, since location of the fluctuations will be somewhat different from that of the average atoms. In fact, Cowley (1965) has reported that the diffuse scattering from an alloy with large size effect is markedly altered through Bragg scattering effects. Rather similar arguments appear to be applicable to thermal scattering; the $\mathbf{q}$-dependence of $R(\mathbf{q},\mathbf{r})$ is expected to provide most useful information in structures with several atoms in the unit cell.

For electronic excitations, the situation is again different. Apart from plasma oscillations, correlations do not play an important part. For one-electron-excitations, the $\mathbf{q}$-dependence, that is the location of fluctuations, may include the interesting information. According to equation (8*a* and *b*), this information is contained in a projection $\int Q\mathrm{d}\mathbf{s}$ of the scattering function. It is known from the theory of anomalous absorption, see Yoshioka (1957), Gjønnes (1962*b*) or Whelan (1965), that a related projection, *viz.*

$$\int \langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h})\rangle\mathrm{d}\mathbf{s}$$

appears in the theory of anomalous absorption. In the next section, we shall derive the connexion between Bragg scattering effects in the diffuse scattering and anomalous absorption in a more direct way.

4. Anomalous absorption, diffuse scattering and secondary radiation

Anomalous absorption refers to the enhancement or reduction of the apparent absorption which occurs when Bragg beams are excited by the incident beam. The intensity which in this way is lost or gained in the discrete beams, relative to normal absorption, must reappear as gain or loss in the background scattering. When emission of secondary radiation accompanies inelastic scattering this emission must be enhanced or reduced in the same way, as has been demonstrated by Hirsch, Howie & Whelan (1962), Duncumb (1962), Hall (1966) and Miyake, Hayakawa & Miida (1968). From the argument presented in the previous section it will appear that structure information can be gained through the study of anomalous absorption effects. Such information may be obtained by studying the Bragg reflexions, the background scattering or the emission of secondary radiation.

Let us now calculate the total intensity in the diffuse scattering from one layer in the crystal, using equation (3) above. In order to achieve this, one can first sum the intensities from corresponding points, $\mathbf{s}+\mathbf{h}$, in different Brillouin zones. Utilizing the relation

$$\sum_h S_{hg}(2)S^*_{hg'}(2) = \delta_{gg'}$$

we get with a simple change of summation variables in equation (3):

$$\sum_h I_{\mathbf{h}+\mathbf{s}} = \sum_g\sum_h \langle f(\mathbf{s}+\mathbf{h})f^*(\mathbf{s}+\mathbf{h}-\mathbf{g})\rangle \sum_f S_{f0}(1)S^*_{f+g,0}(1)$$

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* The equivalence of these two functions, $R(\mathbf{q},0)$ and $R_{(j=j')}(\mathbf{q},\mathbf{r})$ depends upon $\mathbf{r}_{jj'}=0$ for $j=j'$ in equation (6). This is only valid if $\mathbf{r}_j$ and $\mathbf{r}_{j'}$ refers not only to the same particle, but also to the same time; which again demands that scattering at all energy losses should be admitted by the intensity detection system and be subject to the same Bragg scattering.

$$=\sum_{h}\langle|f(\mathbf{s}+\mathbf{h})|^2\rangle+\sum_{h}\sum_{g\neq 0}\langle f(\mathbf{s}+\mathbf{h})f^*(\mathbf{s}+\mathbf{h}-\mathbf{g})\rangle\sum_{f}S_{f0}(1)S^*_{f+g,0}(1)\,. \qquad (9)$$

This result, which was referred in I, brings out clearly the difference between the *direct*, $\langle|f(\mathbf{s}+\mathbf{h})|^2\rangle$ terms and the interference terms, with $g\neq 0$. The sum of the former type of terms is seen to be independent of the Bragg scattering processes and equal to the same sum under kinematical conditions. The last sum in equation (9) represents deviation in total scattering from the kinematical result; that is, enhanced or reduced diffuse scattering. This enhancement or reduction in the diffuse scattering, summed over all interacting beams will, of course, be reflected in enhanced or reduced absorption from the discrete beams, *i.e. anomalous absorption*.

By integrating equation (9) over s, within one Brillouin zone, one now obtains the total intensity, I_t, of diffuse scattering in the pattern:

$$I_t=\int_{\mathrm{B.zone}}\sum_{h}I(\mathbf{s}+\mathbf{h})\mathrm{d}\mathbf{s}=\int I(\mathbf{s})\mathrm{d}\mathbf{s}$$

where the last integral is taken over the whole pattern. With

$$\Phi_g=\sum_{h}\int_{\mathrm{B.zone}}\langle f(\mathbf{s}+\mathbf{h})f^*(\mathbf{s}+\mathbf{h}-\mathbf{g})\rangle\mathrm{d}\mathbf{s}$$

$$=\int\langle f(\mathbf{s})f^*(\mathbf{s}-\mathbf{g})\rangle\mathrm{d}\mathbf{s} \qquad (10a)$$

and

$$F_g=\sum_{f}S_{f0}(1)S^*_{f+g,0}(1)$$

one sees from equation (9) that I_t can be written

$$I_t=\sum_{g}\Phi_gF_g=\int_{\text{unit cell}}\Phi(\mathbf{q})F(\mathbf{q})\mathrm{d}\mathbf{q} \qquad (10b)$$

where Φ_g and F_g are Fourier components of the two-dimensional periodic distributions $\Phi(\mathbf{q})$ and $F(\mathbf{q})$ referring to the level $z=z_1$. Since the wave function for the incident electron is $\Psi(z_1)=\sum S_{f0}(1)\exp\,[i(\mathbf{k}_0+\mathbf{f})\mathbf{r}]$, $F(\mathbf{q})$ will be the probability density, $\Psi\Psi^*$, of the incident electron at the level z_1. However, assuming that $\Phi(\mathbf{q})$ does not vary with z_1, we can substitute the thickness average, $(1/z)\int_0^z F(\mathbf{q})\mathrm{d}z_1$ for $F(\mathbf{q})$.

The distribution $\Phi(\mathbf{q})$ resembles $R(\mathbf{q},0)$ in the previous section. However, it is different from this function in two ways: Firstly, the integration over $\mathbf{s}$ [equation (10a)] is taken over a scattering function which includes the Coulomb denominators s^2 and $(\mathbf{s}+\mathbf{h})^2$, hence it is related to potential fluctuations, instead of charge fluctuations. Further, the integration extends only over a plane section of reciprocal space, the integral is thus related to the projected potential. Thence

$$\Phi(\mathbf{q})=\langle|V|^2\rangle-\langle V\rangle^2$$

where

$$V\equiv V(x,y,\mathbf{r}_j)=\int V(\mathbf{r},\mathbf{r}_j)\mathrm{d}z\,.$$

By the definition [equation (10a)], $\Phi(\mathbf{q})$ is the imaginary potential responsible for anomalous absorption.

It is worth noting that equation (9) may be said to corroborate the simple picture in direct space of anomalous absorption. Due to Bragg reflexion the probability density of the incident electron will not be uniform over the unit cell, but have maxima and minima, as indicated in Fig. 1(a). Since this density distribution $F(\mathbf{q})$ can be changed through changing the diffraction condition of the incident beam, $F(\mathbf{q})$ in a sense can be regarded as a probe which can be used to investigate the distribution of diffuse scattering power within the unit cell. The information about location of scattering centra implied in this picture is reflected in phase information in reciprocal space, Fig. 1(b); the enhancement or reduction of diffuse scattering can be said to result from constructive or destructive interference between diffuse scattering originating from different Bragg beams.

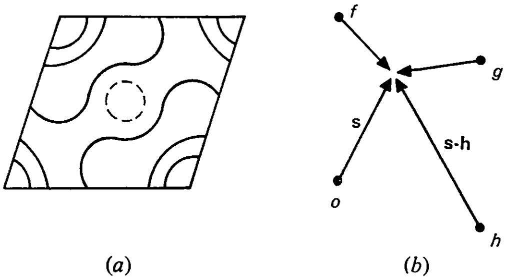


Fig. 1. Schematical description of anomalous absorption with the incident beam near a zone axis. (a) Direct space: distribution of electron probability density in a thickness average. (b) Reciprocal space: interference of diffuse scattering from several discrete beams.

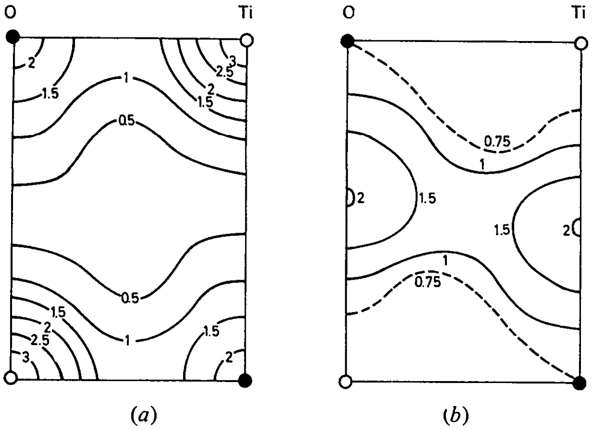


Fig. 2. Calculated electron probability density in a 110 projection of TiO. Voltage: 100 kV in all Figs. 7 beams. (a) Incident beam along zone axis. (b) 004 Bragg condition fulfilled.

Let us end this section with some remarks on anomalous absorption effects from one-electron excitations. It is well known that one-electron excitations give small contributions to anomalous absorption. This is because the outer electrons are localized to a relatively small extent and hence contribute mainly to normal absorption; whereas the inner electrons are responsible for only a small part of the diffuse scattering, so that their contribution to absorption, both normal and anomalous, is swamped by other contributions, mainly from thermal scattering. If, however, anomalous absorption effects from contributions from inner electron excitations are studied in the background scattering or in the accompanying emission of X-rays, this contribution can be separated from other sources by means of energy or wavelength selection.

An application of the present description is thus immediately suggested, that is the location of the site of dissolved atoms through the study of characteristic X-ray emission as a function of the diffraction condition for the incident electron beam.

The simple picture of anomalous absorption illustrated in Fig. 1 is particularly useful in this case, since calculation of the magnitude $\Phi(\mathbf{q})$ for K-shell electrons shows this to be a quite sharply peaked function about the atomic centre (see Appendix). As an approximation we may thus put

$$I_{\text{X-ray}} \propto \int \delta(\mathbf{q}-\mathbf{q}_i)F(\mathbf{q})\mathrm{d}\mathbf{q} \qquad (11)$$

for the contribution to X-ray emission from the site $\mathbf{q}_i$.

Calculations of relative X-ray emission probabilities as a function of diffraction conditions, for a particular distribution of the atom species under consideration, will thus essentially consist of calculations of the probability distribution $F(\mathbf{q})$ at the atomic sites involved.

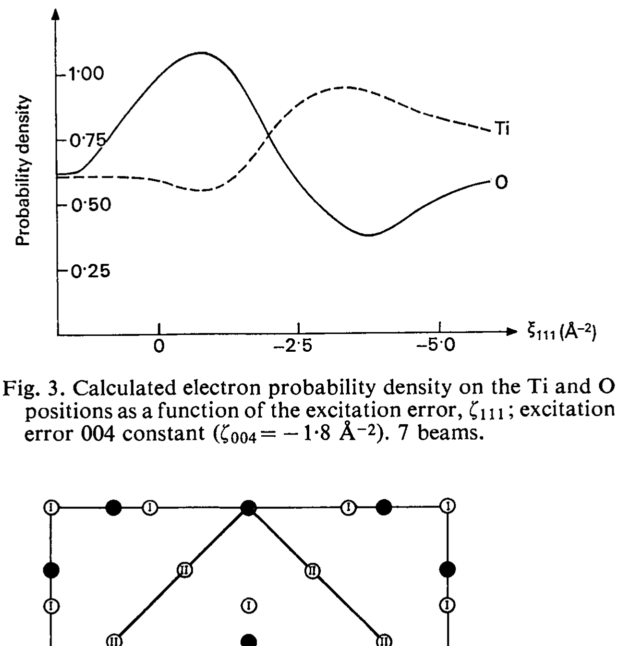


Fig. 3. Calculated electron probability density on the Ti and O positions as a function of the excitation error, ζ_{111}; excitation error 004 constant ($\zeta_{004} = -1{\cdot}8$ Å^{-2}). 7 beams.

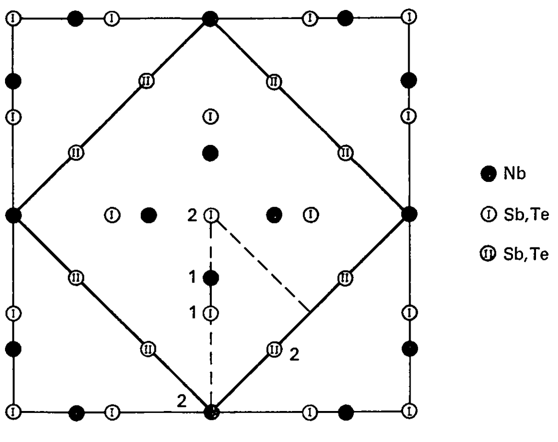


Fig. 4. 100 projection of cubic $Nb_3Sb_2Te_5$. Thin line: unit cell with lattice constant 9·816 Å; thick line: reduced cell used in the calculations; dotted line: area shown in Fig. 6. Numbers show atoms per site in the projection.

5. Calculations

In order to test the possibility of localizing fluctuations in a structure with the method suggested, we have carried out two sets of calculations of $F(\mathbf{q})$ with the incident beam close to a zone axis, (*i.e.* in a many-beam situation). The reason for this was the sharpening of $F(\mathbf{q})$ expected to arise from the presence of many beams. Such sharpening will, of course, facilitate the location of emission sites.

The first set of calculations was carried out for a NaCl type structure. Cubic TiO was chosen as an example, mainly because calculations of the distribution of disorder scattering was started for this structure.

$F(\mathbf{q})$ profiles were computed with the incident beam near a 110 zone axis, since the two types of equivalent lattice sites in TiO are separated in this projection. Examples of such distributions are shown in Fig. 2(*a*) which corresponds to an incident beam along the zone axis, and in Fig. 2(*b*) where the Bragg condition is fulfilled for the 004 reflexion. Only the distribution within $\frac{1}{8}$ of the unit cell is shown since the distribution in the rest of the cell can be obtained from this part through simple symmetry operations. Both height and position of the maxima in $F(\mathbf{q})$ are seen to be strongly dependent on the diffraction conditions. In Fig. 2(*a*) the maxima are found at the atomic sites corresponding to enhanced absorption, when the active absorption mechanisms are associated with these positions. In Fig. 2(*b*) on the other hand, there are minima at the atomic sites giving rise to anomalous transmission. Diffraction conditions for which the electron distribution $F(\mathbf{q})$ has a higher value on one or the other of the two atomic sites in the structure can also be found. In Fig. 3 the value of $F(\mathbf{q})$ at the two sites is shown as a function of the angle between the incident beam and the zone axis. The calculations show that by adjusting the diffraction conditions, it is possible to enhance scattering processes, and hence absorption and emission, associated with one or the other of the atomic positions in the structure, *e.g.* to enhance X-ray emission from one of the sites. Thus, one will expect that it is feasible to determine on which of the two lattices a foreign atom is located from the variation in X-ray emission with the direction of the incident beam. However, in a NaCl-type structure such an application of anomalous absorption effects may appear somewhat superfluous, since in this structure this would be known from general chemical considerations. As a more realistic and more complicated example on such an application, let us discuss the cubic structure $Nb_3Sb_2Te_5$. The crystal structure which has 4 formula groups per unit cell was determined by Jensen & Kjekshus (1967), and is shown in Fig. 4. They could, however, not distinguish between the atomic positions I and II occupied by Sb and Te, due to the very small difference in X-ray scattering factors. Three possible models were suggested: All Sb in I, all Sb in II, and a statistical distribution of Sb in I and II.

The aim of the calculations relating to this structure was to see whether the theoretical variation in X-ray emission probability with atomic position and diffraction condition would be large enough to allow the different models to be distinguished on basis of measurements of X-ray emission as a function of incident beam direction. Thus, $F(\mathbf{q})$ was calculated, as in the previous example, with the incident beam near the 100 zone axis using up to 145 beams. The main features in the distributions were found, however, to be well described by 69 beam calculations. This high number of beams could be handled on a moderate size computer, CDC 3300, by choosing the incident beam directions in such a way that the eigenvectors could be separated in groups with different symmetries (see *e.g.* Hirsch *et al.*, 1965). In the 100 projection a smaller unit cell was chosen (thick line in Fig. 4), and all *hkl* given refer to this cell. Only $\frac{1}{8}$ (dotted line in Fig. 4) of it is discussed below; due to symmetry in $F(\mathbf{q})$ the distribution in the rest of the unit cell is obtained from this part through symmetry operations. In Fig. 5(*a*) and (*b*) is shown computed $F(\mathbf{q})$ distributions when the incident beam is along the zone axis or satisfying the Bragg condition for 440, respectively. This figure is seen to be analogous to Fig. 3, the first case giving enhanced absorption and the second case anomalous transmission. It should be pointed out, however, that the change in peak height is different at the different atomic sites. The variation in $F(\mathbf{q})$ at these positions as a functionof tilt is shown in Fig. 6(*a*). An average value per atomic site is given, since equivalent positions in the three-dimensional structure are not equivalent in the projection. Fig. 6(*b*) shows the variation in X-ray emission probability from Sb with beam tilt for the three models suggested. From this Figure it is seen that on going from incident beam along the zone axis to 220 Bragg condition satisfied, the X-ray emission from Sb is changed by the factors 3·1, 0·8, 1·4 for all Sb in I, all Sb in II, and a statistical distribution of Sb in I and II, respectively. It thus appears possible to distinguish between these three models with the method suggested.

6. Conclusions

The aim of a theoretical description of diffuse scattering in the presence of Bragg scattering may be said to be twofold. On one hand one wants a theory for the various diffraction effects in the background scattering, *e.g.* Kikuchi lines, where the focus of interest frequently lies more with the Bragg scattering than in the non-periodic part of the structure. The second aim is to attain a theoretical basis for comparison of observed patterns of diffuse scattering with physical models for the non-periodic parts of the structure. This aim is pursued in the present paper through the study of the scattering function $I(\mathbf{s},\mathbf{h}) \equiv \langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h})\rangle$ in which all first order contributions from the non-periodic part of the potential are included. It is shown that this function, which actually appeared already in Kainuma's (1955) paper on Kikuchi lines as 'structure factor for the Kikuchi line', can be related to a function $R(\mathbf{q},\mathbf{r})$ of six variables in direct space. The function R may properly be called 'distribution-correlation function', since the dependence on the vector $\mathbf{q}$ reflects the distribution over the average unit cell of the spatial fluctuations

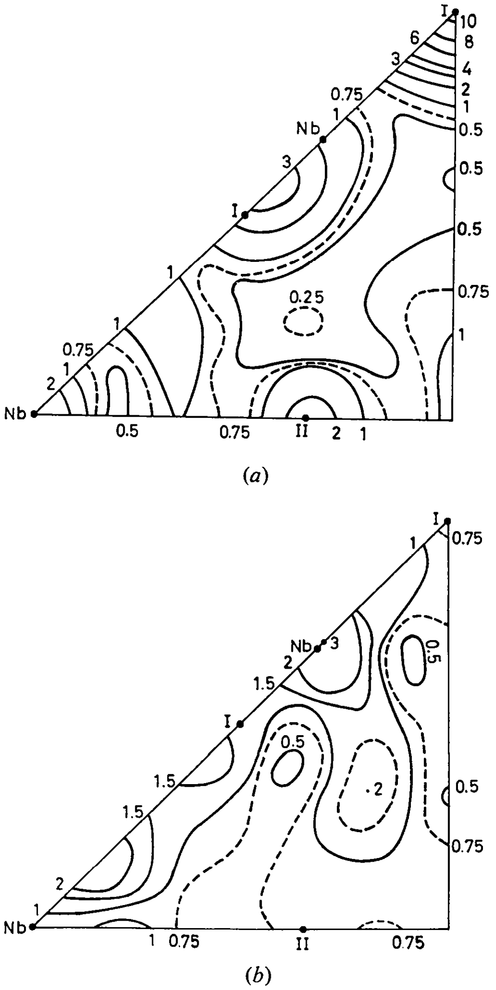
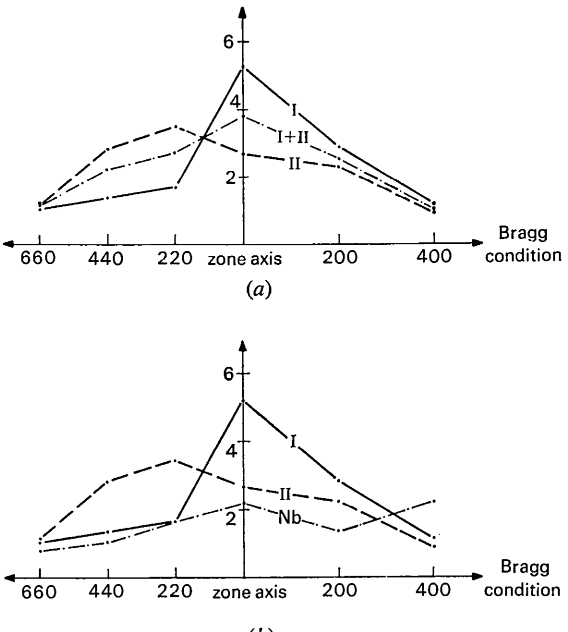


Fig. 5. Calculated electron probability density for $Nb_3Sb_2Te_5$ shown for the area corresponding to the dotted triangle in Fig. 5. I and II are the Sb and Te positions. 69 beams. (*a*) Incident beam along zone axis. (*b*) 440 Bragg condition fulfilled.

responsible for diffuse scattering, whereas the **r**-dependence is related to correlations as in the Patterson or correlation function, $P(\mathbf{r}) \equiv \int R(\mathbf{q},\mathbf{r})d\mathbf{q}$.

The idea that dynamical Bragg scattering may enhance or reduce diffuse scattering from different parts of the unit cell and hence provide information about the positions of sources of diffuse scattering is not new; it may be said to be inherent in the well known description in direct space of the Bormann effect in terms of different probability density distributions across the lattice planes for the various wavefields. The effect of substitutional and interstitial atoms on the anomalous absorption in the two beam case has been studied by Hall, Hirsch & Booker (1966). A similar concept is contained in the classical particle description for the so-called string effect for charged particles (Linhard, 1965). It is doubtful, however, whether Linhard's theory will be successful in complicated cases like the ones treated above (for a discussion see *e.g.* Howie, 1966).

The present theory can be said to corroborate this direct space description from a diffraction viewpoint. In particular, the introduction of the function $R(\mathbf{q},\mathbf{r})$ leads to an interpretation of the imaginary potential – which originally was introduced in a phenomenological way – in terms of potential fluctuations. However, the present theory goes beyond that for anomalous absorption since the absorption contributions from the various points, **s**, in reciprocal space can be analysed in terms of correlations as well as distribution of the fluctuations.



(*a*)

(*b*)

Fig. 6. (*a*) Average value of calculated electron probability density for the incident electron at the sites Nb, I and II shown for different diffraction conditions. (*b*) Relative emission probability of characteristic X-rays from Sb according to the three models: all Sb in I, all Sb in II, Sb statistically distributed I and II. Right-hand side of both figures: incident beam in the 100 plane: left-hand side: incident beam in $\bar{1}10$ plane.

The present theory is restricted to the first order in the non-periodic potential. This limits the application to thin crystals when strong diffuse scattering, *e.g.* from plasmons, is considered. For weaker diffuse scattering this limitation may not be so serious, especially if anomalous absorption is included in the Bragg scattering matrix elements. It ought to be mentioned, however, that even if the validity of the present treatment in this way can be extended, the effects may be gradually washed out in a thicker crystal, as was found by Hall (1966) in his study of X-ray emission in the two beam case. The neglect of thickness oscillations stems from practical considerations, it is hard to see much gain in including such effects at the present stage.

The application of the present theory is simplest in anomalous absorption type experiments, where $\int I(\mathbf{s},\mathbf{h})d\mathbf{s}$ is studied, when for example the anomalous absorption is measured in the emission of secondary radiation. From the theoretical examples studied, it appears that the location of atom positions by means of the variation of emitted X-ray intensity with diffraction condition for the incident electron beam, will be feasible. The inelastic scattering from core electrons may be studied in much the same way, the correlation and hence the angular distribution is here relatively unimportant.

The treatment of anomalous effects in disorder and thermal scattering, according to the present theory is certainly more complicated, but appears to hold out interesting prospects. Here the interesting feature with this representation lies with the possibility of associating correlations with positions in the unit cell. These possibilities of *e.g.* identifying short range order at a particular lattice site or identifying the atoms taking part in a particular lattice vibration, will have to be examined in more detail, however.

APPENDIX

The width of the function ϕ_K (q), § 4

It may be felt sufficient merely to state that the probability density for the 1*s* electron in a medium or heavy atom is so narrow that any distribution associated with the *K*-shell will also be narrow. Let us indicate some calculations pertaining to this question, however.

The Fourier coefficient, or form factor, for Φ_K is

$$F_{1s}(h) = \int \left\{ \left\langle \frac{\exp[i\mathbf{s}\mathbf{r}_j]\exp[i(\mathbf{h}-\mathbf{s})\mathbf{r}_j]}{s^2(\mathbf{h}-\mathbf{s})^2} \right\rangle - \frac{\langle \exp[i\mathbf{s}\mathbf{r}_j]\rangle \langle \exp[i(\mathbf{h}-\mathbf{s})\mathbf{r}_j]\rangle}{s^2(\mathbf{h}-\mathbf{s})^2} \right\} d\mathbf{s} \quad (\text{A}\,1)$$

where $\langle \exp[i\mathbf{s}\mathbf{r}_j]\rangle = f_{1s}(s)$ is the form factor for the 1*s* electron, see *e.g.* Freeman (1959), and the integration is carried out in a section through the origin of reciprocal space. It is convenient to rewrite equation (A 1)

$$F_{1s}(h)=\int\frac{1-f(s)-f(|\mathbf{s}-\mathbf{h})+f(h)}{s^2(\mathbf{s}-\mathbf{h})^2}\,\mathrm{d}\mathbf{s}$$

$$\int\frac{1-f(s)}{s^2}\times\frac{1-f(|\mathbf{s}-\mathbf{h}|)}{(\mathbf{s}-\mathbf{h})^2}\,\mathrm{d}\mathbf{s}\,.$$

The integration can be performed analytically when $f(s)$ is written as a sum of terms of the type $\alpha^2/(\alpha^2+s^2)$. Since we are interested only in an estimate of the width, one such term may be sufficient, α is determined by fitting this to the inner part of the $1s$ form factor; then $\alpha=\sqrt{2}Z/a_H$ where Z is the atomic number, a_H the Bohr radius and a hydrogen type function is used for the $1s$ electron. Then

$$F_{1s}(h)\simeq 2\pi\left\{ln\left(\frac{h^2+\alpha^2}{\alpha h}\right)/(\alpha^2+h^2)\right.$$
$$\left.-\ \mathrm{arc\ tanh}\ (1+\ 4\alpha^2/h^2)^{1/2}/h(h^2+4\alpha^2)^{1/2}\right\}$$

We are here dealing with a single atom; hence, $\Phi_K(\mathbf{q})$ is obtained by a Fourier integral in the plane. Due to the symmetry this leads to a Hankel transform, $\Phi_K(\mathbf{q})=\int F_{1s}(h)J_0(qh)\mathrm{d}h$.

Since α is quite large (150 Å^{-1}), the main contribution apart from very small values of r will come from the region $h\ll\alpha$. Here we have found that $F_{1s}(h)$ is reasonably well represented by $(4\pi/\alpha^2)K_0(2e^{1/4}h/\gamma\alpha)$, so that the Hankel transform leads to

$$\Phi_k(q)\propto(q^2+4e^{1/2}/\gamma^2\alpha^2)^{-1}$$

[see *e.g.* Bateman (1954)] which has a width somewhat less than 0·02 Å for $Z\sim 50$.

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