

The Influence of Bragg Scattering on Inelastic and other Forms of Diffuse Scattering of Electrons

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A method for treatment of the interaction between diffuse and Bragg scattering is developed. The treatment is based on the integral equation for scattering and follows a multiple-scattering approach; representation of the various terms by diagrams is found useful. General expressions for scattered intensity which take diffuse scattering into account in the first order, and include scattering of the incident beam and Bragg interactions between diffuse scattered beams to all orders, are derived. The two-beam case is discussed and a special three-beam case is compared with experiment. Extension to higher-order terms in the diffuse scattering is discussed.

It is shown that the total intensity of diffuse scattering will be either enhanced or reduced when Bragg reflexions are excited by the incident beam. This is due to interference between diffuse scattering amplitudes at corresponding points in different Brillouin zones; effects of this in disorder scattering are discussed. The relationship between this effect and anomalous absorption is pointed out with special reference to inelastic scattering.

1. Introduction

The distribution of diffuse scattering in electron diffraction experiments can be profoundly affected by Bragg scattering; the most well known effects are Kikuchi lines, and the clouds of inelastic scattering which are found around the Bragg spots as well as around the central spot. In the latter case it has been shown by Kamiya & Uyeda (1961) that the diffuse scattering has a definite phase relationship to the nearest Bragg reflexion and can be used to form an image. Recently Dr Watanabe in this laboratory has obtained more complicated patterns of diffuse scattering in cases where several Bragg reflexions are excited by the incident beam. Also, the study of diffuse scattering, especially due to disorder and thermal motion, is receiving increasing attention.

The theory of interaction between diffuse and Bragg scattering (Takagi, 1958; Kainuma, 1955; Fujimoto & Kainuma, 1963; Fukuhara, 1963) has, to a large extent, been developed on basis of the reciprocity theorem (v. Laue, 1948). The recent development of dynamic theories in electron diffraction based on a 'slice' approach (see *e.g.* Cowley & Moodie, 1957 or Kato, 1963) suggests, however, that a reformulation of the general theory with the aim of bringing it into the same framework may be desirable.

The purpose of the present work is to develop a general theory for the modification of the diffuse scattering on such a basis and with the specific aim of explaining the detailed distribution of diffuse intensity when Bragg reflexions are excited by the incident beam.

Effects involving interference between diffuse scattering amplitudes in different Brillouin zones are specifically discussed.

2. General theory

In this section we shall develop a slice formulation of the theory of diffuse scattering in crystals, at first through a direct and somewhat intuitive approach and thence demonstrate the validity of this from the integral equation for scattering. Following the approach in a previous paper (1962) we shall include thermal and inelastic scattering by introducing the Coulomb interaction, $U(\mathbf{r}, \mathbf{r}_j)$, between the incident electron, \mathbf{r} , and the particles, \mathbf{r}_j , of the object in the Schrödinger equation for the scattered electron:

$$\{\nabla^2 + k^2 + U(\mathbf{r}, \mathbf{r}_j)\}\psi(\mathbf{r}, \mathbf{r}_j) = 0, \quad (1a)$$

or in the corresponding integral equation

$$\psi(\mathbf{r}, \mathbf{r}_j) = \psi^o(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}') U(\mathbf{r}', \mathbf{r}_j) \psi(\mathbf{r}', \mathbf{r}_j) d\mathbf{r}'$$

$$G(\mathbf{r}, \mathbf{r}') = (2\pi)^{-3} \int \exp[i\mathbf{\kappa}(\mathbf{r} - \mathbf{r}')] (\kappa^2 - k^2)^{-1} d\mathbf{\kappa}. \quad (1b)$$

From the resulting wave function, $\psi(\mathbf{r}, \mathbf{r}_j)$, for the scattered electron the amplitude of elastic scattering and intensity of the total scattering is obtained in analogy with the expressions for elastic and inelastic ('incoherent') form factors of atoms:

$$\psi(\mathbf{r})_{\text{elastic}} = \langle \psi(\mathbf{r}, \mathbf{r}_j) \rangle, \quad \psi \psi_{\text{total}}^* = \langle |\psi(\mathbf{r}, \mathbf{r}_j)|^2 \rangle \quad (2)$$

where the averages are to be taken as ground state expectation values or thermal averages for inelastic and thermal scattering respectively. The validity of this approach, where the crystal variables, \mathbf{r}_j , are essentially treated as parameters will be discussed at the end of this section.

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Let us first define a z direction close to the direction of the incident beam and to the entrance and exit surfaces; we shall neglect back scattering and envisage the wavefield as propagating through slices normal to the z direction, as in the formulation of Cowley & Moodie (1957) and several later authors (see Kato, 1963). The wavefield is expressed as a sum of Bragg scattering terms and in addition a continuous range of diffuse scattering terms:

$$\psi(\mathbf{r}) = \sum \psi_h(z) \exp [i(\mathbf{k}_0 + \mathbf{h})\mathbf{r}] + \int \psi(\mathbf{s}, z) \exp [i(\mathbf{k}_0 + \mathbf{s})\mathbf{r}] d\mathbf{s}. \quad (3)$$

These two types of term arise initially from two parts of the scattering potential, *viz.*, a periodic part, U_0 and a non-periodic part, U_d , respectively:

$$U(\mathbf{r}) = U_0(\mathbf{r}) + U_d(\mathbf{r}) = \sum V_h \exp [i\mathbf{h}\mathbf{r}] + \int v(\mathbf{s}, z) \exp [i\mathbf{s}\mathbf{r}] d\mathbf{s}, \quad (4)$$

$$v(\mathbf{s}, z) = \int f(\mathbf{s}, \zeta) \exp [i\zeta z] d\zeta,$$

where the vectors \mathbf{g} and \mathbf{s} in direct and reciprocal space are normal to the z axis. U_d and $v(\mathbf{s}, z)$ – and hence $\psi(\mathbf{s}, z)$, and in higher orders also ψ_h – will usually describe thermal or electronic fluctuations and contain the crystal variables, \mathbf{r}_j , according to (1). These may be suppressed at this stage, however, as they need only be

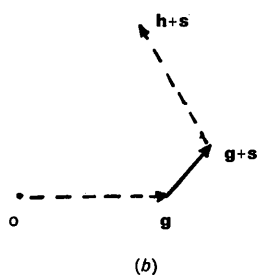
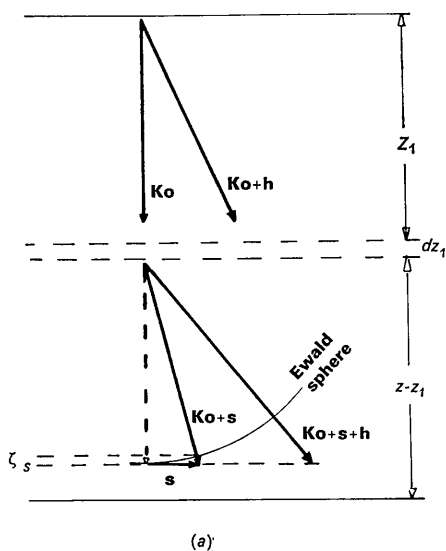


Fig. 1. (a) Diffuse scattering from the slice dz_1 , wave vectors for Bragg and diffuse scattering. (b) Diagrams representing a term in equation (5b). Full-line arrow represents diffuse, broken arrows Bragg scattering.

introduced in the final stage of the calculation as indicated in equation (2).

An expression for the amplitude of diffuse scattering correct to the first order in U_d and including Bragg scattering to all orders can now be formulated. Referring to Fig. 1(a), let us find the contribution to the amplitude of diffuse scattering from the Fourier component $v(\mathbf{s}, z)$ of U_d within the slice $(z_1, dz_1 + z_1)$. The wavefield incident on this slice is given by the first sum in equation (3); we note that the amplitudes, ψ_h , equal the elements $S_{h0}(\mathbf{k}_0, z)$ of the scattering matrix (Fujimoto, 1959; Niehrs, 1959) corresponding to the direction \mathbf{k}_0 of the incident wave and the crystal thickness z_1 . Each of the waves, h , will be scattered by the s component of U_d within the slice and a set of waves

$$(i/2k)v(\mathbf{s}, z_1)S_{h0}(\mathbf{k}_0, z_1) \exp [i(\mathbf{k}_0 + \mathbf{h} + \mathbf{s})\mathbf{r}] dz_1 \quad (5a)$$

results. During the subsequent passage of these waves through the remaining part of the crystal, Bragg scattering will take place between them. The effect of this is described in the matrix formulation as a matrix product between the column vector corresponding to the waves (5a) and the matrix describing Bragg scattering in the slab z_1 to z (final thickness) with the incident wave vector $\mathbf{k}_0 + \mathbf{s}$. We obtain for the resulting set of waves

$$(i/2k) \sum_g S_{hg}(\mathbf{k}_0 + \mathbf{s}, z - z_1) v(\mathbf{s}, z_1) S_{g0}(\mathbf{k}_0, z_1) \times \exp [i(\mathbf{k}_0 + \mathbf{h} + \mathbf{s})\mathbf{r}] dz_1. \quad (5b)$$

The amplitude of diffuse scattering towards $\mathbf{k}_0 + \mathbf{h} + \mathbf{s}$ is now obtained by integrating (5b) over the whole thickness and adding together all contributions $\psi(\mathbf{h}' + \mathbf{s}')$ for which $\mathbf{h}' + \mathbf{s}' = \mathbf{h} + \mathbf{s}$;

$$\psi(\mathbf{h} + \mathbf{s}) = \sum_f \sum_g \int_0^z S_h(\mathbf{k}_0 + \mathbf{s}, z - z_1) S_{f+g,0}(\mathbf{k}_0, z_1) \times v(\mathbf{s} - \mathbf{g}, z_1) dz_1 (i/2k), \quad (6)$$

where \mathbf{s} now can be taken as a vector within the first Brillouin zone. Terms with $\mathbf{g} \neq 0$ may be called 'umklapp' terms. Equation (6) may be compared with the generalized form of the reciprocity theorem derived by Kainuma (1955).

Before we proceed to the intensity expression, let us demonstrate how (6) follows from the integral equation for scattering (1b), which we take in the form (A2) (Appendix I). Upon introducing the expressions (3) and (4) for the amplitude and potential in this integral equation, we obtain

$$\psi(\mathbf{h} + \mathbf{s}, z) = \sum_g (i/2k) \int_0^z \exp [i\zeta_{\mathbf{g}+\mathbf{h}}(z - z_1)] \{ v(\mathbf{s} - \mathbf{g}, z_1) \psi_{\mathbf{h}+\mathbf{g}}(z_1) + \sum_f V_{hf} \psi(\mathbf{s} + \mathbf{f}, z_1) \} dz_1$$

+ higher orders in U_d .

Substitution of $\psi(\mathbf{h} + \mathbf{s}, z)$ from (6) in this equation leads to

$$\begin{aligned} & \int_0^z S_{hf}(z-z_1)v(\mathbf{s}-\mathbf{g}, z_1)\psi_{f+g}(z_1)dz_1 \\ &= \int_0^z \exp[i\zeta_{s+h}(z-z_1)]v(\mathbf{s}-\mathbf{g}, z_1)\psi_{h+g}(z_1)dz_1 \\ &+ (i/2k) \sum_f \int_0^z dz' \int_0^{z'} dz_1 \exp[i\zeta_{h+s}(z-z')] \\ & \quad V_{hf} S_{f,f}(z'-z_1), \end{aligned}$$

which is seen to be satisfied if

$$\begin{aligned} S_{hf}(z-z_1) &= \delta_{hf} \exp[i\zeta_{h+s}(z-z_1)] \\ &+ (i/2k) \sum_f \int_{z_1}^z \exp[i\zeta_{h+s}(z-z')] V_{hf} S_{f,f}(z'-z_1) dz' \end{aligned}$$

which is the equation for the matrix elements $S_{hf}(\mathbf{k}_0 + \mathbf{s}, z-z')$ introduced in equation (6). These elements connect the waves $\mathbf{k}_0 + \mathbf{s} + \mathbf{h}$, where \mathbf{s} is a vector normal to the z axis. We may instead want to use a scattering matrix with a direct wavevector along $\mathbf{k}_0 + \mathbf{s}$ but with length $|\mathbf{k}_0|$. The elements of such matrix will be

$$\begin{aligned} S'_{hf}(\mathbf{k}_0 + \mathbf{s}, z-z_1) \\ = S_{hf}(\mathbf{k}_0 + \mathbf{s}, z-z_1) \exp[-i\zeta_s(z-z_1)]; \quad (7) \end{aligned}$$

the corresponding wave vectors are indicated in Fig. 1(a).

The terms in the double summation in equation (6) can be represented by diagrams as shown in Fig. 1(b); the arrows correspond to the Bragg scattering parts, $0 \rightarrow \mathbf{f} + \mathbf{g}$ and $\mathbf{f} + \mathbf{s} \rightarrow \mathbf{h} + \mathbf{s}$, and to the diffuse scattering part $\mathbf{f} + \mathbf{g} \rightarrow \mathbf{s} + \mathbf{f}$ [$v(\mathbf{s}-\mathbf{g})$]. The summation corresponds to letting the two vertices \mathbf{f} and $\mathbf{g} + \mathbf{s}$ run through all Brillouin zones of the projection. Higher order terms in the diffuse scattering can be represented accordingly and hence written down readily.

Let us now turn to the intensity expression. So far we have not made use of the fact that the scattering resulting from U_a is 'diffuse'; the amplitude expression (6) is, in fact, also valid for a set of crystalline reflexions $\mathbf{h}_i + \mathbf{s}$ weakly coupled to a strongly excited set of reflexions \mathbf{h}_i .

The intensity expression resulting from (6) will, in general, include a double integral over thickness, *i.e.* over contributions from different slices, dz_1 and dz'_1 . The simplest way to introduce the diffuse nature of the scattering is to assume the diffuse scatterers to be independent over distances small compared with the z_1 variation in the Bragg scattering matrix elements. Interference between scattering from different slices can then be neglected, and we obtain the intensity as an integral over intensity contributions from the slices. We can study this assumption in more detail by expressing $v(\mathbf{s}, z_1)$ *etc.* as sums over normal coordinates, $l_r = 2\pi r/z$ and the scattering matrix elements as sums over the different branches j , of the dispersion surface. An expression similar to Fujimoto & Kainuma's (1963) results when the normal modes, r , are assumed to be independent; we get terms of the type

$$\begin{aligned} & \sum_r \iint \exp[i(\Delta z_1 - \Delta' z'_1 - l_r(z_1 - z'_1))] \\ & \quad \times |f(\mathbf{s}, l_r)|^2 dz_1 dz'_1. \quad (8) \end{aligned}$$

Δ and Δ' are here combinations of 'anpassungen'. If $\Delta = \Delta'$ the kinematical value of the diffuse intensity $|f(\mathbf{s}, \Delta)|^2$ results. If $|f(\mathbf{s}, \Delta)|^2$ is a slowly varying function of Δ , the summation over r will yield $\delta(z_1 - z'_1)$ and the intensity reduces to a sum over intensity contributions from different slices with common form factors $|f(\mathbf{s}, 0)|^2$ *etc.* or, slightly better, $|f(\mathbf{s}, \zeta_s)|^2$ - the value of the kinematic intensity at the Ewald sphere:

$$\begin{aligned} & I(\mathbf{s} + \mathbf{h})/z \\ &= (1/z)(1/2k)^2 \text{Re} \sum_g \sum_g \int_0^z \left\{ \sum_f S(2)_{hf} S(1)_{f+g, 0} \right\} \\ & \quad \times \left\{ \sum_f S^*(2)_{hf} S^*(1)_{f+g, 0} \right\} dz_1 \langle f(\mathbf{s}-\mathbf{g}) f^*(\mathbf{s}-\mathbf{g}') \rangle, \quad (9) \end{aligned}$$

where the abbreviated arguments, 1 and 2, stand for (\mathbf{k}_0, z_1) and $(\mathbf{k}_0 + \mathbf{s}, z - z_1)$ respectively. In the form factor parts, the appropriate averages over crystal variables, \mathbf{r}_j , are indicated, these correspond to the 'structure factors for the Kikuchi lines' introduced by Kainuma (1955). The terms with $g \neq g'$ will be called 'interference terms'. The calculation of the form factors $\langle f(\mathbf{s}) f^*(\mathbf{s}-\mathbf{h}) \rangle$ is discussed further in §5.

It might appear, as indicated by Fujimoto & Kainuma (1963) when discussing their intensity expressions, that the rapid variation of the inelastic scattering cross section for small \mathbf{s} , *i.e.* s of the order of the Δ 's in equation (8), would invalidate the procedure leading to equation (9). This, corresponds, however, to very small angles ($s \lesssim 10^{-1} \text{ \AA}^{-1}$ or $2\theta \lesssim 10^{-3}$ radian), so that the matrix elements $S_{hg}(z)$ and $S_{g0}(1)$ refer to virtually the same direction of the central beam. The sum in (5) will then be

$$\simeq \sum_f S_{hf}(\mathbf{k}_0, z-z_1) S_{f0}(\mathbf{k}_0, z_1) = S_{h0}(\mathbf{k}_0, z)$$

which is independent of z_1 , so that the intensity expression (9) is still valid. Similar arguments can be produced when $|f(\mathbf{s}-\mathbf{h}, \zeta)|^2$ varies rapidly for small s and ζ , as in phonon scattering; this case will not be treated here, however. Only when the 'diffuse' intensity function varies rapidly with the z component of the scattering vector *between* the spots, as for sharp streaks in or near the equator plane, do we expect (9) to break down.

It now remains to discuss the treatment of the crystal variables, \mathbf{r}_j , as parameters during the calculation of the interaction with the Bragg scattering; with the average over \mathbf{r}_j performed only in the form factor part, $f(\mathbf{s}-\mathbf{g})$ as in equation (9). Although we shall treat inelastic scattering (from electronic excitations) the development will be applicable also to scattering from thermal motion.

The total system of the crystal, \mathbf{r}_j , plus incident electron, \mathbf{r} , is described by a wavefunction Φ which can be expanded in the eigenfunctions of the crystal

$$\Phi(\mathbf{r}, \mathbf{r}_j) = \sum_n \psi_n(\mathbf{r}) \varphi_n(\mathbf{r}_j).$$

Let us define an operator $\psi = \psi(\mathbf{r}, \mathbf{r}_j)$ such that

$$\psi(\mathbf{r}, \mathbf{r}_j) |\varphi_0(\mathbf{r}_j)\rangle = |\Phi(\mathbf{r}, \mathbf{r}_j)\rangle.$$

We have

$$\psi_n(\mathbf{r}) = \int \varphi_n^*(\mathbf{r}_j) \Phi(\mathbf{r}, \mathbf{r}_j) d\tau_{r_j} = \int \varphi_n^* \psi \varphi_0 d\tau_{r_j} \equiv \langle n | \psi | 0 \rangle,$$

e.g. $\psi_0(\mathbf{r}) = \langle 0 | \psi | 0 \rangle$

and $\sum_n |\psi_n(\mathbf{r})|^2 = \langle 0 | \psi \psi^* | 0 \rangle.$

Φ is a solution of the Schrödinger equation

$$\{\nabla_r^2 + k^2 - (H_0 - E_0)2m/\hbar^2 + U(\mathbf{r}, \mathbf{r}_j)\} \Phi = 0,$$

where H_0 and E_0 are the Hamilton operator and ground state energy of the scattering system and U was introduced in equation (1). The corresponding integral equation for scattering is quite analogous to (1b); see e.g. Lippman & Schwinger (1950);

$$\Phi(\mathbf{r}, \mathbf{r}_j) = \psi^0(\mathbf{r}) \varphi_0(\mathbf{r}_j) + \int G(\mathbf{r}, \mathbf{r}', \mathbf{r}_j) U(\mathbf{r}', \mathbf{r}_j) \Phi(\mathbf{r}', \mathbf{r}_j) d\mathbf{r}', \quad (10)$$

where the Green's function now depends on \mathbf{r}_j through the operator $H_0 - E_0$ in the energy denominator:

$$G(\mathbf{r}, \mathbf{r}', \mathbf{r}_j) = (2\pi)^{-3} \int \exp[i\mathbf{k}(\mathbf{r} - \mathbf{r}')] \times (\kappa^2 - k^2 - (E_0 - H_0)2m/\hbar^2)^{-1} d\kappa.$$

Equation (10) can be rewritten as an equation for the operator ψ ,

$$\psi(\mathbf{r}, \mathbf{r}_j) = \psi^0(\mathbf{r}) + \int G(\mathbf{r}, \mathbf{r}', \mathbf{r}_j) U(\mathbf{r}', \mathbf{r}_j) \psi(\mathbf{r}', \mathbf{r}_j) d\mathbf{r}', \quad (11)$$

which is equivalent to equation (1b) if the operator $(E_0 - H_0)$ can be neglected in the Green's function. In order to find the criteria for this, we may bring the integral equation (11) on the form (A2) (Appendix I). By proceeding exactly as in Appendix I, noting that H_0 commutes with \mathbf{r} , we find that the only change to be made in the formulae (A1) and (A2) is the introduction of an excitation energy *operator*, through the substitution.

$$\zeta_s \rightarrow \zeta_s - (H_0 - E_0)(2m/\hbar^2)/2\kappa \equiv \zeta_s - \zeta(H_0).$$

To estimate the order of magnitude to be expected, we may use an excitation $0 \rightarrow n$ with energy 20 eV as an example; this corresponds to

$$\langle n | \zeta(H_0) | n \rangle \sim 2 \cdot 10^{-2} \text{ \AA}^{-1}.$$

The effect of the addition $\zeta(H_0)$, to the excitation error will be to substitute the value of the kinematical intensity at $[\mathbf{s}, \zeta(H_0)]$ for its value at $(\mathbf{s}, 0)$; cf. the remark following equation (8). This will only lead to significant change in the form factor when \mathbf{s} is of the same order of magnitude as $\zeta(H_0)$, i.e. for very small angles*.

The above development may also be carried out by taking $U(\mathbf{r}, \mathbf{r}_j)$ as a time dependent operator, $\exp(-iH_0 t/\hbar) U(\mathbf{r}, \mathbf{r}_j) \exp(iH_0 t/\hbar)$, in the time dependent wave equation. This may be used to extend the formalism given by van Hove (1954) for purely kinematical scattering to include interaction with the Bragg scattering.

* Calculations of the kinematic inelastic scattering at very small angles were presented at the I.U.Cr. Congress in Rome (Gjønnnes, 1963).

Our equations for the amplitude (6) and intensity (9) can be brought into the forms given by previous authors by expansion of U_a or f in eigenfunctions for the Bragg scattering. The advantage of our presentation appears to lie in a more simple description in terms of successive forward scattering processes. This picture lends itself very readily to representation by diagrams, of which examples are given in the following section. Also, a more complete separation in the Bragg scattering calculations, and an essentially kinematic calculation of diffuse scattering form factors has been achieved.

We may remark here that the sum over the $|f(\mathbf{s})|^2$ terms, which are the most important ones for inelastic scattering, in the integrand of equation (9) equals the intensity expression for diffraction from a bi-crystal with a tilt boundary of angle $s/2k$ at the level z_1 . Higher order terms in U_a can be described in a similar analogy through several tilt boundaries at z_1, z_2 etc., so that the expressions for intensity contributions from higher orders upon integration over z_1, z_2 become similar to the intensity expression for a mosaic crystal with a 'mosaic spread' given by $\langle |f(\mathbf{s})|^2 \rangle$. Hence we expect these contributions around the Bragg reflexions to be proportional to the kinematical value for the integrand intensity, from which we can explain Kuwabara's (1963) measurements of the contributions to the integrated intensities of powder lines from electrons which had suffered energy losses. With increasing energy loss, the intensity contributions to different lines became proportional to the kinematical intensities, as would be expected from the above picture if the higher energy losses are assumed to arise mainly through multiple scattering (Marton, Simpson, Fowler & Swanson, 1962).

3. The two-beam case

To gain information on the pattern of diffuse scattering, let us now consider the general two beam case, i.e. when one Bragg reflexion, h , is excited by the incident beam and there is Bragg interaction between the diffuse scattering towards $\mathbf{k}_0 + \mathbf{s}$ and $\mathbf{k}_0 + \mathbf{s} + \mathbf{h}$. Several aspects of this case have been studied before, notably the Kikuchi line case (Kainuma, 1955) and the electron microscope contrast from regions close to the diffraction spots (Fukuhara, 1963; Fujimoto & Kainuma, 1963), and we shall here confine ourselves to a general discussion, mainly of the intensity distribution $I(\mathbf{s})$, near the central spot.

From equation (6)

$$\begin{aligned} \psi(\mathbf{s}, z) = & \int_0^z \{ (S(2)_{00} S(1)_{00} + S(2)_{0h} S(1)_{h0}) f(\mathbf{s}) \\ & + S(2)_{00} S(1)_{h0} f(\mathbf{s} - \mathbf{h}) + S(2)_{0h} S(1)_{00} f(\mathbf{s} + \mathbf{h}) \} dz_1 \\ \equiv & (A + B) f(\mathbf{s}) + C f(\mathbf{s} - \mathbf{h}) + D f(\mathbf{s} + \mathbf{h}). \quad (12) \end{aligned}$$

These four terms can be represented by the diagrams of Fig. 2. A and D are the terms left when Bragg scattering of the incident beam is neglected, as in the usual treatment of Kikuchi lines; the resulting intensity con-

tributions $|A|^2$, $|D|^2$ and $\text{Re}(AD^*)$ represent a white line, a dark line and an asymmetric band respectively. When s is small; *i.e.* near the diffraction spots, the terms involving $f(s)$ will be the most important in inelastic scattering, whereas the last two terms, C and D , will dominate the thermal scattering. In disorder scattering all four terms will be important. The inelastic scattering is usually by far the strongest; the $|A+B|^2$ term and the corresponding dark field term will then determine the intensity distribution and electron microscope contrast from diffuse scattering close to the spots. The calculation of the amplitudes A , B , *etc.* is straightforward; the main steps are indicated in Appendix II. The resulting intensity terms $|A+B|^2$, $2\text{Re}[(A+B)C^*]$ *etc.* can each be divided into a thickness independent term plus four terms which oscillate with thickness and with the direction of scattering. As only some of the resulting 30 intensity terms have been given before (Fujimoto & Kainuma), a full list is given in Table 1 with the corresponding scattering factors $\langle |f(s)|^2 \rangle$, $\langle f(s)f^*(s-h) \rangle$, *etc.* indicated in the first column and the thickness dependent factors given in the top row. The excitation errors ζ_1 and ζ_2 describe the directions of the incident and the scattered beam in the usual way, $4A_1^2 = \zeta_1^2 + 4V_h^2$, $4A_2^2 = \zeta_1\zeta_2 + 4V_h^2$.

For thick crystals, the thickness independent terms will determine the intensity distribution. In the limit $\zeta_1 \rightarrow \infty$, these tend to the well known expressions for the Kikuchi-line profile. It is seen, that also in the general case considered here, the line profile will be of the form given by Kainuma (1954); *viz.* $a + b/\Delta_2^2 + c\zeta_2/\Delta_2^2$, that is a constant, plus a symmetric, plus an asymmetric term. The magnitude of these contributions depends now, however, on the direction of the incident beam, *i.e.* on ζ_1 . In particular it is seen that an asymmetric part is contained also in the $\langle |f(s)|^2 \rangle$ -term, whereas in the standard Kikuchi-line expression the asymmetric part arises only through the interference term $\langle f(s)f^*(s+h) \rangle$. When the incident beam

satisfies the Bragg condition ($\zeta_1=0$) the Kikuchi-line vanishes – only the constant term is left.

Of the thickness dependent parts, the third column (upper sign) will be of the greater importance for moderately thick crystals, as the denominator here can be zero, for $\zeta_2 = \zeta_1$. Hence this term is expected to be responsible for the oscillations in diffuse intensity as a function of angle, *e.g.* the fine structure in the Kikuchi-lines observed by Uyeda, Fukano & Ichinokawa (1954) and also to include the main contribution to the microscope contrast from diffuse scattering. When $\zeta_1 \rightarrow \infty$ these terms vanish; the only oscillating parts are then those containing $\sin(2A_2)/2A_2z$, which for thin crystals may lead to the very weak fine structure of the Kikuchi line discussed by Fujimoto & Kainuma (1963).

Fig. 3 indicates the intensity distribution across a Kikuchi-line pair for four values of ζ_1 . The intensity oscillations are seen to be centered around $\zeta_2 = \zeta_1$, *i.e.* lines through the central and the diffracted spot. It is also seen that the asymmetric parts tend to increase the intensity between these lines when $\zeta_1 < 0$ (the diffraction spot outside the Laue circle) and to reduce the intensity in this region when $\zeta_1 > 0$.

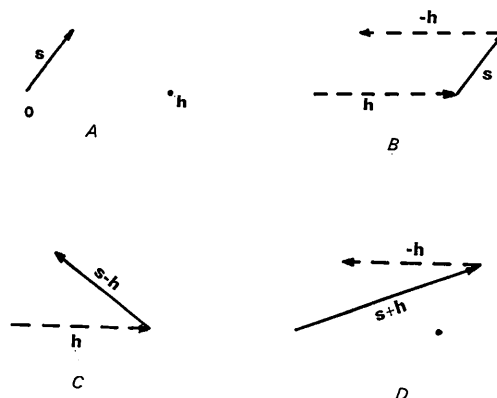


Fig. 2. Diagrams representing the four terms of equation (12).

Table 1. Coefficients for the different form factors and oscillating parts in the two-beam cases

		Thickness-dependent parts			
Form factor	1	$\frac{\sin(\Delta_1 \mp \Delta_2)z}{(\Delta_1 \mp \Delta_2)z}$	$\cos(\Delta_1 \pm \Delta_2)z$	$\frac{\sin 2\Delta_2 z}{2\Delta_2 z}$	$\frac{\sin 2\Delta_1 z}{2\Delta_1 z}$
$ f(s) ^2$	$\frac{1}{2} + \frac{\zeta_1 \zeta_2 \Delta^2}{8\Delta_1^2 \Delta_2^2}$	$\frac{v^2 \Delta^2 \pm \Delta_1 \Delta_2}{4\Delta_1^2 \Delta_2^2}$		$\frac{v^2 \zeta_1 (\zeta_1 - \zeta_2)}{8\Delta_1^2 \Delta_2^2}$	$\frac{v^2 \zeta_2 (\zeta_2 - \zeta_1)}{8\Delta_1^2 \Delta_2^2}$
$ f(s-h) ^2$	$\frac{v^2(2v^2 + \zeta_2^2)}{8\Delta_1^2 \Delta_2^2}$	$\frac{-v^4}{8\Delta_1^2 \Delta_2^2}$		$\frac{-v^2(2v^2 + \zeta_2^2)}{8\Delta_1^2 \Delta_2^2}$	$\frac{v^4}{4\Delta_1^2 \Delta_2^2}$
$ f(s+h) ^2$		As for $ f(s-h) ^2$ but with interchange of subscripts			
$f(s)f^*(s-h)$	$\frac{v(\Delta^2 \zeta_2 + \Delta_2^2 \zeta_1)}{2\Delta_1^2 \Delta_2^2}$	$\frac{v^3(\zeta_2 - \zeta_1)}{4\Delta_1^2 \Delta_2^2}$		$\frac{v^3(\zeta_1 - \zeta_2)}{2\Delta_1^2 \Delta_2^2}$	$\frac{v(\Delta^2 \zeta_2 + \Delta_2^2 \zeta_1)}{2\Delta_1^2 \Delta_2^2}$
$f(s)f^*(s+h)$		As for $f(s)f^*(s-h)$ but with interchange of subscripts			
$f(s-h)f^*(s+h)$	$\frac{v^2 \zeta_1 \zeta_2}{4\Delta_1^2 \Delta_2^2}$	$\frac{v^2(\zeta_1 \zeta_2 \mp 4\Delta_1 \Delta_2)}{8\Delta_1^2 \Delta_2^2}$		$\frac{-v^2 \zeta_1 \zeta_2}{2\Delta_1^2 \Delta_2^2}$	$\frac{-v^2 \zeta_1 \zeta_2}{2\Delta_1^2 \Delta_2^2}$

The intensity distribution, $I(\mathbf{s}+\mathbf{h})$, around the Bragg spot (the dark field) can be obtained in the same way. The $\langle |f(\mathbf{s})|^2 \rangle$ part is complementary to the corresponding bright field term. This is not the case for the $\langle |f(\mathbf{s}+\mathbf{h})|^2 \rangle$ -terms, as these scattering factors also lead to diffuse scattering toward $\mathbf{s}+2\mathbf{h}$ and $\mathbf{s}-\mathbf{h}$. Neither

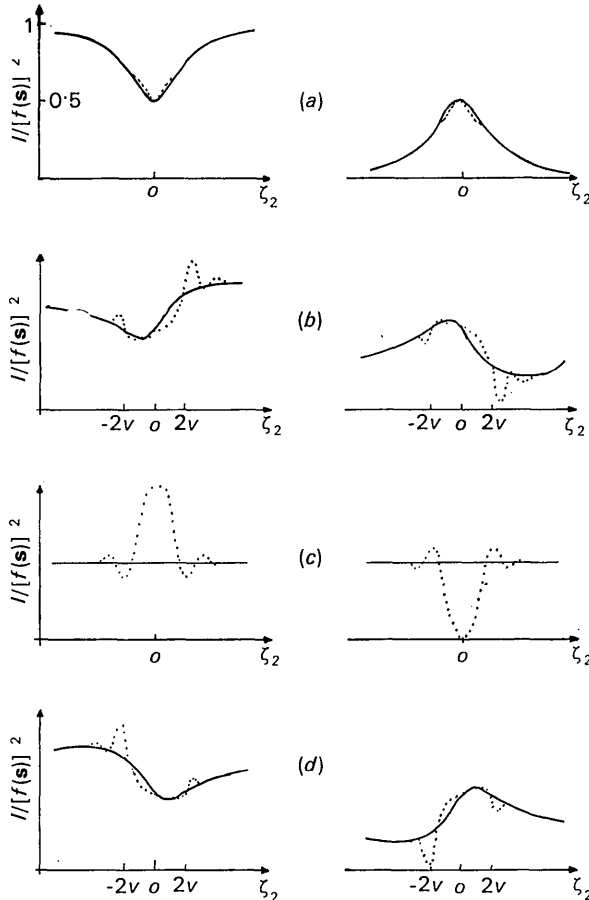


Fig. 3. The $\langle |f(\mathbf{s})|^2 \rangle$ -contributions to the diffuse intensity in the two-beam cases. Intensity profiles, excluding the form factor, as a function of ζ_2 , for different values of ζ_1 : (a) $\zeta_1 = \infty$, (b) $\zeta_1 = 2v$, (c) $\zeta_1 = 0$, (d) $\zeta_1 = -2v$. Full-line: thickness independent part; broken line: including oscillating term for $z = 2\pi/v$. Right hand side, excess; left hand side deficient part.

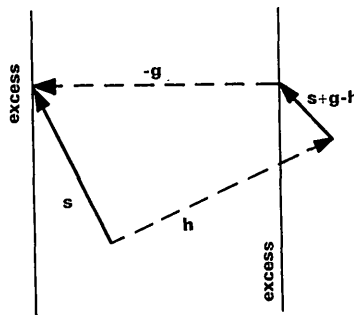


Fig. 4. Diagrams representing two amplitude terms for a Kikuchi-line pair, g , when the reflexion \mathbf{h} is excited by the incident beam.

are the interference terms complementary; this is discussed in more detail in § 5.

To conclude this section, let us mention the case indicated in Fig. 4; here a Kikuchi-line pair g is considered when the reflexion h is excited by the incident beam. There will, as in the case above, be four amplitude terms, of which two, $S(2)_{00}S(1)_{00}f(\mathbf{s})$ and $S(2)_{0g}S(1)_{h0}f(\mathbf{s}-\mathbf{g}+\mathbf{h})$, are shown in the figure. If we neglect the interference terms, the line profile will consist of a white line and a dark line term with the same width as in standard Kikuchi-line expressions. The relative magnitude of these parts will depend on the form factors, and vary along the line pair; the regions where the dark line term dominates are indicated in the figure. Such reversal of contrast along a Kikuchi line has been observed in this laboratory (Watanabe & Gjønnes, 1965).

4. Intensity distribution in a three-beam case

Although the two beam case reveals most of the essential features of the interaction between diffuse and Bragg scattering, in actual cases it is often necessary to take more beams into account. In this section we outline a calculation of the inelastic scattering from magnesium oxide between the 200 and $\bar{2}00$ reflexions when the incident beam is parallel to the (200) planes.

The amplitude contributions according to equation (6) can be written in matrix form:

$$\begin{pmatrix} S(2)_{00} & S(2)_{0h} & S(2)_{0\bar{h}} \\ S(2)_{h0} & S(2)_{hh} & S(2)_{h\bar{h}} \\ S(2)_{\bar{h}0} & S(2)_{\bar{h}h} & S(2)_{\bar{h}\bar{h}} \end{pmatrix} \begin{pmatrix} S(1)_{00} \\ S(1)_{h0} \\ S(1)_{\bar{h}0} \end{pmatrix} f(\mathbf{s}) \quad (13)$$

+ $f(\mathbf{s} \pm \mathbf{h})$ -terms,

where we may take the matrix elements in the form $\Sigma S_{00}^{(m)} \exp [i\xi_m z]$ etc. where ξ_m is the eigenvalue ('an-passing') for the m th branch of the dispersion surface. The amplitude terms can then be represented by the coefficients of the six different oscillating parts (only two branches of the dispersion surface are excited by the incident beam in the symmetrical case),

$$\exp [i\xi_m z_1] \exp [i\eta_n (z - z_1)],$$

where η_n are the eigenvalues for the beams \mathbf{s} , $\mathbf{s}+\mathbf{h}$, $\mathbf{s}-\mathbf{h}$. In the intensity expression we then have, before the integration over z_1 , the thickness dependent factors

$$\exp [i(\xi_m - \xi_{m'})z_1] \exp [i(\eta_n - \eta_{n'}) (z - z_1)].$$

Through the integration over z_1 a denominator, $\xi_m - \xi_{m'} - \eta_n + \eta_{n'}$, results. The most important terms are those for which this denominator can be small; firstly $m=m'$, $n=n'$, which gives the constant terms. The main oscillating terms arise when $m=n$, $m'=n'$; these will produce oscillations around $\zeta_2 = \zeta_1$ (analogous to the third row in Table 1). The terms with $m=m'$, $n=n'$ give weak oscillations around the Kikuchi-line position. The denominator may be zero also at some values of $\zeta_2 \neq \zeta_1$ when two branches of the dispersion

surface are separated by a distance $\Delta_{n,n'}$ equal to the distance $\Delta_{m,m}$ between two of the points excited by the incident beam.

In this way the constant term and the most important oscillating terms were readily found, once the three-beam solutions for the eigenvalues and the corresponding elements of the scattering matrix had been obtained, by solution of the dispersion equation and fitting of boundary conditions in the usual way.

The form factors, including $\langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h}) \rangle$ were obtained from the one-electron form factors given by Freeman (1959). Anomalous absorption, based on the values found by Lehmppuhl & Molière (1962), were included in the matrix elements. The resulting intensity distribution shown in Fig. 5 corresponds to a section parallel to the line through the 200-reflexion and the central spot, at a distance $\frac{1}{2}(200)$ from this line. The experimental curve is a photometer trace along the same line on a diffraction pattern taken at 80 kV (Fig. 5).

The main discrepancy between the experimental and calculated curve lies in the magnitude of the oscillations in the central region, *i.e.* far from $\zeta_2 = \zeta_1$. Also in patterns involving other reflexions it was found that the oscillations were stronger than expected in such regions. Several reasons for this have been considered: effect of higher order terms, failure of the assumption of independent normal modes, and the effect of a non-uniform distribution of diffuse scatterers. The latter effect has been suggested by Heidenreich (1963) who invokes plasmon scattering in an 'advance excitation zone' in order to describe the electron-microscope contrast from diffuse scattering. Although such a mechanism does not appear necessary to explain the microscope contrast when the objective aperture is close to a diffraction spot, it would be of importance for the intensity distribution and microscope contrast at some distance from the spots, as this would reduce the effect of the denominator $(\xi_m - \xi_{m'} - \eta_n + \eta_{n'})z$ arising from the integration over z_1 . In order to resolve this question, and also to investigate the effect of multiple inelastic scattering, intensity measurements with energy analysis would be desirable.

It is also seen that the inclusion of the interference or $\langle f(\mathbf{s})f^*(\mathbf{s}+\mathbf{h}) \rangle$ -term does not improve the agreement. This is somewhat difficult to assess; the justification for using one-electron form factors in this term may be doubtful; also multiple scattering effects must be expected in the background.

5. Interference terms: an example from disorder scattering

As mentioned in § 3, the bright and dark field terms are not all complementary. This was pointed out for the electron-microscope contrast in the two-beam case by Fujimoto & Kainuma (1963). A general expression for the total excess or deficient diffuse scattering can be found by summing the intensity contributions in

all Brillouin zones from one particular form factor according to equation (7) (omitting the average over z_1). We obtain for this sum

$$\begin{aligned} & \text{Re} \sum_h \sum_f \sum_f \langle f(\mathbf{s}-\mathbf{g})f^*(\mathbf{s}-\mathbf{g}') \rangle S(2)_{hf} S(1)_{f+g,0} \\ & \quad S^*(2)_{hf'} S^*(1)_{f+g',0} \\ & = \text{Re} \langle f(\mathbf{s}-\mathbf{g})f^*(\mathbf{s}-\mathbf{g}') \rangle \sum_f S(1)_{f+g,0} S^*(1)_{f+g',0} \end{aligned} \quad (14)$$

by using the unitary property of the scattering matrix. For $\mathbf{g}=\mathbf{g}'$ the last sum is unity, so that the $|f(\mathbf{s}-\mathbf{g})|^2$ -terms are complimentary when the contributions from all Brillouin zones are included. The interference terms give rise to an excess or deficient intensity, which in the two beam case becomes:

$$-2 \langle f(\mathbf{s})f^*(\mathbf{s}-\mathbf{h}) \rangle (1 - \sin(2\Delta_1 z) / 2\Delta_1 z) V_h \zeta_1 / (\zeta_1^2 + 4V_h^2)$$

when the average over z_1 has been taken. The last factor, which depends only upon the direction of the incident beam, is negative when the reflexion, h , is inside, and positive when h is outside the Laue circle and has maximum magnitude for $|\zeta_1| = 2v_h$.

When several beams are excited, as when the incident wave is along a principal direction, many of the beams may be in phase, and the last sum (14) can be appreciable. As an example, consider diffuse scattering from short range order in cubic alloys. Here the diffuse scattering amplitudes $f_{sro}(\mathbf{s}+\mathbf{h})$ have the same phase in all Brillouin zones; they vary with \mathbf{h} only through the atomic scattering factor difference $f_A - f_B$. Hence the interference form factor $\langle f(\mathbf{s}-\mathbf{g}')f(\mathbf{s}-\mathbf{g}) \rangle$ is always positive. In order to obtain an estimate of the modification to the kinematical intensities $|f_{sro}(110)|^2$ through Bragg scattering, let us include only these scattering processes which are indicated in Fig. 6(a). That is, Bragg spots beyond the four 200's, diffuse scattering amplitudes beyond 110 and Bragg interaction between the 110 and 310 spots are all disregarded. We

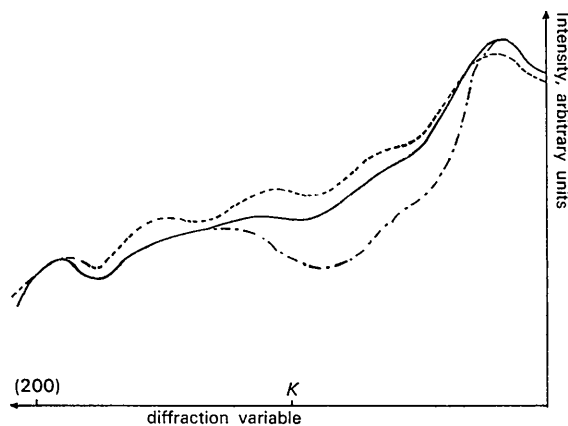


Fig. 5. Calculated and experimental intensity curves for a magnesium oxide crystal, incident beam in the (200) plane. Section parallel to (200) at a distance $\frac{1}{2}(200)$ from the central spot. Broken curve: experimental curve, primary energy 80 kV. Full-line: calculated intensity for 630 Å thickness, without interference terms. Dash-dot: calculated intensity including interference terms. K is Kikuchi-line position.

then get for the intensity at 110, remembering that $\psi_{200} = \psi_{020}$ etc. owing to symmetry:

$$[\psi_0(1) + 2\psi_{200}(1)]f_{sro}(110) \times c.c. \\ = \{1 + 4\text{Re}[\psi_0(1)\psi_{200}^*(1)]\}|f_{sro}(110)|^2$$

and similarly for the diffuse intensity at (100) [Fig. 6(b)]:

$$[\psi_0(1) + \psi_{200}(1)]f_{sro}(100) \times c.c. \\ = [1 - 3|\psi_0(1)|^2 + 2\text{Re}\psi_0(1)\psi_{200}^*(1)]|f_{sro}(100)|^2.$$

The $f_{sro}(110)$ -contribution to the intensity at 110 is seen to be above its kinematical value, when $\text{Re}\psi_0\psi_{200} > 0$, even though there are contributions also to the (310)-spots. This shows that the total diffuse intensity is considerably enhanced, mainly through interference between the terms $\psi_{200}(1)f_{sro}(110)$ and $\psi_{020}(1)f_{sro}(110)$ [Fig. 6(a)].

The $f_{sro}(100)$ contributions to the scattering are also spread out over a number of spots, and here there is not such an effective interference to build up the total intensity. If we take $|\psi_{200}(1)|^2$ to be $\frac{1}{8}$ and neglect $\psi_0\psi_{200}^*$, the dynamic correction factors to the short range order scattering become:

$$1 \text{ at } 110, \frac{5}{8} \text{ at } 100.$$

Calculations for particular alloys (AuAg, CuAu₃) including more interactions lead to results quite close to these estimates; so the 110 is expected to be appreciably stronger than the 100 diffuse peak, as is also seen in the diffraction patterns from these alloys. Fur-

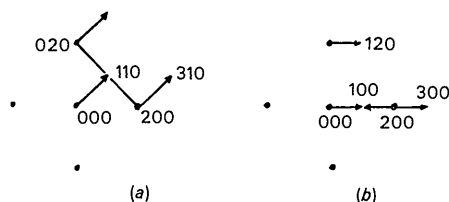


Fig. 6. Diagrams representing short range order scattering contribution to 110 (a) and 100 (b) in a face-centered alloy. Incident beam along [001]; only diffuse scattering processes are indicated.

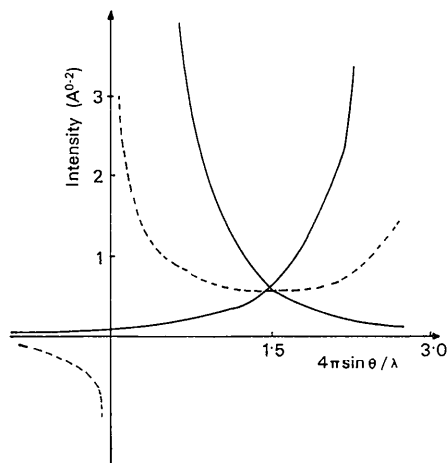


Fig. 7. The inelastic form factors $\langle |f(\mathbf{s})|^2 \rangle$ (full-line curve) and $\langle f(\mathbf{s})f^*(\mathbf{s}-\mathbf{h}) \rangle$ (broken curve) for magnesium oxide; $\mathbf{h} = 200$, \mathbf{s} parallel to (200).

ther work on dynamical corrections to short range order diffuse scattering is in progress in this laboratory (Fisher, 1965).

For thermal and inelastic scattering the phase relationships between amplitudes in different Brillouin zones is more involved. In phonon scattering the amplitudes will, to the first approximation, depend on the scalar product $\mathbf{a}(\mathbf{s}+\mathbf{h})$, where \mathbf{a} is the phonon polarization vector. For a primitive lattice:

$$f_{\mathbf{a}}(\mathbf{s}-\mathbf{h})f_{\mathbf{a}}^*(\mathbf{s}-\mathbf{g}) = \pm |f_{\mathbf{a}}(\mathbf{s}-\mathbf{h})| \cdot |f_{\mathbf{a}}(\mathbf{s}-\mathbf{g})|,$$

where the upper and lower signs should be used when the \mathbf{a} -components of $\mathbf{s}+\mathbf{h}$ and $\mathbf{s}-\mathbf{g}$ have the same or opposite directions respectively. We may note that the two terms $\psi_{200}(1)f_{\mathbf{a}}(110)$ and $\psi_{020}(1)f_{\mathbf{a}}(110)$, referring to Fig. 6(a), will always cancel.

For inelastic scattering the interference form factors $\langle f(\mathbf{s})f^*(\mathbf{s}-\mathbf{h}) \rangle$ have previously been studied in connection with the anomalous absorption, where they occur as the integrand in the calculation of the absorption coefficients C_{h0}^i (Yoshika, 1957; Gjønnes, 1962). The excess or deficient intensity calculated above corresponds, of course, to enhanced and reduced absorption respectively. The dependence on the excitation error is reflected in the two-beam case into asymmetry of the direct beam as a function of the excitation error – a well known result from the theory of anomalous absorption.

Calculations have so far been based upon one-electron wave functions for free atoms or ions; an expression in terms of Hartree-Fock functions has been given by the present author (1962):

$$\langle f(\mathbf{s})f^*(\mathbf{s}-\mathbf{h}) \rangle \\ = \frac{\sum_m f_m(\mathbf{h}) - f_m(\mathbf{s})f_m(\mathbf{h}-\mathbf{s}) - \sum_{m \neq n} f_{mn}(\mathbf{s})f_{mn}(\mathbf{h}-\mathbf{s})}{s^2(\mathbf{h}-\mathbf{s})^2},$$

where the f 's are one-electron scattering factors and the last sum is to be taken over wave functions with the same spin only. For non-primitive unit cells, a factor $\exp(i\mathbf{h}\mathbf{R}_j)$ should be included for an atom at \mathbf{R}_j . Fig. 7 shows the result of a calculation for magnesium oxide with $\mathbf{h} = 200$ based on the one-electron scattering factors given by Freeman (1959). The interference form factor is negative in a roughly circular region around $\mathbf{s} = \mathbf{h}/2$; it appears more sensitive to the wave functions and state of ionization than the $|f(\mathbf{s})|^2$.

At small values of \mathbf{s} , we must expect plasmon excitation to be important. Fukuhara (1963) has mentioned the possibility of 'Umklapp'-processes $[f(\mathbf{s}+\mathbf{h})]$ in plasmon excitation. So far no calculation has been made for such a process, which should determine the interference term in plasmon scattering, and the plasmon contribution to anomalous absorption.

6. Multiple scattering

Our theory has so far taken only single diffuse scattering into account. Extension of the theory to include

higher order scattering is straightforward, but calculations become laborious in the general case. In the simple Kikuchi-line case when Bragg scattering of the incident beam and of the intermediate diffuse scattered beam are neglected, double scattering expressions can be represented as in Fig. 8(a) which leads to the same form of the profile function as before, but with the form factors replaced by the intensity convolutions

$$\langle |f(\mathbf{s})|^2 \rangle \star \langle |f(\mathbf{s})|^2 \rangle, \quad \langle |f(\mathbf{s})|^2 \rangle \star \langle f(\mathbf{s}) f^*(\mathbf{s}-\mathbf{h}) \rangle.$$

The third-order diffuse scattering terms represented by Fig. 8(b) are included when anomalous absorption is taken into account in the matrix elements S_{h_0} , etc. This may lead to an additional asymmetry in the Kikuchi line, which, however, will be largely independent of the position of the line, in contrast to the asymmetry discussed in § 5.

7. Conclusion

The method presented here for calculation of diffuse scattering in the presence of Bragg scattering follows the multiple scattering approach by Cowley & Moodie (1957), and Fujiwara (1959). One advantage of this appears to be that the various terms can be represented very simply by diagrams which are of help in analysing particular situations and picking the most important terms. The main theory is independent of the nature of diffuse scattering, although normal modes for inelastic scattering have been assumed to be independent. Extension to multiple diffuse scattering is feasible at least in simple cases; appreciable multiple scattering will probably occur only for inelastic scattering where it is possible to avoid multiple scattering experimentally through energy analysis.

Apart from the application to Kikuchi and similar patterns and to correction of diffuse scattering for dynamic effects, it is hoped that the present theory will be of value in the study of the interference terms which depend on the Bragg interaction and do not appear in kinematic diffuse scattering. In particular, the study of these terms for inelastic scattering offers an alternative way of investigating the anomalous absorption of electrons.

APPENDIX I

By performing the integration over κ_z in equation (1b) in the manner shown by Fujiwara (1959), *i.e.* by choosing integration contours consistent with waves travelling along the positive z direction and neglecting back scattering, we obtain:

$$\begin{aligned} \mathbf{G}(\mathbf{r}, \mathbf{r}') &\simeq (i/4\pi^2) \int \exp [i\mathbf{s}(\mathbf{q}-\mathbf{q}')] \exp [ik_s(z-z')] ds/2k \\ &\simeq 0 \end{aligned} \quad \begin{array}{l} z > z' \\ z < z' \end{array} \quad (A1)$$

where $k_s = (k^2 - s^2)^{\frac{1}{2}} = k_{0z} + \zeta_s$; ζ_s is here an excitation error. On introducing this form in the integral equation

for scattering [(equation 1(b)) for *e.g.* a continuous set of waves,

$$\psi(\mathbf{s}, z) = \delta(\mathbf{s}) + i \int ds' \int_0^z (v(\mathbf{s}-\mathbf{s}')/2k) \exp [i\zeta_s(z-z')] \psi(\mathbf{s}', z') dz' \quad (A2)$$

where the integrand in the ds' -integration is of the type called $I(\mathbf{h})$ by Fujiwara (1959). It may be of interest to quote the integral equation for Bragg scattering matrix elements between discrete waves, taking z_0 as the entrance surface:

$$\begin{aligned} \psi_{hg}(z-z_0) &= \delta_{hg} \exp [i\zeta_h(z-z_0)] \\ &+ i \sum_f \int \exp [i\zeta_h(z-z')] \psi_{fg}(z'-z_0) dz' \end{aligned}$$

where ζ_h is the excitation error of the reflexion \mathbf{h} . The Born approximation corresponding to this expression was given by Kato (1963).

APPENDIX II

Let us write the elements of the two-beam scattering matrix for an excitation error, ζ , and a Fourier potential $v_h = v$, as

$$\begin{aligned} S_{00}(z) &= S_{hh}^*(z) = \cos \Delta z + ix \sin \Delta z, \quad S_{h_0}(z) \\ &= S_{0h}(z) = iy \sin \Delta z, \end{aligned}$$

where $x = \zeta/2\Delta$, $y = v/\Delta$, $\Delta = \sqrt{(\zeta/2)^2 + v^2}$, and a factor of modulus unity has been omitted. We then have in equation (12), *e.g.*,

$A = (\cos \Delta_2 z_2 + ix_2 \sin \Delta_2 z_2)(\cos \Delta_1 z_1 + ix_1 \sin \Delta_1 z_1)$, $Z_2 = z - z_1$, which can be written as a sum of sines and cosines of $\Delta_1 z_1 + \Delta_2 z_2 = \alpha$ and $\Delta_1 z_1 - \Delta_2 z_2 = \beta$; in this way we obtain

$$\begin{aligned} A+B &= \frac{1}{2}(1+x_1x_2+y_1y_2) \cos \alpha + (1-x_1x_2-y_1y_2) \cos \beta + \\ &+ i(x_1+x_2) \sin \alpha + i(x_1x_2) \sin \alpha \\ C &= \frac{1}{2}\{y_1x_2(\cos \alpha - \cos \beta) + iy_1(\sin \alpha + \sin \beta)\} \\ D &= \frac{1}{2}\{y_2x_1(\cos \alpha - \cos \beta) + iy_2(\sin \alpha - \sin \beta)\}, \end{aligned}$$

which leads to the intensity formulae summarized in Table 1.

The author is indebted to Dr D. Watanabe for his kind cooperation and also wishes to express his gratitude to Professor J.M. Cowley for the generous hos-

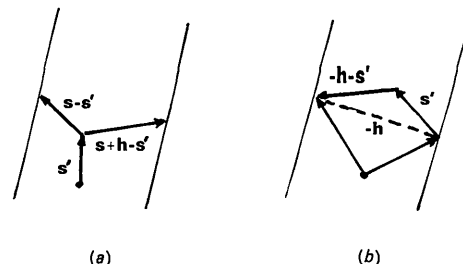


Fig. 8. Diagrams showing multiple diffuse scattering. (a) 2-order diagram representing double incoherent scattering. (b) 3-order diagram including virtual inelastic scattering leading to anomalous absorption.

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The Conformation of Non-Aromatic Ring Compounds.*

XVI. The Crystal Structure of 2 β , 3 α -dichloro-5 α -cholestane (Modification β) at -120°C

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The crystal structure of 2 β ,3 α -dichloro-5 α -cholestane has been determined by comparison with the isomorphous structure of the corresponding 2 β -chloro-3 α -bromo-derivative. The unit-cell dimensions at -120°C (of the former compound) are: $a = 13.31$, $b = 10.47$, $c = 9.88$ Å; $\beta = 113^{\circ} 37'$. The space group is $P2_1$ and $Z = 2$.

The rings A , B and C of the steroid skeleton are in the chair form. The conformation of ring D is best represented by a half chair with approximate symmetry C_2 . The angle between the bonds C(2)–Cl(2) and C(3)–Cl(3), having an average length of 1.81 Å, is 157° . The mean value of the carbon bond angles (111.2°) within the cyclohexane rings deviates significantly from the ideal tetrahedral value and this deviation is connected with the flattening of the perhydrophenanthrene skeleton. The bonds C(10)–C(19) and C(13)–C(18) are not strictly parallel, but are inclined to each other at an angle of 9° , which is an indication of the slightly bent shape of the molecule. A proof of the structures and configuration of 2 β -chloro-3 α -bromo- and 2 β -bromo-3 α -chloro-5 α -cholestane is given.

Introduction

The investigation presented in this paper is a part of a series of physico-chemical and conformational studies on steroid compounds and on more simple six-membered ring systems, such as cyclohexane and dioxane derivatives. For a complete survey of this work we refer to the preceding papers of this series and to the publications cited therein.

In a preliminary communication on the optical properties, cell dimensions and space groups (Geise, Romers & Hartman, 1962) we announced the crystal structure determinations of 2 β ,3 α -dichloro- and 2 α ,3 β -dichloro-5 α -cholestane. It proved possible to obtain more accurate data at low temperature of the 2 β ,3 α -dichloro compound and of the 2 α ,3 β -dibromo derivative, the latter being isomorphous with 2 α ,3 β -dichloro-5 α -cholestane. Meanwhile the crystal structure of the synthetic steroid 4-bromo-9 β ,10 α -pregna-4,6-diene-3,20-dione was carried out and a short communication of this work appeared elsewhere (Romers, v. Heijkoop, Hesper &

* Part XIV, Kalf & Romers (1965); Part XV, Romers, v. Heijkoop, Hesper & Geise (1965).