International Tables for Crystallography (2010). Vol. B, Section 4.3.4, pp. 542–544.

$$\frac{d\sigma}{d\Omega} = \frac{E_p}{2\pi a_H mvN}[1/(\theta^2 + \theta_E^2)G(\theta, \theta_c)], \qquad (4.3.2.4)$$

where $G(\theta, \theta_c)$ takes account of the cut-off angle Θ_c. Inner-shell excitations have been studied because of their importance to spectroscopy. The most realistic calculations may be those of Leapman *et al.* (1980) where one-electron wavefunctions are determined for the excited states in order to obtain 'generalized oscillator strengths' which may then be used to modify equation (4.3.1.2).

At high energies and high momentum transfer, the scattering will approach that of free electrons, *i.e.* a maximum at the so-called Bethe ridge, $E = h^2u^2/2m$.

A complete and detailed picture of inelastic scattering of electrons as a function of energy and angle (or scattering variable) is lacking, and may possibly be the least known area of diffraction by solids. It is further complicated by the dynamical scattering, which involves the incident and diffracted electrons and also the ejected atomic electron (see *e.g.* Maslen & Rossouw, 1984*a*,*b*).

4.3.3. Kinematical and pseudo-kinematical scattering

Kinematical expressions for TDS or defect and disorder scattering according to equation (4.3.1.3) can be obtained by inserting the appropriate atomic scattering factors in place of the X-ray scattering factors in Chapter 4.1. The complications introduced by dynamical diffraction are considerable (see Section 4.3.4). In the most general case, a complete specification of the disordered structure may be needed. However, for thin specimens, approximate treatments of the deviations from kinematical scattering may lead to relatively simple forms. Two such cases are treated in this section, both relying on the small-angle nature of electron scattering. The first is based upon the phase-object approximation, which applies to small angles and thin specimens.

The amplitude at the exit surface of a specimen can always be written as a sum of a periodic and a nonperiodic part, and may in analogy with the kinematical case [equation (4.3.1.1)] be written

$$\psi(\mathbf{r}) = \bar{\psi}(\mathbf{r}) + \Delta\psi(\mathbf{r}), \qquad (4.3.3.1)$$

where $\mathbf{r}$ is a vector in two dimensions. The intensities can be separated in the same way [*cf.* equation (4.3.1.3)].

When the phase-object approximation applies [Section 2.5.2.4(*b*)]

$$\begin{aligned}\psi(\mathbf{r}) &= \exp\{-i\sigma\varphi(\mathbf{r})\}\\ &= \exp\{-i\sigma\bar{\varphi}(\mathbf{r})\}[1 - i\sigma\Delta\varphi(\mathbf{r}) - \ldots]. \qquad (4.3.3.2)\end{aligned}$$

Then the Bragg reflections are given by Fourier transform of the periodic part, *viz*:

$$\langle\exp\{-i\sigma\varphi(\mathbf{r})\}\rangle = \exp\{-i\sigma\bar{\varphi}(\mathbf{r})\}\exp\left\{-\tfrac{1}{2}\sigma^2\langle\Delta\varphi^2(\mathbf{r})\rangle\right\}; \qquad (4.3.3.3)$$

note that an absorption function is introduced.

The diffuse scattering derives from

$$-i\sigma\Delta\varphi(\mathbf{r})\exp\{-i\sigma\bar{\varphi}(\mathbf{r})\}, \qquad (4.3.3.4)$$

so that

$$I_d(\mathbf{u}) = \sigma^2|\Delta\Phi(\mathbf{u}) * \Phi_{av}(\mathbf{u})|^2. \qquad (4.3.3.5)$$

Thus, the kinematical diffuse-scattering amplitude is convoluted with the amplitude function for the average structure, *i.e.* the set of sharp Bragg beams. When the direct beam, $\Phi_{av}(0)$, is relatively strong, the kinematical diffuse scattering will be modified to only a limited extent by convolution with the Bragg reflections. To the extent that the diffuse scattering is periodic in reciprocal space, the effect will be to modify the intensity by a slowly varying function. Thus the shapes of local diffuse maxima will not be greatly affected.

The electron-microscope image contrast derived from the diffuse scattering will be obtained by inserting equation (4.3.3.4) in the appropriate intensity expressions of Section 4.3.8 of *IT* C (2004).

Another approach may be used for extended crystal defects in thin films, *e.g.* faults normal or near-normal to the film surface. Often, an average periodic structure may not readily be defined, as in the case of a set of incommensurate stacking faults. Kinematically, the projection of the structure in the simplest case may be described by convoluting the projection of a unit-cell structure with a nonperiodic set of delta functions which constitute a distribution function:

$$\varphi(\mathbf{r}) = \varphi_0(\mathbf{r}) * \sum_n \delta(\mathbf{r} - \mathbf{r}_n) = \varphi_0(\mathbf{r}) * \mathrm{d}(\mathbf{r}). \qquad (4.3.3.6)$$

Then the diffraction-pattern intensity is

$$I(\mathbf{u}) = |\Phi_0(\mathbf{u})|^2|D(\mathbf{u})|^2. \qquad (4.3.3.7)$$

Here, $\Phi_0(\mathbf{u})$ is the scattering amplitude of the unit whereas the function $|D(\mathbf{u})|^2$, where $D(\mathbf{u}) = \mathscr{F}\{d(\mathbf{r})\}$, gives the configuration of spots, streaks or other diffraction maxima corresponding to the faulted structure (see *e.g.* Marks, 1985).

In the projection (column) approximation to dynamical scattering, the wavefunction at the exit surface may be given by an expression identical to (4.3.3.6), but with a wavefunction, $\psi_0(\mathbf{r})$, for the unit in place of the projected potential, $\varphi_0(\mathbf{r})$.

An intensity expression of the same form as (4.3.3.7) then applies, with a dynamical scattering amplitude Ψ_0 for the scattering unit substituted for the kinematical amplitude Φ_0.

$$I(\mathbf{u}) = |\Psi_0(\mathbf{u})|^2|D(\mathbf{u})|^2, \qquad (4.3.3.8)$$

which in the simplest case describes a diffraction pattern with the same features as in the kinematical case. Note that $\Psi_0(\mathbf{u})$ may have different symmetries when the incident beam is tilted away from a zone axis, leading to diffuse streaks *etc.* appearing also in positions where the kinematical diffuse scattering is zero. More complicated cases have been considered by Cowley (1976*a*) who applied this type of analysis to the case of nonperiodic faulting in magnesium fluorogermanate (Cowley, 1976*b*).

4.3.4. Dynamical scattering: Bragg scattering effects

The distribution of diffuse scattering is modified by higher-order terms in essentially two ways: Bragg scattering of the incident and diffuse beams or multiple diffuse scattering, or by a combination.

Theoretical treatment of the Bragg scattering effects in diffuse scattering has been given by many authors, starting with Kainuma's (1955) work on Kikuchi-line contrast (Howie, 1963; Fujimoto & Kainuma, 1963; Gjønnes, 1966; Rez *et al.*, 1977; Maslen & Rossouw, 1984*a*,*b*; Wang, 1995; Allen *et al.*, 1997). Mathematical formalism may vary but the physical pictures and results are essentially the same. They may be discussed with reference to a Born-series expansion, *i.e.* by introducing the potential φ in the integral equation, as a sum of a periodic and a nonperiodic part [*cf.* equation (4.3.1.1)] and arranging the terms by orders of $\Delta\varphi$.

$$\begin{aligned}\psi &= \psi_0 + G\varphi\psi \\ &= [1 + G\varphi + (G\varphi)^2 + \ldots]\psi_0 \\ &= [1 + G\bar{\varphi} + (G\bar{\varphi})^2 + \ldots]\psi_0 \\ &\quad + [1 + G\bar{\varphi} + (G\bar{\varphi})^2 + \ldots] \\ &\quad \times G(\Delta\varphi)[1 + G\bar{\varphi} + (G\bar{\varphi})^2 + \ldots]\psi_0 \\ &\quad + \text{higher-order terms.} \end{aligned} \quad (4.3.4.1)$$

Some of the higher-order terms contributing to the Bragg scattering can be included by adding the essentially imaginary term $\langle\Delta\varphi G(\Delta\varphi)\rangle$ to the static potential $\bar{\varphi}$.

Theoretical treatments have mostly been limited to the first-order diffuse scattering. With the usual approximation to forward scattering, the expression for the amplitude of diffuse scattering in a direction $\mathbf{k}_0 + \mathbf{u} + \mathbf{g}$ can be written as

$$\begin{aligned}\psi(\mathbf{u} + \mathbf{g}) &= \sum_g \sum_f \int_0^z S_{hg}(\mathbf{k}_0 + \mathbf{u}, z - z_1) \\ &\quad \times \Delta\Phi(\mathbf{u} + \mathbf{g} - \mathbf{f}) S_{f0}(\mathbf{k}_0, z_1)\, \mathrm{d}z_1 \end{aligned} \quad (4.3.4.2)$$

and read (from right to left): S_{f0}, Bragg scattering of the incident beam above the level z_1; $\Delta\Phi$, diffuse scattering within a thin layer $\mathrm{d}z_1$ through the Fourier components $\Delta\Phi$ of the nonperiodic potential $\Delta\Phi$; S_{hg}, Bragg scattering between diffuse beams in the lower part of the crystal. It is commonly assumed that diffuse scattering at different levels can be treated as independent (Gjønnes, 1966), then the intensity expression becomes

$$\begin{aligned}I(\mathbf{u} + \mathbf{g}) &= \sum_h \sum_{h'} \sum_f \sum_{f'} \int_0^z S_{gh}(2) S^*_{gh'}(2) \\ &\quad \times \langle \Delta\Phi(\mathbf{u} + \mathbf{h} - \mathbf{f}) \Delta\Phi^*(\mathbf{u} + \mathbf{h}' - \mathbf{f}') \rangle \\ &\quad \times S_{f0}(1) S^*_{f'0}(1)\, \mathrm{d}z_1, \end{aligned} \quad (4.3.4.3)$$

where (1) and (2) refer to the regions above and below the diffuse-scattering layer. This expression can be manipulated further, *e.g.* by introducing Bloch-wave expansion of the scattering matrices, *viz*

$$\begin{aligned}I(\mathbf{u} + \mathbf{g}) &= \sum_{hh'} \sum_{ff'} \sum_{jj'} \sum_{ii'} C^j_g(2) C^{j'*}_g(2) C^{j*}_h(2) C^{j'}_{h'}(2) \\ &\quad \times \frac{\exp[i(\gamma^i - \gamma^{i'})z] - \exp[i(\gamma^j - \gamma^{j'})z]}{\gamma^i - \gamma^{i'} - \gamma^j + \gamma^{j'}} \\ &\quad \times \langle f(\mathbf{u} + \mathbf{h} - \mathbf{f}) f^*(\mathbf{u} + \mathbf{h}' - \mathbf{f}') \rangle \\ &\quad \times C^{i*}_f(1) C^{i'}_{f'}(1) C^i_0(1) C^{i*}_0(1), \end{aligned} \quad (4.3.4.4)$$

which may be interpreted as scattering by $\Delta\varphi$ between Bloch waves belonging to the same branch (intraband scattering) or different branches (interband scattering). Another alternative is to evaluate the scattering matrices by multislice calculations (Section 4.3.5).

Expressions such as (4.3.4.2) contain a large number of terms. Unless very detailed calculations relating to a precisely defined model are to be carried out, attention should be focused on the most important terms.

In Kikuchi-line contrast, the scattering in the upper part of the crystal is usually not considered and frequently the angular variation of the $\Phi(\mathbf{u})$ is also neglected. In diffraction contrast from small-angle inelastic scattering, it may be sufficient to consider the intraband terms [$i = i'$, $j = j'$ in (4.3.4.3)].

In studies of diffuse-scattering distribution, the factor $\langle\Phi(\mathbf{u} + \mathbf{h})\Phi(\mathbf{u} + \mathbf{h}')\rangle$ will produce two types of terms: Those with $\mathbf{h} = \mathbf{h}'$ result only in a redistribution of intensity between corresponding points in the Brillouin zones, with the same total intensity. Those with $\mathbf{h} \neq \mathbf{h}'$ lead to enhancement or reduction of the total diffuse intensity and hence absorption from the Bragg beam and enhanced/reduced intensity of secondary radiation, *i.e.* anomalous absorption and channelling effects. They arise through interference between different Fourier components of the diffuse scattering and carry information about position of the sources of diffuse scattering, referred to the projected unit cell. This is exploited in channelling experiments, where beam direction is used to determine atom reaction (Taftø & Spence, 1982; Taftø & Lehmpfuhl, 1982).

Gjønnes & Høier (1971) expressed this information in terms of the Fourier transform R of the generalized or Kikuchi-line form factor;

$$\langle\Delta\Phi(\mathbf{u})\Delta\Phi^*(\mathbf{u} + \mathbf{h})\rangle \mathbf{u}^2(\mathbf{u} + \mathbf{h})^2 = Q(\mathbf{u} + \mathbf{h}) = \mathscr{F}\{R(\mathbf{r}, \mathbf{g})\} \quad (4.3.4.5)$$

includes information both about correlations between sources of diffuse scattering and about their position in the projected unit cell. It is seen that $Q(\mathbf{u}, 0)$ represents the kinematical intensity, hence $\int R(\mathbf{r}, \mathbf{g})\, \mathrm{d}\mathbf{g}$ is the Patterson function. The integral of $Q(\mathbf{u}, \mathbf{h})$ in the plane gives the anomalous absorption (Yoshioka, 1957) which is related to the distribution $R(\mathbf{r}, 0)$ of scattering centres across the unit cell.

The scattering factor $\langle\Delta\Phi(\mathbf{u})\Delta\Phi^*(\mathbf{u} - \mathbf{h})\rangle$ can be calculated for different modes. For one-electron excitations as an extension of the Waller–Hartree expression (Gjønnes, 1962; Whelan, 1965):

$$\begin{aligned}\langle\Delta\Phi(\mathbf{u})\Delta\Phi^*(\mathbf{u} - \mathbf{h})\rangle &= \sum_i \frac{f_{ii}(\mathbf{h}) - f_{ii}(\mathbf{u}) f_{ii}(|\mathbf{h} - \mathbf{u}|)}{u^2(\mathbf{h} - \mathbf{u})^2} \\ &\quad - \sum_i \sum_{i \neq j} \frac{f_{ij}(\mathbf{u}) f_{ij}(|\mathbf{h} - \mathbf{u}|)}{u^2(\mathbf{h} - \mathbf{u})^2}, \end{aligned} \quad (4.3.4.6)$$

where f_{ij} are the one-electron amplitudes (Freeman, 1959).

A similar expression for scattering by phonons is obtained in terms of the scattering factors $G_j(\mathbf{u}, \mathbf{g})$ for the branch j, wave-vector $\mathbf{g}$ and a polarization vector $\mathbf{l}_{j,q}$ (see Chapter 4.1):

$$\langle\Delta\Phi(\mathbf{u})\Delta\Phi^*(\mathbf{u} - \mathbf{h})\rangle = G_j(\mathbf{u}, \mathbf{q}) G^*_j(\mathbf{u} - \mathbf{h}, \mathbf{q}), \quad (4.3.4.7)$$

independent phonons being assumed.

For scattering from substitutional order in a binary alloy with ordering on one site only, we obtain simply

$$\Delta\Phi(\mathbf{u})\Delta\Phi^*(\mathbf{u} - \mathbf{h}) = |\Delta\varphi(\mathbf{u})|^2 \frac{f_A(|\mathbf{u} - \mathbf{h}|) - f_B(|\mathbf{u} - \mathbf{h}|)}{f_A(\mathbf{u}) - f_B(\mathbf{u})}, \quad (4.3.4.8)$$

where $f_{A,B}$ are atomic scattering factors. It is seen that $Q(\mathbf{u})$ then does not contain any new information; the location of the site involved in the ordering is known.

When several sites are involved in the ordering, the dynamical scattering factor becomes less trivial, since scattering factors for the different ordering parameters (for different sites) will include a factor $\exp(2\pi i \mathbf{r}_m \cdot \mathbf{h})$ (see Andersson *et al.*, 1974).

From the above expressions, it is found that the Bragg scattering will affect diffuse scattering from different sources differently: Diffuse scattering from substitutional order will usually be enhanced at low and intermediate angles, whereas scattering from thermal and electronic fluctuations will be reduced at low angles and enhanced at higher angles. This may be used to study substitutional order and displacement order (size effect) separately (Andersson, 1979).

The use of such expressions for quantitative or semi-quantitative interpretation raises several problems. The Bragg scattering effects occur in all diffuse components, in particular the inelastic scattering, which thus may no longer be represented by a smooth, monotonic background. It is best to eliminate this experimentally. When this cannot be done, the experiment should be arranged so as to minimize Kikuchi-line excess/deficient terms, by aligning the incident beam along a not too dense zone. In this way, one may optimize the diffuse-scattering information and minimize the dynamical corrections, which then are used partly as guides to conditions, partly as refinement in calculations.

The multiple scattering of the background remains as the most serious problem. Theoretical expressions for multiple scattering in the absence of Bragg scattering have been available for some time (Moliere, 1948), as a sum of convolution integrals

$$I(\mathbf{u}) = [(\mu t)I_1(\mathbf{u}) + (1/2)(\mu t)^2 I_2(\mathbf{u}) + \ldots]\exp(-\mu t), \quad (4.3.4.9)$$

where $I_2(\mathbf{u}) = I_1(\mathbf{u}) * I_1(\mathbf{u}) \ldots$ *etc.*, and $I_1(\mathbf{u})$ is normalized.

A complete description of multiple scattering in the presence of Bragg scattering should include Bragg scattering between diffuse scattering at all levels z_1, z_2, *etc.* This quickly becomes unwieldy. Fortunately, the experimental patterns seem to indicate that this is not necessary: The Kikuchi-line contrast does not appear to be very sensitive to the exact Bragg condition of the incident beam. Høier (1973) therefore introduced Bragg scattering only in the last part of the crystal, *i.e.* between the level z_n and the final thickness z for n-times scattering. He thus obtained the formula:

$$I(\mathbf{u}+\mathbf{h}) = \sum_j |C_h^j|^2 \left\{ A_1^j \sum_g \sum_{g\neq g'} F_1(\mathbf{u},\mathbf{g},\mathbf{g}')C_g^j C_{g'}^{j*} + \sum_n \sum_g A_{ng}^j F_n(\mathbf{u},\mathbf{g})|C_g^j|^2 \right\}, \quad (4.3.4.10)$$

where F_n are normalized scattering factors for nth-order multiple diffuse scattering and A_n^j are multiple-scattering coefficients which include absorption.

When the thickness is increased, the variation of $F_n(\mathbf{u},\mathbf{g})$ with angle becomes slower, and an expression for intensity of the channelling pattern is obtained (Gjønnes & Taftø, 1976):

$$\begin{aligned} I(\mathbf{u}+\mathbf{h}) &= \sum_j \sum_g \sum_n |C_h^j|^2 |C_g^j|^2 A_n^j \\ &= \sum_j |C_h^j|^2 \sum_n A_n^j \rightarrow |C_h^j|^2/\mu^j(\mathbf{u}). \end{aligned} \quad (4.3.4.11)$$

Another approach is the use of a modified diffusion equation (Ohtsuki *et al.*, 1976).

These expressions seem to reproduce the development of the general background with thickness over a wide range of thicknesses. It may thus appear that the contribution to the diffuse background from known sources can be treated adequately – and that such a procedure must be included together with adequate filtering of the inelastic component in order to improve the quantitative interpretation of diffuse scattering.

4.3.5. Multislice calculations for diffraction and imaging

The description of dynamical diffraction in terms of the progression of a wave through successive thin slices of a crystal (Chapter 5.2) forms the basis for the multislice method for the calculation of electron-diffraction patterns and electron-microscope images [see Section 4.3.6.1 in *IT* C (2004)]. This method can be applied directly to the calculations of diffuse scattering in electron diffraction due to thermal motion and positional disorder and for calculating the images of defects in crystals.

It is essentially an amplitude calculation based on the formulation of equation (4.3.4.1) [or (4.3.4.2)] for first-order diffuse scattering. The Bragg scattering in the first part of the crystal is calculated using a standard multislice method for the set of beams **h**. In the nth slice of the crystal, a diffuse-scattering amplitude $\Psi_d(\mathbf{u})$ is convoluted with the incident set of Bragg beams. For each **u**, propagation of the set of beams $\mathbf{u}+\mathbf{h}$ is then calculated through the remaining slices of the crystal. The intensities for the exit wave at the set of points $\mathbf{u}+\mathbf{h}$ are then calculated by adding either amplitudes or intensities. Amplitudes are added if there is correlation between the defects in successive slices. Intensities are added if there are no such correlations. The process is repeated for all **u** values to obtain a complete mapping of the diffuse scattering.

Calculations have been made in this way, for example, for short-range order in alloys [Fisher (1969); see also Cowley (1981) ch. 17] and also for TDS on the assumption of both correlated and uncorrelated atomic motions (Doyle, 1969). The effects of the correlations were shown to be small.

This computing method is not practical for electron-microscope images in which individual defects are to be imaged. The perturbations of the exit wavefunction due to individual defects (vacancies, replaced atoms, displaced atoms) or small groups of defects may then be calculated with arbitrary accuracy by use of the 'periodic continuation' form of the multislice computer programs in which an artificial, large, superlattice unit cell is assumed [Section 4.3.6.1 in *IT* C (2004)]. The corresponding images and microdiffraction patterns from the individual defects or clusters may then be calculated (Fields & Cowley, 1978). A more recent discussion of the image calculations, particularly in relation to thermal diffuse scattering, is given by Cowley (1988).

In order to calculate the diffuse-scattering distributions from disordered systems or from a crystal with atoms in thermal motion by the multislice method with periodic continuation, it would be necessary to calculate for a number of different defect configurations sufficiently large to provide an adequate representation of the statistics of the disordered system. However, it has been shown by Cowley & Fields (1979) that, if the single-diffuse-scattering approximation is made, the perturbations of the exit wave due to individual defects are characteristic of the defect type and of the slice number and may be added, so that a considerable simplification of the computing process is possible. Methods for calculating diffuse scattering in electron-diffraction patterns using the multislice approach are described by Tanaka & Cowley (1987) and Cowley (1989). Loane *et al.* (1991) introduced the concept of 'frozen phonons' for multislice calculations of thermal scattering.

4.3.6. Qualitative interpretation of diffuse scattering of electrons

Quantitative interpretation of the intensity of diffuse scattering by calculation of *e.g.* short-range-order parameters has been the exception. Most studies have been directed to qualitative features

references