

4.3. Diffuse scattering in electron diffraction

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4.3.1. Introduction

The origins of diffuse scattering in electron-diffraction patterns are the same as in the X-ray case: inelastic scattering due to electronic excitations, thermal diffuse scattering (TDS) from atomic motions, scattering from crystal defects or disorder. For diffraction by crystals, the diffuse scattering can formally be described in terms of a nonperiodic deviation $\Delta\varphi$ from the periodic, average crystal potential, $\bar{\varphi}$:

$$\varphi(\mathbf{r}, t) = \bar{\varphi}(\mathbf{r}) + \Delta\varphi(\mathbf{r}, t), \quad (4.3.1.1)$$

where $\Delta\varphi$ may have a static component from disorder in addition to time-dependent fluctuations of the electron distribution or atomic positions.

In the kinematical case, the diffuse scattering can be treated separately. The intensity I_d as a function of the scattering variable \mathbf{u} ($|\mathbf{u}| = 2 \sin \theta / \lambda$) and energy transfer $h\nu$ is then given by the Fourier transform \mathcal{F} of $\Delta\varphi$

$$I(\mathbf{u}, \nu) = |\Delta\Phi(\mathbf{u}, \nu)|^2 = |\mathcal{F}\{\Delta\varphi(\mathbf{r}, t)\}|^2 = \mathcal{F}\{P_d(\mathbf{r}, \nu)\} \quad (4.3.1.2)$$

and may also be written as the Fourier transform of a correlation function P_d representing fluctuations in space and time (see Cowley, 1981). When the energy transfers are small – as with TDS – and hence not measured, the observed intensity corresponds to an integral over ν :

$$\begin{aligned} I(\mathbf{u}) &= I_d(\mathbf{u}) + I_{av}(\mathbf{u}) \\ I_d(\mathbf{u}) &= \int I_d(\mathbf{u}, \nu) d\nu = \mathcal{F}\{P_d(\mathbf{r}, \mathbf{0})\} \end{aligned}$$

and also

$$I_d(\mathbf{u}) = \langle |\Phi(\mathbf{u})|^2 \rangle - |\langle \Phi(\mathbf{u}) \rangle|^2, \quad (4.3.1.3)$$

where the brackets may indicate a time average, an expectation value, or a spatial average over the periodicity of the lattice in the case of static deviations from a periodic structure.

The considerations of TDS and static defects and disorder of Chapters 4.1 and 4.2 thus may be applied directly to electron diffraction in the kinematical approximation when the differences in experimental conditions and diffraction geometry are taken into account.

The most prominent contribution to the diffuse background in electron diffraction, however, is the inelastic scattering at low angles arising mainly from the excitation of outer electrons. This is quite different from the X-ray case where the inelastic ('incoherent') scattering, $S(\mathbf{u})$, goes to zero at small angles and increases to a value proportional to Z for high values of $|\mathbf{u}|$. The difference is due to the Coulomb nature of electron scattering, which leads to the kinematical intensity expression S/u^4 , emphasizing the small-angle region. At high angles, the inelastic scattering from an atom is then proportional to Z/u^4 , which is considerably less than the corresponding elastic scattering $(Z - f)^2/u^4$ which approaches Z^2/u^4 (Section 2.5.2) (see Fig. 4.3.1.1).

The kinematical description can be used for electron scattering only when the crystal is very thin (10 nm or less) and composed of light atoms. For heavy atoms such as Au or Pb, crystals of thickness 1 nm or more in principal orientations show strong deviations from kinematical behaviour. With increasing thickness, dynamical scattering effects first modify the sharp Bragg reflections and then have increasingly significant effects on the diffuse scattering. Bragg scattering of the diffuse scattering produces Kikuchi lines and other effects. Multiple diffuse scattering broadens the distribution and smears out detail. As the thickness increases further, the diffuse

scattering increases and the Bragg beams are reduced in intensity until there is only a diffuse 'channelling pattern' where the features depend in only a very indirect way on the incident-beam direction or on the sources of the diffuse scattering (Uyeda & Nonoyama, 1968).

The multiple-scattering effects make the quantitative interpretation of diffuse scattering more difficult and complicate the extraction of particular components, *e.g.* disorder scattering. Much of the multiple scattering involves inelastic scattering processes. However, electrons that have lost energy of the order of 1 eV or more can be subtracted experimentally by use of electron energy filters (Krahl *et al.*, 1990; Krivanek *et al.*, 1992) which are commercially available. Measurement can be made also of the complete scattering function $I(\mathbf{u}, \nu)$, but such studies have been rare. Another significant improvement to quantitative measurement of diffuse electron scattering is offered by new recording devices: slow-scan charge-couple-device cameras (Krivanek & Mooney, 1993) and imaging plates (Mori *et al.*, 1990).

There are some advantages in the use of electrons which make it uniquely valuable for particular applications.

(1) Diffuse-scattering distributions can be recorded from very small specimen regions, a few nm in diameter and a few nm thick. The diameter of the specimen area may be varied readily up to several μm .

(2) Diffraction information on defects or disorder may be correlated with high-resolution electron-microscope imaging of the same specimen area [see Section 4.3.8 in *IT C* (1999)].

(3) The electron-diffraction pattern approximates to a planar section of reciprocal space, so that complicated configurations of diffuse scattering may be readily visualized (see Fig. 4.3.1.2).

(4) Dynamical effects may be exploited to obtain information about localization of sources of the diffuse scattering within the unit cell.

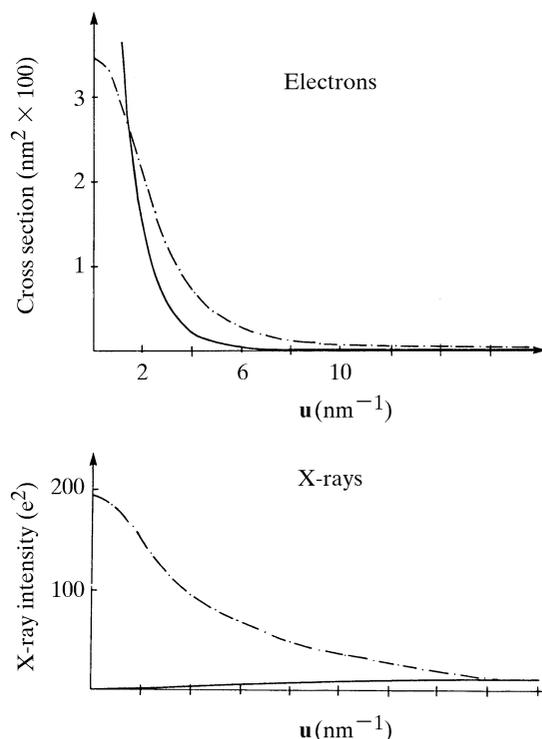


Fig. 4.3.1.1. Comparison between the kinematical inelastic scattering (full line) and elastic scattering (broken) for electrons and X-rays. Values for silicon [Freeman (1960) and *IT C* (1999)].

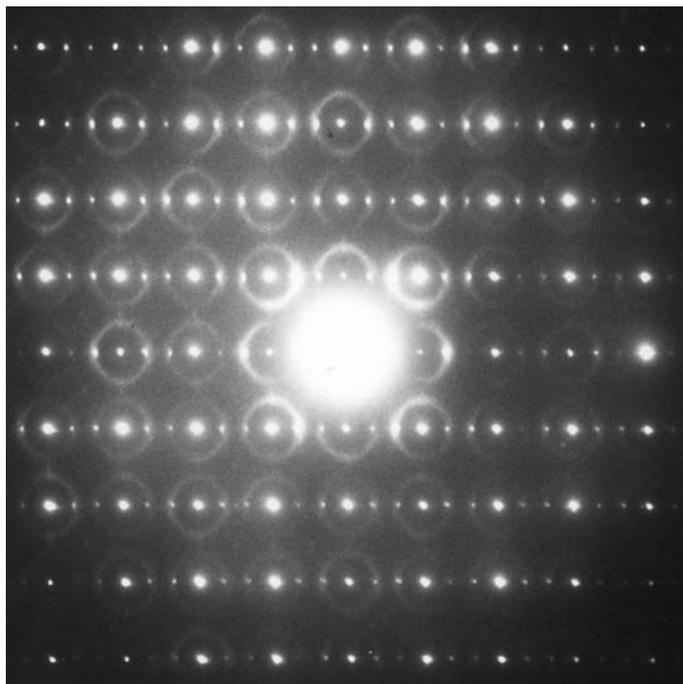


Fig. 4.3.1.2. Electron-diffraction pattern from a disordered crystal of $17\text{Nb}_2\text{O}_5.48\text{WO}_3$ close to the [001] orientation of the tetragonal tungsten-bronze-type structure (Iijima & Cowley, 1977).

These experimental and theoretical aspects of electron diffraction have influenced the ways in which it has been applied in studies of diffuse scattering.

In general, we may distinguish three different approaches to the interpretation of diffuse scattering:

(a) The crystallographic way, in which the Patterson- or correlation-function representation of the local order is emphasized, *e.g.* by use of short-range-order parameters.

(b) The physical model in terms of excitations. These are usually described in reciprocal (momentum) space: phonons, plasmons *etc.*

(c) Structure models in direct space. These must be derived by trial or by chemical considerations of bonds, coordinates *etc.*

Owing to the difficulties of separating the different components in the diffuse scattering, most work on diffuse scattering of electrons has followed one or both of the two last approaches, although Patterson-type interpretation, based upon kinematical scattering including some dynamical corrections, has also been tried.

4.3.2. Inelastic scattering

In the kinematical approximation, a general expression which includes inelastic scattering can be written in the form quoted by Van Hove (1954)

$$I(\mathbf{u}, \nu) = \frac{m^3 k}{2^2 h^6 k_o} \times W(\mathbf{u}) \sum_{\eta} P_{n_o} \sum_{j=1}^Z |\langle n_o | \exp\{2\pi i \mathbf{u} \cdot \mathbf{R}_j\} | n \rangle|^2 \times \delta\left(\nu + \frac{E_n - E_{n_o}}{h}\right) \quad (4.3.2.1)$$

for the intensity of scattering as function of energy transfer and momentum transfer from a system of Z identical particles, \mathbf{R}_j . Here m and h have their usual meanings; k_o and k , E_{n_o} and E_n are

wavevectors and energies before and after the scattering between object states n_o and n ; P_{n_o} are weights of the initial states; $W(\mathbf{u})$ is a form factor (squared) for the individual particle.

In equation (4.3.2.1), \mathbf{u} is essentially momentum transfer. When the energy transfer is small ($\Delta E/E \ll \theta$), we can still write $|\mathbf{u}| = 2 \sin \theta/\lambda$, then the sum over final states n is readily performed and an expression of the Waller–Hartree type is obtained for the total inelastic scattering as a function of angle:

$$I_{\text{inel}}(\mathbf{u}) \propto \frac{S}{u^4},$$

where

$$S(u) = Z - \sum_{j=1}^Z |f_{jj}(u)|^2 - \sum_j \sum_{j \neq k}^Z |f_{jk}(u)|^2, \quad (4.3.2.2)$$

and where the one-electron f 's for Hartree–Fock orbitals, $f_{jk}(\mathbf{u}) = \langle j | \exp(2\pi i \mathbf{u} \cdot \mathbf{r}) | k \rangle$, have been calculated by Freeman (1959, 1960) for atoms up to $Z = 30$. The last sum is over electrons with the same spin only.

The Waller–Hartree formula may be a very good approximation for Compton scattering of X-rays, where most of the scattering occurs at high angles and multiple scattering is no problem. With electrons, it has several deficiencies. It does not take into account the electronic structure of the solid, which is most important at low values of u . It does not include the energy distribution of the scattering. It does not give a finite cross section at zero angle, if u is interpreted as an angle. In order to remedy this, we should go back to equation (4.3.1.2) and decompose \mathbf{u} into two components, one tangential part which is associated with angle in the usual way and one normal component along the beam direction, u_n , which may be related to the excitation energy $\Delta E = E_n - E_{n_o}$ by the expression $u_n = \Delta E_k/2E$. This will introduce a factor $1/(u^2 + u_n^2)$ in the intensity at small angles, often written as $1/(\theta^2 + \theta_E^2)$, with ΔE estimated from ionization energies *etc.* (Strictly speaking, ΔE is not a constant, not even for scattering from one shell. It is a weighted average which will vary with u .)

Calculations beyond this simple adjustment of the Waller–Hartree-type expression are few. Plasmon scattering has been treated on the basis of a nearly free electron model by Ferrel (1957):

$$\frac{d^2\sigma}{d(\Delta E) d\Omega} = (1/\pi^2 a_H m v^2 N) (-\text{Im}\{1/\varepsilon\})/(\theta^2 + \theta_E^2), \quad (4.3.2.3)$$

where m , v are relativistic mass and velocity of the incident electron, N is the density of the valence electrons and $\varepsilon(\Delta E, \theta)$ their dielectric constant. Upon integration over ΔE :

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

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, $E = h^2 u^2/2m$.

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).