4. DIFFUSE SCATTERING AND RELATED TOPICS
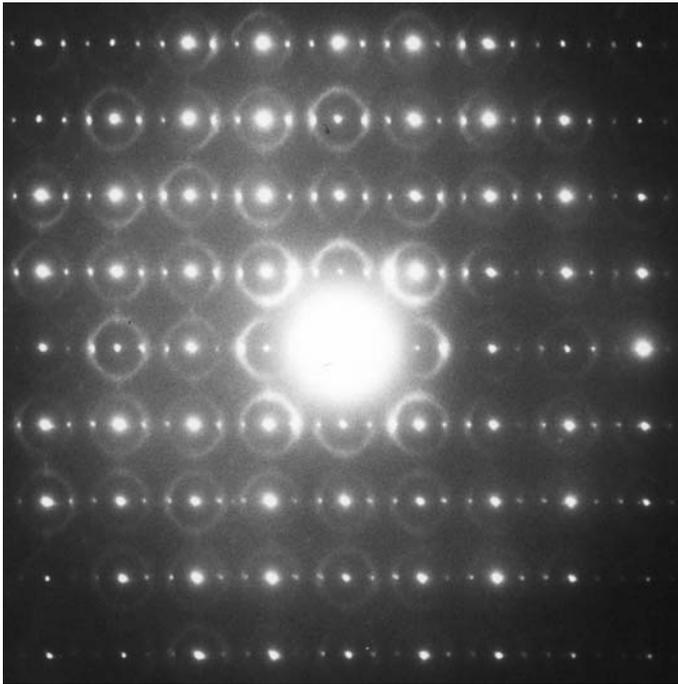

Fig. 4.3.1.2. Electron-diffraction pattern from a disordered crystal of $17Nb_2O_5.48WO_3$ close to the [001] orientation of the tetragonal tungsten-bronze-type structure (Iijima & Cowley, 1977).

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)

$$I(\mathbf{u}, \nu) = \frac{m^3}{2^2 h^6} \frac{k}{k_o}$$

$$\times W(\mathbf{u}) \sum P_{n_o} \sum_{\eta} \sum_{j=1}^{Z} |\langle n_o | \exp\{2\pi i \mathbf{u} \cdot \mathbf{R}_j\} | n \rangle|^2$$

$$\times \delta\left(\nu + \frac{E_n - E_{n_o}}{h}\right) \qquad (4.3.2.1)$$

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

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

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:

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

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

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).