

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

possible in many cases to obtain information on the structure of crystals and of crystal defects by direct inspection of electron micrographs.

The electromagnetic electron lenses may also be used to form electron beams of very small diameter and very high intensity. In particular, by the use of cold field-emission electron guns, it is possible to obtain a current of 10^{-10} A in an electron beam of diameter 10 Å or less with a beam divergence of less than 10^{-2} rad, *i.e.* a current density of 10^4 A cm $^{-2}$ or more. The magnitudes of the electron scattering amplitudes then imply that detectable signals may be obtained in diffraction from assemblies of fewer than 10^2 atoms. On the other hand, electron beams may readily be collimated to better than 10^{-6} rad.

The cross sections for inelastic scattering processes are, in general, less than for the elastic scattering of electrons, but signals may be obtained by the observation of electron energy losses, or the production of secondary radiations, which allow the analysis of chemical compositions or electronic excited states for regions of the crystal 100 Å or less in diameter.

On the other hand, the transfer to the sample of large amounts of energy through inelastic scattering processes produces radiation damage which may severely limit the applicability of the imaging and diffraction techniques, especially for biological and organic materials, unless the information is gathered from large specimen volumes with low incident electron beam densities.

Structure analysis of crystals can be performed using electron diffraction in the same way as with X-ray or neutron diffraction. The mathematical expressions and the procedures are much the same. However, there are peculiarities of the electron-diffraction case which should be noted.

(1) Structure analysis based on electron diffraction is possible for thin specimens for which the conditions for kinematical scattering are approached, *e.g.* for thin mosaic single-crystal specimens, for thin polycrystalline films having a preferred orientation of very small crystallites or for very extensive, very thin single crystals of biological molecules such as membranes one or a few molecules thick.

(2) Dynamical diffraction effects are used explicitly in the determination of crystal symmetry (with no Friedel's law limitations) and for the measurement of structure amplitudes with high accuracy.

(3) For many radiation-resistant materials, the structures of crystals and of some molecules may be determined directly by imaging atom positions in projections of the crystal with a resolution of 2 Å or better. The information on atom positions is not dependent on the periodicity of the crystal and so it is equally possible to determine the structures of individual crystal defects in favourable cases.

(4) Techniques of microanalysis may be applied to the determination of the chemical composition of regions of diameter 100 Å or less using the same instrument as for diffraction, so that the chemical information may be correlated directly with morphological and structural information.

(5) Crystal-structure information may be derived from regions containing as few as 10^2 or 10^3 atoms, including very small crystals and single or multiple layers of atoms on surfaces.

2.5.2.2. The interactions of electrons with matter

(1) The *elastic* scattering of electrons results from the interaction of the charged electrons with the electrostatic potential distribution, $\varphi(\mathbf{r})$, of the atoms or crystals. An incident electron of kinetic energy eW gains energy $e\varphi(\mathbf{r})$ in the potential field. Alternatively it may be stated that an incident electron wave of wavelength $\lambda = h/mv$ is diffracted by a region of variable refractive index

$$n(\mathbf{r}) = k/K_0 = \{[W + \varphi(\mathbf{r})]/W\}^{1/2} \simeq 1 + \varphi(\mathbf{r})/2W.$$

(2) The most important *inelastic* scattering processes are:

(a) thermal diffuse scattering, with energy losses of the order of 2×10^{-2} eV, separable from the elastic scattering only with specially devised equipment; the angular distribution of thermal diffuse scattering shows variations with $(\sin \theta)/\lambda$ which are much the same as for the X-ray case in the kinematical limit;

(b) bulk plasmon excitation, or the excitation of collective energy states of the conduction electrons, giving energy losses of 3 to 30 eV and an angular range of scattering of 10^{-4} to 10^{-3} rad;

(c) surface plasmons, or the excitation of collective energy states of the conduction electrons at discontinuities of the structure, with energy losses less than those for bulk plasmons and a similar angular range of scattering;

(d) interband or intraband excitation of valence-shell electrons giving energy losses in the range of 1 to 10^2 eV and an angular range of scattering of 10^{-4} to 10^{-2} rad;

(e) inner-shell excitations, with energy losses of 10^2 eV or more and an angular range of scattering of 10^{-3} to 10^{-2} rad, depending on the energy losses involved.

(3) In the original treatment by Bethe (1928) of the elastic scattering of electrons by crystals, the Schrödinger equation is written for electrons in the periodic potential of the crystal; *i.e.*

$$\nabla^2 \psi(\mathbf{r}) + K_0^2 [1 + \varphi(\mathbf{r})/W] \psi(\mathbf{r}) = 0, \quad (2.5.2.1)$$

where

$$\begin{aligned} \varphi(\mathbf{r}) &= \int V(\mathbf{u}) \exp\{-2\pi i \mathbf{u} \cdot \mathbf{r}\} \, d\mathbf{u} \\ &= \sum_{\mathbf{h}} V_{\mathbf{h}} \exp\{-2\pi i \mathbf{h} \cdot \mathbf{r}\}, \end{aligned} \quad (2.5.2.2)$$

\mathbf{K}_0 is the wavevector in zero potential (outside the crystal) (magnitude $2\pi/\lambda$) and W is the accelerating voltage. The solutions of the equation are Bloch waves of the form

$$\psi(\mathbf{r}) = \sum_{\mathbf{h}} C_{\mathbf{h}}(\mathbf{k}) \exp\{-i(\mathbf{k}_0 + 2\pi\mathbf{h}) \cdot \mathbf{r}\}, \quad (2.5.2.3)$$

where \mathbf{k}_0 is the incident wavevector in the crystal and \mathbf{h} is a reciprocal-lattice vector. Substitution of (2.5.2.2) and (2.5.2.3) in (2.5.2.1) gives the dispersion equations

$$(\kappa^2 - k_{\mathbf{h}}^2) C_{\mathbf{h}} + \sum_{\mathbf{g}}' V_{\mathbf{h}-\mathbf{g}} C_{\mathbf{g}} = 0. \quad (2.5.2.4)$$

Here κ is the magnitude of the wavevector in a medium of constant potential V_0 (the 'inner potential' of the crystal). The refractive index of the electron in the average crystal potential is then

$$n = \kappa/K = (1 + V_0/W)^{1/2} \simeq 1 + V_0/2W. \quad (2.5.2.5)$$

Since V_0 is positive and of the order of 10 V and W is 10^4 to 10^6 V, $n - 1$ is positive and of the order of 10^{-4} .

Solution of equation (2.5.2.4) gives the Fourier coefficients $C_{\mathbf{h}}^{(i)}$ of the Bloch waves $\psi^{(i)}(\mathbf{r})$ and application of the boundary conditions gives the amplitudes of individual Bloch waves (see Chapter 5.2).

(4) The experimentally important case of transmission of high-energy electrons through thin specimens is treated on the assumption of a plane wave incident in a direction almost perpendicular to an infinitely extended plane-parallel lamellar crystal, making use of the *small-angle scattering approximation* in which the forward-scattered wave is represented in the paraboloidal approximation to the sphere. The incident-beam direction, assumed to be almost parallel to the z axis, is unique and the z component of \mathbf{k} is factored out to give

2.5. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY IN STRUCTURE DETERMINATION

$$\nabla^2\psi + 2k\sigma\varphi\psi = \pm i2k\frac{\partial\psi}{\partial z}, \quad (2.5.2.6)$$

where $k = 2\pi/\lambda$ and $\sigma = 2\pi m_e\lambda/h^2$. [See Lynch & Moodie (1972), Portier & Gratiat (1981), Tournarie (1962), and Chapter 5.2.]

This equation is analogous to the time-dependent Schrödinger equation with z replacing t . Retention of the \pm signs on the right-hand side is consistent with both ψ and ψ^* being solutions, corresponding to propagation in opposite directions with respect to the z axis. The double-valued solution is of importance in consideration of reciprocity relationships which provide the basis for the description of some dynamical diffraction symmetries. (See Section 2.5.3.)

(5) The integral form of the wave equation, commonly used for scattering problems, is written, for electron scattering, as

$$\psi(\mathbf{r}) = \psi^{(0)}(\mathbf{r}) + (\sigma/\lambda) \int \frac{\exp\{-i\mathbf{k}|\mathbf{r} - \mathbf{r}'|\}}{|\mathbf{r} - \mathbf{r}'|} \varphi(\mathbf{r}')\psi(\mathbf{r}') d\mathbf{r}'. \quad (2.5.2.7)$$

The wavefunction $\psi(\mathbf{r})$ within the integral is approximated by using successive terms of a Born series

$$\psi(\mathbf{r}) = \psi^{(0)}(\mathbf{r}) + \psi^{(1)}(\mathbf{r}) + \psi^{(2)}(\mathbf{r}) + \dots \quad (2.5.2.8)$$

The first Born approximation is obtained by putting $\psi(\mathbf{r}) = \psi^{(0)}(\mathbf{r})$ in the integral and subsequent terms $\psi^{(n)}(\mathbf{r})$ are generated by putting $\psi^{(n-1)}(\mathbf{r})$ in the integral.

For an incident plane wave, $\psi^{(0)}(\mathbf{r}) = \exp\{-i\mathbf{k}_0 \cdot \mathbf{r}\}$ and for a point of observation at a large distance $\mathbf{R} = \mathbf{r} - \mathbf{r}'$ from the scattering object ($|\mathbf{R}| \gg |\mathbf{r}'|$), the first Born approximation is generated as

$$\psi^{(1)}(\mathbf{r}) = \frac{i\sigma}{\lambda R} \exp\{-i\mathbf{k} \cdot \mathbf{R}\} \int \varphi(\mathbf{r}') \exp\{i\mathbf{q} \cdot \mathbf{r}'\} d\mathbf{r}',$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}_0$ or, putting $\mathbf{u} = \mathbf{q}/2\pi$ and collecting the pre-integral terms into a parameter μ ,

$$\Psi(\mathbf{u}) = \mu \int \varphi(\mathbf{r}) \exp\{2\pi i\mathbf{u} \cdot \mathbf{r}\} d\mathbf{r}. \quad (2.5.2.9)$$

This is the Fourier-transform expression which is the basis for the *kinematical scattering approximation*. It is derived on the basis that all $\psi^{(n)}(\mathbf{r})$ terms for $n \neq 0$ are very much smaller than $\psi^{(0)}(\mathbf{r})$ and so is a weak scattering approximation.

In this approximation, the scattered amplitude for an atom is related to the atomic structure amplitude, $f(\mathbf{u})$, by the relationship, derived from (2.5.2.8),

$$\psi(\mathbf{r}) = \exp\{-i\mathbf{k}_0 \cdot \mathbf{r}\} + i \frac{\exp\{-i\mathbf{k} \cdot \mathbf{r}\}}{R\lambda} \sigma f(\mathbf{u}),$$

$$f(\mathbf{u}) = \int \varphi(\mathbf{r}) \exp\{2\pi i\mathbf{u} \cdot \mathbf{r}\} d\mathbf{r}. \quad (2.5.2.10)$$

For centrosymmetrical atom potential distributions, the $f(\mathbf{u})$ are real, positive and monotonically decreasing with $|\mathbf{u}|$. A measure of the extent of the validity of the first Born approximation is given by the fact that the effect of adding the higher-order terms of the Born series may be represented by replacing $f(\mathbf{u})$ in (2.5.2.10) by the complex quantities $f(\mathbf{u}) = |\mathbf{f}| \exp\{i\eta(\mathbf{u})\}$ and for single heavy atoms the phase factor η may vary from 0.2 for $|\mathbf{u}| = 0$ to 4 or 5 for large $|\mathbf{u}|$, as seen from the tables of *IT C* (1999, Section 4.3.3).

(6) Relativistic effects produce appreciable variations of the parameters used above for the range of electron energies considered. The relativistic values are

$$m = m_0(1 - v^2/c^2)^{-1/2} = m_0(1 - \beta^2)^{-1/2}, \quad (2.5.2.11)$$

$$\lambda = h[2m_0|e|W(1 + |e|W/2m_0c^2)]^{-1/2} \quad (2.5.2.12)$$

$$= \lambda_c(1 - \beta^2)^{1/2}/\beta, \quad (2.5.2.13)$$

where λ_c is the Compton wavelength, $\lambda_c = h/m_0c = 0.0242 \text{ \AA}$, and

$$\sigma = 2\pi m_e\lambda/h^2 = (2\pi m_0e/h^2)(\lambda_c/\beta)$$

$$= 2\pi/\{\lambda W[1 + (1 - \beta^2)^{1/2}]\}. \quad (2.5.2.14)$$

Values for these quantities are listed in *IT C* (1999, Section 4.3.2). The variations of λ and σ with accelerating voltage are illustrated in Fig. 2.5.2.1. For high voltages, σ tends to a constant value, $2\pi m_0e\lambda_c/h^2 = e/hc$.

2.5.2.3. Recommended sign conventions

There are two alternative sets of signs for the functions describing wave optics. Both sets have been widely used in the literature. There is, however, a requirement for internal consistency within a particular analysis, independently of which set is adopted. Unfortunately, this requirement has not always been met and, in fact, it is only too easy at the outset of an analysis to make errors in this way. This problem might have come into prominence somewhat earlier were it not for the fact that, for centrosymmetric crystals (or indeed for centrosymmetric projections in the case of planar diffraction), only the signs used in the transmission and propagation functions can affect the results. It is not until the origin is set away from a centre of symmetry that there is a need to be consistent in every sign used.

Signs for electron diffraction have been chosen from two points of view: (1) defining as positive the sign of the exponent in the structure-factor expression and (2) defining the forward propagating free-space wavefunction with a positive exponent.

The second of these alternatives is the one which has been adopted in most solid-state and quantum-mechanical texts.

The first, or *standard crystallographic* convention, is the one which could most easily be adopted by crystallographers accustomed to retaining a positive exponent in the structure-factor equation. This also represents a consistent *International Tables* usage. It is, however, realized that both conventions will continue to be used in crystallographic computations, and that there are by now a large number of operational programs in use.

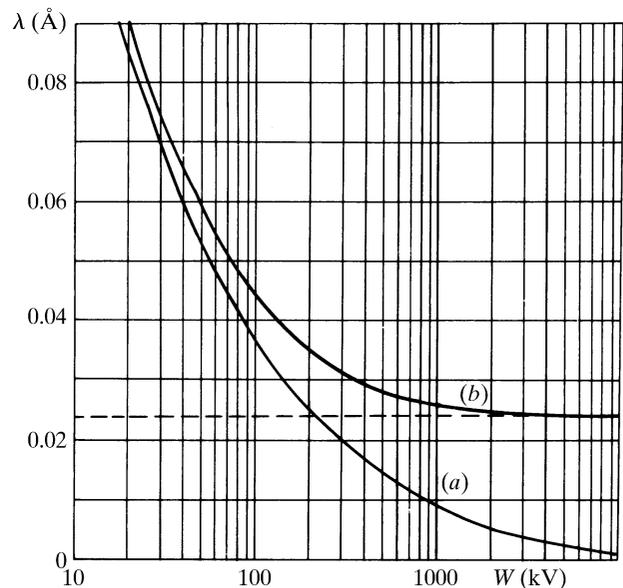


Fig. 2.5.2.1. The variation with accelerating voltage of electrons of (a) the wavelength, λ and (b) the quantity $\lambda[1 + (h^2/m_0^2c^2\lambda^2)] = \lambda_c/\beta$ which is proportional to the interaction constant σ [equation (2.5.2.14)]. The limit is the Compton wavelength λ_c (after Fujiwara, 1961).