

## 2.5. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY IN STRUCTURE DETERMINATION

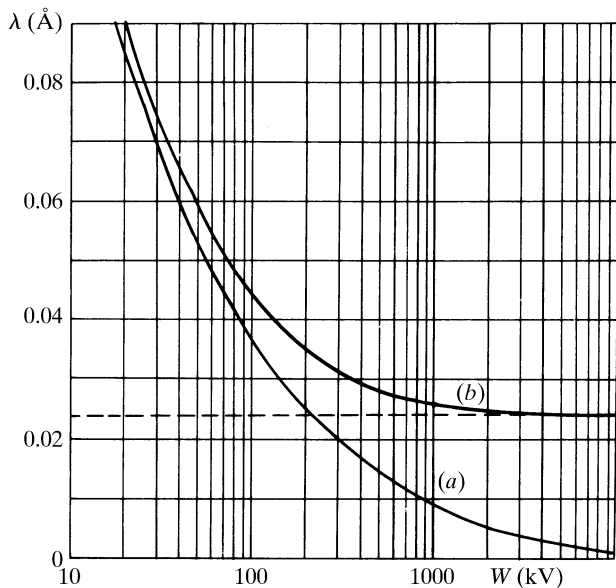


Fig. 2.5.2.1. The variation with accelerating voltage of electrons of (a) the wavelength,  $\lambda$  and (b) the quantity  $\lambda[1 + (h^2/m_0^2c^2\lambda^2)] = \lambda_c/\beta$  which is proportional to the interaction constant  $\sigma$  [equation (2.5.2.14)]. The limit is the Compton wavelength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

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

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

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  $\eta$  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* (2004, 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

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

$$\lambda = h[2m_0e|W(1 + |e|W/2m_0c^2)]^{-1/2} \quad (2.5.2.12)$$

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

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

$$\sigma = 2\pi m e \lambda / h^2 = (2\pi m_0 e / h^2)(\lambda_c / \beta)$$

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

Values for these quantities are listed in *IT C* (2004, Section 4.3.2). The variations of  $\lambda$  and  $\sigma$  with accelerating voltage are illustrated in Fig. 2.5.2.1. For high voltages,  $\sigma$  tends to a constant value,  $2\pi m_0 e \lambda_c / h^2 = e / \hbar c$ .

## 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.

It is therefore recommended (a) that a particular sign usage be indicated as either *standard crystallographic* or *alternative crystallographic* to accord with Table 2.5.2.1, whenever there is a need for this to be explicit in publication, and (b) that either one or other of these systems be adhered to throughout an analysis in a self-consistent way, even in those cases where, as indicated above, some of the signs appear to have no effect on one particular conclusion.

## 2.5.2.4. Scattering of electrons by crystals; approximations

The forward-scattering approximation to the many-beam dynamical diffraction theory outlined in Chapter 5.2 provides the basis for the calculation of diffraction intensities and electron-microscope image contrast for thin crystals. [See Cowley (1995), Chapter 5.2 and *IT C* (2004) Sections 4.3.6 and 4.3.8.] On the other hand, there are various approximations which provide relatively simple analytical expressions, are useful for the determination of diffraction geometry, and allow estimates to be made of the relative intensities in diffraction patterns and electron micrographs in favourable cases.

(a) *The kinematical approximation*, derived in Section 2.5.2.2 from the first Born approximation, is analogous to the corresponding approximation of X-ray diffraction. It assumes that the scattering amplitudes are directly proportional to the three-dimensional Fourier transform of the potential distribution,  $\varphi(\mathbf{r})$ .

$$V(\mathbf{u}) = \int \varphi(\mathbf{r}) \exp\{2\pi i \mathbf{u} \cdot \mathbf{r}\} d\mathbf{r}, \quad (2.5.2.15)$$

so that the potential distribution  $\varphi(\mathbf{r})$  takes the place of the charge-density distribution,  $\rho(\mathbf{r})$ , relevant for X-ray scattering.

The validity of the kinematical approximation as a basis for structure analysis is severely limited. For light-atom materials, such as organic compounds, it has been shown by Jap & Glaeser (1980) that the thickness for which the approximation gives reasonable accuracy for zone-axis patterns from single crystals is of the order of  $100 \text{ \AA}$  for 100 keV electrons and increases, approximately as  $\sigma^{-1}$ , for higher energies. The thickness limits quoted for polycrystalline samples, having crystallite dimensions smaller than the sample thickness, are usually greater (Vainshstein, 1956). For heavy-atom materials the approximation is more limited since it may fail significantly for single heavy atoms.

(b) *The phase-object approximation* (POA), or high-voltage limit, is derived from the general many-beam dynamical