

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

Table 2.5.2.1. Standard crystallographic and alternative crystallographic sign conventions for electron diffraction

	Standard	Alternative
Free-space wave	$\exp[-i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$	$\exp[+i(\mathbf{k} \cdot \mathbf{r} - \omega t)]$
Fourier transforming from real space to reciprocal space	$\int \psi(\mathbf{r}) \exp[+2\pi i(\mathbf{u} \cdot \mathbf{r})] \, d\mathbf{r}$	$\int \psi(\mathbf{r}) \exp[-2\pi i(\mathbf{u} \cdot \mathbf{r})] \, d\mathbf{r}$
Fourier transforming from reciprocal space to real space	$\psi(\mathbf{r}) = \int \Psi(\mathbf{u}) \exp[-2\pi i(\mathbf{u} \cdot \mathbf{r})] \, d\mathbf{u}$	$\int \Psi(\mathbf{u}) \exp[+2\pi i(\mathbf{u} \cdot \mathbf{r})] \, d\mathbf{u}$
Structure factors	$V(\mathbf{h}) = (1/\Omega) \sum_j f_j(\mathbf{h}) \exp(+2\pi i\mathbf{h} \cdot \mathbf{r}_j)$	$(1/\Omega) \sum_j f_j(\mathbf{h}) \exp(-2\pi i\mathbf{h} \cdot \mathbf{r}_j)$
Transmission function (real space)	$\exp[-i\sigma\varphi(x, y)\Delta z]$	$\exp[+i\sigma\varphi(x, y)\Delta z]$
Phenomenological absorption	$\sigma\varphi(\mathbf{r}) - i\mu(\mathbf{r})$	$\sigma\varphi(\mathbf{r}) + i\mu(\mathbf{r})$
Propagation function $P(h)$ (reciprocal space) within the crystal	$\exp(-2\pi i\zeta_h\Delta z)$	$\exp(+2\pi i\zeta_h\Delta z)$
Iteration (reciprocal space)	$\Psi_{n+1}(\mathbf{h}) = [\Psi_n(\mathbf{h}) \cdot P(\mathbf{h})] * Q(\mathbf{h})$	
Unitarity test (for no absorption)	$T(\mathbf{h}) = Q(\mathbf{h}) * Q^*(-\mathbf{h}) = \delta(\mathbf{h})$	
Propagation to the image plane-wave aberration function, where $\chi(U) = \pi\lambda\Delta f U^2 + \frac{1}{2}\pi C_s\lambda^3 U^4$, $U^2 = u^2 + v^2$ and Δf is positive for overfocus	$\exp[i\chi(U)]$	$\exp[-i\chi(U)]$

σ = electron interaction constant = $2\pi me\lambda/h^2$; m = (relativistic) electron mass; λ = electron wavelength; e = (magnitude of) electron charge; h = Planck's constant; $k = 2\pi/\lambda$; Ω = volume of the unit cell; \mathbf{u} = continuous reciprocal-space vector, components u, v ; \mathbf{h} = discrete reciprocal-space coordinate; $\varphi(x, y)$ = crystal potential averaged along beam direction (positive); Δz = slice thickness; $\mu(\mathbf{r})$ = absorption potential [positive; typically $\leq 0.1\sigma\varphi(\mathbf{r})$]; Δf = defocus (defined as negative for underfocus); C_s = spherical aberration coefficient; ζ_h = excitation error relative to the incident-beam direction and defined as negative when the point h lies outside the Ewald sphere; $f_j(\mathbf{h})$ = atomic scattering factor for electrons, f_e , related to the atomic scattering factor for X-rays, f_X , by the Mott formula $f_e = (e/\pi U^2)(Z - f_X)$. $Q(\mathbf{h})$ = Fourier transform of periodic slice transmission function.

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* (1999) 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 Å for 100 keV electrons and increases, approximately as σ^{-1} , for higher energies. The thickness limits quoted for polycrystalline samples, having crystallite dimensions smaller than the sample thickness, are usually greater (Vainshtein, 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 diffraction expression, equation (5.2.13.1), Chapter 5.2, by assuming the Ewald sphere curvature to approach zero. Then the scattering by a thin sample can be expressed by multiplying the incoming wave amplitude by the transmission function

$$q(xy) = \exp\{-i\sigma\varphi(xy)\}, \quad (2.5.2.16)$$

where $\varphi(xy) = \int \varphi(\mathbf{r}) \, dz$ is the projection of the potential distribution of the sample in the z direction, the direction of the incident beam. The diffraction-pattern amplitudes are then given by two-dimensional Fourier transform of (2.5.2.16).

This approximation is of particular value in relation to the electron microscopy of thin crystals. The thickness for its validity for 100 keV electrons is within the range 10 to 50 Å, depending on the accuracy and spatial resolution involved, and increases with accelerating voltage approximately as $\lambda^{-1/2}$. In computational work, it provides the starting point for the multi-slice method of dynamical diffraction calculations (*IT C*, 1999, Section 4.3.6.1).

(c) *The two-beam approximation* for dynamical diffraction of electrons assumes that only two beams, the incident beam and one diffracted beam (or two Bloch waves, each with two component amplitudes), exist in the crystal. This approximation has been adapted, notably by Hirsch *et al.* (1965), for use in the electron microscopy of inorganic materials.

It forms a convenient basis for the study of defects in crystals having small unit cells (metals, semiconductors *etc.*) and provides good preliminary estimates for the determination of crystal thicknesses and structure amplitudes for orientations well removed from principal axes, and for electron energies up to 200–500 keV, but it has decreasing validity, even for favourable cases, for higher energies. It has been used in the past as an 'extinction correction' for powder-pattern intensities (Vainshtein, 1956).

(d) *The Bethe second approximation*, proposed by Bethe (1928) as a means for correcting the two-beam approximation for the