

## 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 $\Delta f$ is positive for overfocus	$\exp[i\chi(U)]$	$\exp[-i\chi(U)]$

$\sigma$  = electron interaction constant =  $2\pi m e \lambda / h^2$ ;  $m$  = (relativistic) electron mass;  $\lambda$  = electron wavelength;  $e$  = (magnitude of) electron charge;  $h$  = Planck's constant;  $k = 2\pi/\lambda$ ;  $\Omega$  = 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);  $\Delta z$  = slice thickness;  $\mu(\mathbf{r})$  = absorption potential [positive; typically  $\leq 0.1\sigma\varphi(\mathbf{r})$ ];  $\Delta f$  = defocus (defined as negative for underfocus);  $C_s$  = spherical aberration coefficient;  $\zeta_h$  = 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.

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 multislice method of dynamical diffraction calculations (ITC, 2004, 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 effects of weakly excited beams, replaces the Fourier coefficients of potential by the ‘Bethe potentials’

$$U_{\mathbf{h}} = V_{\mathbf{h}} - 2k_0\sigma \sum_{\mathbf{g}} \frac{V_{\mathbf{g}} \cdot V_{\mathbf{h}-\mathbf{g}}}{\kappa^2 - k_{\mathbf{g}}^2}. \quad (2.5.2.17)$$

Use of these potentials has been shown to account well for the deviations of powder-pattern intensities from the predictions of two-beam theory (Horstmann & Meyer, 1965) and to predict accurately the extinctions of Kikuchi lines at particular accel-

erating voltages due to relativistic effects (Watanabe *et al.*, 1968), but they give incorrect results for the small-thickness limit.

## 2.5.2.5. Kinematical diffraction formulae

(1) *Comparison with X-ray diffraction.* The relations of real-space and reciprocal-space functions are analogous to those for X-ray diffraction [see equations (2.5.2.2), (2.5.2.10) and (2.5.2.15)]. For diffraction by crystals

$$\varphi(\mathbf{r}) = \sum_{\mathbf{h}} V_{\mathbf{h}} \exp\{-2\pi i\mathbf{h} \cdot \mathbf{r}\},$$

$$V_{\mathbf{h}} = \int \varphi(\mathbf{r}) \exp\{2\pi i\mathbf{h} \cdot \mathbf{r}\} \, d\mathbf{r} \quad (2.5.2.18)$$

$$= \frac{1}{\Omega} \sum_i f_i(\mathbf{h}) \exp\{2\pi i\mathbf{h} \cdot \mathbf{r}_i\}, \quad (2.5.2.19)$$

where the integral of (2.5.2.18) and the summation of (2.5.2.19) are taken over one unit cell of volume (see Dawson *et al.*, 1974).

Important differences from the X-ray case arise because

(a) the wavelength is relatively small so that the Ewald-sphere curvature is small in the reciprocal-space region of appreciable scattering amplitude;

(b) the dimensions of the single-crystal regions giving appreciable scattering amplitudes are small so that the ‘shape transform’ regions of scattering power around the reciprocal-lattice points are relatively large;

(c) the spread of wavelengths is small ( $10^{-5}$  or less, with no white-radiation background) and the degree of collimation is better ( $10^{-4}$  to  $10^{-6}$ ) than for conventional X-ray sources.

As a consequence of these factors, single-crystal diffraction patterns may show many simultaneous reflections, representing almost-planar sections of reciprocal space, and may show fine structure or intensity variations reflecting the crystal dimensions and shape.

(2) Kinematical diffraction-pattern intensities are calculated in a manner analogous to that for X-rays except that

(a) no polarization factor is included because of the small-angle scattering conditions;

(b) integration over regions of scattering power around reciprocal-lattice points cannot be assumed unless appropriate experimental conditions are ensured.

For a thin, flat, lamellar crystal of thickness  $H$ , the observed intensity is