International Tables for Crystallography (2006). Vol. B, Section 2.5.3.1, pp. 285–286.

(*c*) the diffraction intensity $|\Phi(U)|^2$ is a radially symmetric, smoothly varying function such as is normally produced by a sufficiently large area of the image of an amorphous material;

(*d*) there is no astigmatism present and no drift of the specimen; either of these factors would remove the radial symmetry.

From the form of (2.5.2.54) and a preknowledge of $|\Phi(U)|^2$, the zero crossings of $\sin\chi$ and the form of $E(U)$ may be deduced. Analysis of a through-focus series of images provides more complete and reliable information.

(2) Detail on a scale much smaller than the resolution of the electron microscope, as defined above, is commonly seen in electron micrographs, especially for crystalline samples. For example, lattice fringes, having the periodicity of the crystal lattice planes, with spacings as small as 0.6 Å in one direction, have been observed using a microscope having a resolution of about 2.5 Å (Matsuda *et al.*, 1978), and two-dimensionally periodic images showing detail on the scale of 0.5 to 1 Å have been observed with a similar microscope (Hashimoto *et al.*, 1977).

Such observations are possible because

(*a*) for periodic objects the diffraction amplitude $\Psi_0(uv)$ in (2.5.2.31) is a set of delta functions which may be multiplied by the corresponding values of the transfer function that will allow strong interference effects between the diffracted beams and the zero beam, or between different diffracted beams;

(*b*) the envelope functions for the WPOA, arising from incoherent imaging effects, do not apply for strongly scattering crystals; the more general expression (2.5.2.36) provides that the incoherent imaging factors will have much less effect on the interference of some sets of diffracted beams.

The observation of finely spaced lattice fringes provides a measure of some important factors affecting the microscope performance, such as the presence of mechanical vibrations, electrical interference or thermal drift of the specimen. A measure of the fineness of the detail observable in this type of image may therefore be taken as a measure of ‘instrumental resolution’.

2.5.2.10. *Electron diffraction in electron microscopes*

Currently most electron-diffraction patterns are obtained in conjunction with images, in electron microscopes of one form or another, as follows.

(*a*) Selected-area electron-diffraction (SAED) patterns are obtained by using intermediate and projector lenses to form an image of the diffraction pattern in the back-focal plane of the objective lens (Fig. 2.5.2.2). The area of the specimen from which the diffraction pattern is obtained is defined by inserting an aperture in the image plane of the objective lens. For parallel illumination of the specimen, sharp diffraction spots are produced by perfect crystals.

A limitation to the area of the specimen from which the diffraction pattern can be obtained is imposed by the spherical aberration of the objective lens. For a diffracted beam scattered through an angle α, the spread of positions in the object for which the diffracted beam passes through a small axial aperture in the image plane is $C_s\alpha^3$, *e.g.* for $C_s = 1$ mm, $\alpha = 5\times10^{-2}$ rad (10,0,0 reflection from gold for 100 keV electrons), $C_s\alpha^3 = 1250$ Å, so that a selected-area diameter of less than about 2000 Å is not feasible. For higher voltages, the minimum selected-area diameter decreases with λ^2 if the usual assumption is made that C_s increases for higher-voltage microscopes so that $C_s\lambda$ is a constant.

(*b*) Convergent-beam electron-diffraction (CBED) patterns are obtained when an incident convergent beam is focused on the specimen, as in an STEM instrument or an STEM attachment for a conventional TEM instrument.

For a large, effectively incoherent source, such as a conventional hot-filament electron gun, the intensities are added for each incident-beam direction. The resulting CBED pattern has an intensity distribution

$$I(uv) = \int |\Psi_{u_1v_1}(uv)|^2 \,\mathrm{d}u_1\,\mathrm{d}v_1, \qquad (2.5.2.55)$$

where $\Psi_{u_1v_1}(uv)$ is the Fourier transform of the exit wave at the specimen for an incident-beam direction u_1, v_1.

(*c*) Coherent illumination from a small bright source such as a field emission gun may be focused on the specimen to give an electron probe having an intensity distribution $|t(xy)|^2$ and a diameter equal to the STEM dark-field image resolution [equation (2.5.2.47)] of a few Å. The intensity distribution of the resulting microdiffraction pattern is then

$$|\Psi(uv)|^2 = |\Psi_0(uv) * T(uv)|^2, \qquad (2.5.2.56)$$

where $\Psi_0(uv)$ is the Fourier transform of the exit wave at the specimen. Interference occurs between waves scattered from the various incident-beam directions. The diffraction pattern is thus an in-line hologram as envisaged by Gabor (1949).

(*d*) Diffraction patterns may be obtained by using an optical diffractometer (or computer) to produce the Fourier transform squared of a small selected region of a recorded image. The optical diffraction-pattern intensity obtained under the ideal conditions specified under equation (2.5.2.54) is given, in the case of weak phase objects, by

$$I(uv) = \delta(uv) + 4\sigma^2|\Phi(uv)|^2\cdot\sin^2\chi(uv)\cdot E^2(uv) \qquad (2.5.2.57)$$

or, more generally, by

$$I(uv) = c\delta(uv) + |\Psi(uv)\cdot T(uv) * \Psi^*(uv)\cdot T^*(uv)|^2,$$

where $\Psi(uv)$ is the Fourier transform of the wavefunction at the exit face of the specimen and c is a constant depending on the characteristics of the photographic recording medium.

2.5.3. Space-group determination by convergent-beam electron diffraction* (P. Goodman)

2.5.3.1. *Introduction*

2.5.3.1.1. *CBED*

Convergent-beam electron diffraction, originating in the experiments of Kossel and Möllenstedt (Kossel & Möllenstedt, 1938) has been established over the past two decades as a powerful technique for the determination of space group in inorganic materials, with particular application when only microscopic samples are available. Relatively recently, with the introduction of the analytical electron microscope, this technique – abbreviated as CBED – has become available as a routine, so that there is now a considerable accumulation of data from a wide range of materials. A significant extension of the technique in recent times has been the introduction of LACBED (large-angle CBED) by Tanaka & Terauchi (1985). This technique allows an extensive angular range of single diffraction orders to be recorded and, although this method cannot be used for microdiffraction (since it requires an extensive single-crystal area), new LACBED applications appear regularly, particularly in the field of semiconductor research (see Section 2.5.3.6).

The CBED method relies essentially on two basic properties of transmission electron diffraction, namely the radical departure from Friedel’s law and the formation of characteristic extinction bands

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within space-group-forbidden reflections. Departure from Friedel's law in electron diffraction was first noted experimentally by Miyake & Uyeda (1950). The prediction of space-group-forbidden bands (within space-group-forbidden reflections) by Cowley & Moodie (1959), on the other hand, was one of the first successes of *N*-beam theory. A detailed explanation was later given by Gjønnes & Moodie (1965). These are known variously as 'GM' bands (Tanaka *et al.*, 1983), or more simply and definitively as 'GS' (glide–screw) bands (this section). These extinctions have a close parallel with space-group extinctions in X-ray diffraction, with the reservation that only screw axes of order two are accurately extinctive under *N*-beam conditions. This arises from the property that only those operations which lead to identical *projections* of the asymmetric unit can have *N*-beam dynamical symmetries (Cowley *et al.*, 1961).

Additionally, CBED from perfect crystals produces high-order defect lines in the zero-order pattern, analogous to the defect Kikuchi lines of inelastic scattering, which provide a sensitive measurement of unit-cell parameters (Jones *et al.*, 1977; Fraser *et al.*, 1985; Tanaka & Terauchi, 1985).

The significant differences between X-ray and electron diffraction, which may be exploited in analysis, arise as a consequence of a much stronger interaction in the case of electrons (Section 2.5.2). Hence, thin, approximately parallel-sided crystal regions must be used in high-energy (100 kV–1 MV) electron transmission work, so that diffraction is produced from crystals effectively infinitely periodic in only two dimensions, leading to the relaxation of three-dimensional diffraction conditions known as 'excitation error' (Chapter 5.2). Also, there is the ability in CBED to obtain data from microscopic crystal regions of around 50 Å in diameter, with corresponding exposure times of several seconds, allowing a survey of a material to be carried out in a relatively short time.

In contrast, single-crystal X-ray diffraction provides much more limited symmetry information in a direct fashion [although statistical analysis of intensities (Wilson, 1949) will considerably supplement this information], but correspondingly gives much more direct three-dimensional geometric data, including the determination of unit-cell parameters and three-dimensional extinctions.

The relative strengths and weaknesses of the two techniques make it useful where possible to collect both convergent-beam and X-ray single-crystal data in a combined study. However, all parameters *can* be obtained from convergent-beam and electron-diffraction data, even if in a somewhat less direct form, making possible space-group determination from microscopic crystals and microscopic regions of polygranular material. Several reviews of the subject are available (Tanaka, 1994; Steeds & Vincent, 1983; Steeds, 1979). In addition, an atlas of characteristic CBED patterns for direct phase identification of metal alloys has been published (Mansfield, 1984), and it is likely that this type of procedure, allowing *N*-beam analysis by comparison with standard simulations, will be expanded in the near future.

2.5.3.1.2. *Zone-axis patterns from CBED*

Symmetry analysis is necessarily tied to examination of patterns near relevant zone axes, since the most intense *N*-beam interaction occurs amongst the zero-layer zone-axis reflections, with in addition a limited degree of upper-layer (higher-order Laue zone) interaction. There will generally be several useful zone axes accessible for a given parallel-sided single crystal, with the regions between axes being of little use for symmetry analysis. Only one such zone axis can be parallel to a crystal surface normal, and a microcrystal is usually chosen at least initially to have this as the principal symmetry axis. Other zone axes from that crystal may suffer mild symmetry degradation because the *N*-beam lattice component ('excitation error' extension) will not have the symmetry of the structure (Goodman, 1974; Eades *et al.*, 1983).

Upper-layer interactions, responsible for imparting three-dimensional information to the zero layer, are of two types: the first arising from 'overlap' of dynamic shape transforms and causing smoothly varying modulations of the zero-layer reflections, and the second, caused by direct interactions with the upper-layer, or higher-order Laue zone lines, leading to a sharply defined fine-line structure. These latter interactions are especially useful in increasing the accuracy of space-group determination (Tanaka *et al.*, 1983), and may be enhanced by the use of low-temperature specimen stages. The presence of these defect lines in convergent-beam discs, occurring especially in low-symmetry zone-axis patterns, allows symmetry elements to be related to the three-dimensional structure (Section 2.5.3.5; Fig. 2.5.3.4*c*).

To the extent that such three-dimensional effects can be ignored or are absent in the zero-layer pattern the *projection approximation* (Chapter 5.2) can be applied. This situation most commonly occurs in zone-axis patterns taken from relatively thin crystals and provides a useful starting point for many analyses, by identifying the projected symmetry.

2.5.3.2. *Background theory and analytical approach*

2.5.3.2.1. *Direct and reciprocity symmetries: types I and II*

Convergent-beam diffraction symmetries are those of Schrödinger's equation, *i.e.* of crystal potential, plus the diffracting electron. The appropriate equation is given in Section 2.5.2 [equation (2.5.2.6)] and Chapter 5.2 [equation (5.2.2.1)] in terms of the real-space wavefunction ψ. The symmetry elements of the crystal responsible for generating pattern symmetries may be conveniently classified as of two types (I and II) as follows.

I. The *direct* (type I: Table 2.5.3.1) symmetries imposed by this equation on the transmitted wavefunction given *z*-axis illumination ($\mathbf{k}_0$, the incident wavevector parallel to *Z*, the surface normal) are just the symmetries of φ whose operation leaves both crystal and *z* axis unchanged. These are also called 'vertical' symmetry elements, since they contain *Z*. These symmetries apply equally in real and reciprocal space, since the operator ∇^2 has circular symmetry in both spaces and does nothing to degrade the symmetry in

Table 2.5.3.1. *Listing of the symmetry elements relating to CBED patterns under the classifications of 'vertical' (I), 'horizontal' (II) and combined or roto-inversionary axes*

I. Vertical symmetry elements		
	International symbols	
	$2, 3, 4, 6$ $(2_1, 3_1, \ldots)$	
	m (c)	
	a, b (n)	
II. Horizontal symmetry elements		
	Diperiodic symbols	BESR symbols
	$2'$	m
	$2'_1$	
	m'	1_R
	a', b', n'	
	$\bar{1}'$	2_R
I + II	$\bar{4}'$	4_R
I × II	$\bar{3}' = 3 \times \bar{1}'$	$6_R = 3 \cdot 2_R$
	$\bar{6}' = 3 \times m'$	31_R

references