

2. RECIPROCAL SPACE IN CRYSTAL-STRUCTURE DETERMINATION

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 Gjønnnes & 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. 2.5.3.4c).

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 , ...)
	<i>m</i>	(<i>c</i>)
	<i>a, b</i>	(<i>n</i>)
II. Horizontal symmetry elements		
	Diperiodic symbols	BESR symbols
	2'	<i>m</i>
	2' ₁	
	<i>m'</i>	1 _R
	<i>a', b', n'</i>	
	$\bar{1}'$	2 _R
I + II	$\bar{4}'$	4 _R
I × II	$\bar{3}' = 3 \times \bar{1}'$	6 _R = 3 · 2 _R
	$\bar{6}' = 3 \times m'$	31 _R