2.5. ELECTRON DIFFRACTION AND ELECTRON MICROSCOPY IN STRUCTURE DETERMINATION

(*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, $\alpha = 5 \times 10^{-2}$ 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

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

where $\Psi_{u_1 v_1}(uv)$ 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. Point-group and space-group determination by convergent-beam electron diffraction

By M. Tanaka

2.5.3.1. Introduction

Because the cross section for electron scattering is at least a thousand times greater than that for X-rays, and because multiple Bragg scattering preserves information on symmetry (such as the absence of inversion symmetry), electron diffraction is exquisitely sensitive to symmetry. The additional ability of modern electron-optical lenses to focus an electron probe down to nanometre dimensions, and so allow the study of nanocrystals too small for analysis by X-rays, has meant that the method of convergent-beam diffraction described here has now become the preferred method of symmetry determination for very small crystals, domains, twinned structures, quasicrystals, incommensurate structures and other imperfectly crystalline materials.

Convergent-beam electron diffraction (CBED) originated with the experiments of Kossel & Möllenstedt (1938). However, modern crystallographic investigations by CBED began with the studies performed by Goodman & Lehmpfuhl (1965) in a modified transmission electron microscope. They obtained CBED patterns by converging a conical electron beam with an angle of more than 10^{-3} rad on an ~30 nm diameter specimen area, which had uniform thickness and no bending. Instead of the

usual diffraction spots, diffraction discs (in Laue or transmission geometry) were produced. The diffraction intensity within a disc shows a specific symmetry, which enables one to determine the point groups and space groups of microcrystals. Unlike X-ray diffraction, the method is extremely sensitive to the presence or absence of inversion symmetry.

The method corresponding to CBED in the field of light optics is the conoscope method. Using a conoscope, we can identify whether a crystal is isotropic, uniaxial or biaxial, and determine the optic axis and the sign of birefringence of a crystal. When CBED, a conoscope method using an electron beam, is utilized, more basic properties of a crystal – the crystal point group and space group – can be determined.

Point- and space-group determinations are routinely also carried out by X-ray diffraction. This method, to which kinematical diffraction is applicable, cannot determine whether a crystal is polar or nonpolar unless anomalous absorption is utilized. As a result, the X-ray diffraction method can only identify 11 Laue groups among 32 point groups. CBED, based fully upon dynamical diffraction, can distinguish polar crystals from nonpolar crystals using only a nanometre-sized crystal, thus allowing the unique identification of all the point groups by inspecting the symmetries appearing in CBED discs.

As pointed out above, an unambiguous experimental determination of crystal symmetry, in the case of X-ray diffraction, is usually not possible because of the apparent centrosymmetry of the diffraction pattern, even for noncentrosymmetric crystals. However, methods based on structure-factor and X-ray intensity statistics remain useful for the resolution of space-group ambiguities, and are routinely applied to structure determinations from X-ray data. These methods are described in Chapter 2.1 of this volume.

In the field of materials science, correct space-group determination by CBED is often requested prior to X-ray or neutron structure refinement, in particular in the case of Rietveld refinements based on powder diffraction data.

CBED can determine not only the point and space groups of crystals but also crystal structure parameters – lattice parameters, atom positions, Debye–Waller factors and low-order structure factors. The lattice parameters can be determined from sub-micron regions of thin crystals by using higher-order Laue zone (HOLZ) reflections with an accuracy of 1×10^{-4}. Cherns *et al.* (1988) were the first to perform strain analysis of artificial multilayer materials using the large-angle technique (LACBED) (Tanaka *et al.*, 1980). Since then, many strain measurements at interfaces of various multilayer materials have been successfully conducted. In recent years, strain analysis has been conducted using automatic analysis programs, which take account of dynamical diffraction effects (Krämer *et al.*, 2000). We refer to the book of Morniroli (2002), which carries many helpful figures, clear photographs and a comprehensive list of papers on this topic.

Vincent *et al.* (1984*a*,*b*) first applied the CBED method to the determination of the atom positions of AuGeAs. They analysed the intensities of HOLZ reflections by applying a quasi-kinematical approximation. Tanaka & Tsuda (1990, 1991) and Tsuda & Tanaka (1995) refined the structural parameters of $SrTiO_3$ by applying the dynamical theory of electron diffraction. The method was extended to the refinements of CdS, $LaCrO_3$ and hexagonal $BaTiO_3$ (Tsuda & Tanaka, 1999; Tsuda *et al.*, 2002; Ogata *et al.*, 2004). Rossouw *et al.* (1996) measured the order parameters of TiAl through a Bloch-wave analysis of HOLZ reflections in a CBED pattern. Midgley *et al.* (1996) refined two positional parameters of $AuSn_4$ from the diffraction data obtained with a small convergence angle using multislice calculations.

Low-order structure factors were first determined by Goodman & Lehmpfuhl (1967) for MgO. After much work on low-order structure-factor determination, Zuo & Spence determined the 200 and 400 structure factors of MgO in a very modern

way, by fitting energy-filtered patterns and many-beam dynamical calculations using a least-squares procedure. For the low-order structure-factor determinations, the excellent comprehensive review of Spence (1993) should be referred to. Saunders *et al.* (1995) succeeded in obtaining the deformation charge density of Si using the low-order crystal structure factors determined by CBED. For the reliable determination of the low-order X-ray crystal structure factors or the charge density of a crystal, accurate determination of the Debye–Waller factors is indispensable. Zuo *et al.* (1999) determined the bond-charge distribution in cuprite. Simultaneous determination of the Debye–Waller factors and the low-order structure factors using HOLZ and zeroth-order Laue zone (ZOLZ) reflections was performed to determine the deformation charge density of $LaCrO_3$ accurately (Tsuda *et al.*, 2002).

CBED can also be applied to the determination of lattice defects, dislocations (Cherns & Preston, 1986), stacking faults (Tanaka, 1986) and twins (Tanaka, 1986). Since this topic is beyond the scope of the present chapter, readers are referred to pages 156 to 205 of the book by Tanaka *et al.* (1994).

We also mention the book by Spence & Zuo (1992), which deals with the whole topic of CBED, including the basic theory and a wealth of literature.

2.5.3.2. Point-group determination

When an electron beam traverses a thin slab of crystal parallel to a zone axis, one can easily imagine that symmetries parallel to the zone axis should appear in the resulting CBED pattern. It is, however, more difficult to imagine what symmetries appear due to symmetries perpendicular to the incident beam. Goodman (1975) pioneered the clarification of CBED symmetries for the twofold rotation axis and mirror plane perpendicular to the incident beam, and the symmetry of an inversion centre, with the help of the reciprocity theorem of scattering theory. Tinnappel (1975) solved many CBED symmetries at various crystal settings with respect to the incident beam using a group-theoretical treatment. Buxton *et al.* (1976) also derived these results from first principles, and generalized them to produce a systematic method for the determination of the crystal point group. Tanaka, Saito & Sekii (1983) developed a method to determine the point group using simultaneously excited many-beam patterns. The point-group-determination method given by Buxton *et al.* (1976) is described with the aid of the description by Tanaka, Saito & Sekii (1983) in the following.

2.5.3.2.1. Symmetry elements of a specimen and diffraction groups

Since CBED uses the Laue geometry, Buxton *et al.* (1976) assumed a perfectly crystalline specimen in the form of a parallel-sided slab which is infinite in two dimensions. The symmetry elements of the *specimen* (as distinct from those of an infinite crystal) form 'diffraction groups', which are isomorphic to the point groups of the diperiodic plane figures and Shubnikov groups of coloured plane figures. The diffraction groups of a specimen are determined from the symmetries of CBED patterns taken at various orientations of the specimen. The *crystal* point-group of the specimen is identified by referring to Fig. 2.5.3.4, which gives the relation between diffraction groups and crystal point groups.

A specimen that is parallel-sided and is infinitely extended in the x and y directions has ten symmetry elements. The symmetry elements consist of six two-dimensional symmetry elements and four three-dimensional ones. The operation of the former elements transforms an arbitrary coordinate (x, y, z) into (x', y', z), with z remaining the same. The operation of the latter transforms a coordinate (x, y, z) into (x', y', z'), where $z' \neq z$. A vertical mirror plane m and one-, two-, three-, four- and sixfold rotation axes that are parallel to the surface normal $\mathbf{z}$ are the two-