

2.4. POWDER AND RELATED TECHNIQUES: ELECTRON AND NEUTRON TECHNIQUES

By integrating the two-beam intensity expression over excitation error, Blackman (1939) obtained the expression for the ratio of dynamical to kinematical intensities:

$$I_{\text{dyn}}/I_{\text{kin}} = A_h^{-1} \int_0^{A_h} J_0(2x) dx, \quad (2.4.1.4)$$

where $J_0(x)$ is the zero-order Bessel function, $A_h = \sigma H \Phi_h$ with the interaction constant $\sigma = 2\pi m e \lambda / h^2$, and H is the crystal thickness. Careful measurements on ring patterns from thin aluminium films by Horstmann & Meyer (1962) showed agreement with the 'Blackman curve' [from equation (2.4.1.4)] to within about 5% with some notable exceptions. Deviations of up to 40 to 50% from the Blackman curve occurred for several reflections, such as 222 and 400, which are second-order reflections from strong inner reflections. A practical algorithm for implementing Blackman corrections has been published by Dvoryankina & Pinsker (1958).

Such deviations result from plural-beam *systematic interactions*, the coherent multiple scattering between different orders of a strong inner reflection. When the Bragg condition is satisfied for one order, the excitation errors for the other orders are the same for all possible crystal orientations and these other orders contribute systematically to the ring-pattern intensities. A correction for the effects of systematic interactions may be made by use of the Bethe second approximation (Bethe, 1928) (see Chapter 8.8).

For non-systematic reflections, corresponding to reciprocal-lattice points not collinear with the origin and the reciprocal-lattice point of interest, the averaging over all crystal orientations ensures that the powder-pattern intensity calculated from the two-beam formula will not be appreciably affected. Appreciable effects from non-systematic interactions may, however, occur when the averaging is over a limited range of crystal orientations, as in the case of strong preferred orientations. It was shown theoretically by Turner & Cowley (1969) and experimentally by Imamov, Pannhorst, Avilov & Pinsker (1976) that appreciable modifications of intensities of oblique-texture patterns may result from non-systematic interactions for particular tilt angles, especially for heavy-atom materials [see also Avilov, Parmon, Semiletov & Sirota (1984)].

The techniques for the measurement of electron diffraction intensities are described in Chapter 7.2. Most commonly electron diffraction powder patterns are recorded by photographic methods and a microdensitometer is used for quantitative intensity measurement. The Grigson scanning method, using a scintillator and photomultiplier to record intensities as the pattern is scanned over a fine slit, has considerable advantages in terms of linearity and range of the intensity scale (Grigson, 1962). This method also has the advantage that it may readily be combined with an energy filter so that only elastically scattered electrons (or electrons inelastically scattered with a particular energy loss) may be recorded.

Small-angle electron diffraction may give useful information in some cases, but must be interpreted carefully because the features may result from multiple scattering or other artefacts. It may give additional details of periodicity (super-periods) and deviations of the real symmetry from the ideal symmetry suggested by other data. Care must be taken with the interpretation of additional reflections, as they may relate to the structure of small regions that are not typical of the bulk specimens such as are examined by X-ray diffraction.

The techniques for interpretation of electron diffraction powder-pattern intensities follow those for X-ray patterns when the kinematical approximation is valid. For very small crystals,

giving very broad rings, it is possible to use the method, commonly applied for diffraction by gases, of performing a Fourier transform to obtain a radial distribution function (Goodman, 1963).

2.4.1.5. Crystal-size analysis

The methods used in X-ray diffraction for the determination of average crystal size or size distributions may be applied to electron diffraction powder patterns. Except in the case of very small crystal dimensions, several factors peculiar to electrons should be taken into consideration.

(a) Unless energy filtering is used to remove inelastically scattered electrons, a component is added to the rings broadened by the effects of inelastic scattering involving electronic excitations. Since the mean free paths for such processes are of the order of 10^3 \AA and the angular spread of the scattered electrons is 10^{-3} to 10^{-4} rad, the ring broadening for thick samples may be equivalent to the broadening for a crystal size of the order of 100 \AA .

(b) When a powder sample consists of separated crystallites having faces not predominantly parallel or perpendicular to the incident beam, the diffraction rings may be appreciably broadened by refraction effects. The refractive index for electrons is given, to a first approximation, by

$$n = 1 + \Phi_0/2E,$$

where Φ_0 is the mean inner potential of the crystal, typically 10 to 20 V, and E is the accelerating voltage of the incident electron beam. For the beam passing through the two faces of a 90° wedge, each at an angle $\alpha = 45^\circ$ to the beam, for example, the beam is deflected by an amount

$$\Delta = \Phi_0/E = 1.5 \times 10^{-4} \text{ rad}$$

for an inner potential of 15 V and $E = 100 \text{ kV}$. The broadening of the ring by such deflections can correspond to the broadening due to a particle size of $\lambda/2\Delta \simeq 120 \text{ \AA}$.

For crystallites of regular habit, such as the small cubic crystals of MgO smoke, the ring broadening from this source is strongly dependent on the crystallographic planes involved (Sturkey & Frevel, 1945; Cowley & Rees, 1947; Honjo & Mihama, 1954). For more isometric crystal shapes, this dependence is less marked and the broadening has been estimated (Cowley & Rees, 1947) as equivalent to that due to a particle size of about 200 \AA .

2.4.1.6. Unknown-phase identification: databases

To a limited extent, the compilations of data for X-ray diffraction, such as the ICDD Powder Diffraction File, may be used for the identification of phases from electron diffraction data. The nature of the electron diffraction data and the circumstances of its collection have prompted the compilation of databases specifically for use with electron diffraction. Factors taken into consideration include the following.

(a) Because of the increasing use of single-crystal patterns obtained in the SAED mode in an electron microscope, the use of single-crystal spot patterns, in addition to powder patterns, must be considered for purposes of identification. Methods for the analysis of single-crystal patterns are summarized in Section 5.4.1.

(b) The deviations from kinematical scattering conditions may be large, especially for single-crystal patterns, so that little reliance can be placed on relative intensities, and reflections kinematically forbidden may be present.