2.4. Powder and related techniques: electron and neutron techniques

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2.4.1. Electron techniques (By J. M. Cowley)

2.4.1.1. *Powder-pattern geometry*

The electron wavelengths normally used to obtain powder patterns from thin films of polycrystalline materials lie in the range 8×10^{-2} to 2×10^{-2} Å (20 to 200 kV accelerating voltages). The maximum scattering angles ($2\theta_B$) observed are usually less than 10^{-1} rad.

Patterns are usually recorded on flat photographic plates or films and a small-angle approximation is applied. For a camera length L, the distance from the specimen to the photographic plate in the absence of any intervening electron lenses, the approximation is made that, for a diffraction ring of radius r,

$$\lambda/d = 2\sin\theta \simeq \tan 2\theta = r/L,$$

or the interplanar spacing, d, is given by

$$d = L\lambda/r. \qquad (2.4.1.1)$$

For a scattering angle of 10^{-1} rad, the error in this expression is 0.5%. A better approximation, valid to better than 0.1% at 10^{-1} rad, is

$$d = (L\lambda/r)(1 + 3r^2/8L^2). \qquad (2.4.1.2)$$

The 'camera constant' $L\lambda$ may be obtained by direct measurement of L and the accelerating voltage if there are no electron lenses following the specimen.

Direct electronic recording of intensities has great advantages over photographic recording (Tsypursky & Drits, 1977).

In recent years, electron diffraction patterns have been obtained most commonly in electron microscopes with three or more post-specimen lenses. The camera-constant values are then best obtained by calibration using samples of known structure.

With electron-optical instruments, it is possible to attain collimations of 10^{-6} rad so that for scattering angles of 10^{-1} rad an accuracy of 10^{-5} in d spacings should be possible in principle but is not normally achievable. In practice, accuracies of about 1% are expected. Some factors limiting the accuracy of measurement are mentioned in the following sections. The small-angle-scattering geometry precludes application of any of the special camera geometries used for high-accuracy measurements with X-rays (Chapter 2.3).

2.4.1.2. *Diffraction patterns in electron microscopes*

The specimens used in electron microscopes may be self-supporting thin films or fine powders supported on thin films, usually made of amorphous carbon. Specimen thicknesses must be less than about 10^3 Å in order to avoid perturbations of the diffraction patterns by strong multiple-scattering effects. The selected-area electron-diffraction (SAED) technique [see Section 2.5.1 in *IT* B (1993)] allows sharply focused diffraction patterns to be obtained from regions 10^3 to 10^5 Å in diameter. For the smaller ranges of selected-area regions, specimens may give single-crystal patterns or very spotty ring paterns, rather than continuous ring patterns, because the number of crystals present in the field of view is small unless the crystallite size is of the order of 100 Å or less. By use of the convergent-beam electron-diffraction (CBED) technique, diffraction patterns can be obtained from regions of diameter 100 Å [see Section 2.5.2 in *IT* B (1993)] or, in the case of some specialized instruments, regions less than 10 Å in diameter. For these reasons, the methods for phase identification from electron diffraction patterns and the corresponding databases (see Subsection 2.4.1.6) are increasingly concerned with single-crystal spot patterns in addition to powder patterns.

Instrument manufacturers usually provide values of camera lengths, L, or camera constants, $L\lambda$, for a wide range of designated lens-current settings. It is advisable to check these calibrations with samples of known structure and to determine calibrations for non-standard lens settings.

The effective camera length, L, is dependent on the specimen height within the objective-lens pole-piece. If a specimen-height adjustment (a z-lift) is provided, it should be adjusted to give a predetermined lens current, and hence focal length, of the objective lens.

In some microscopes, at particular lens settings the projector lenses may introduce a radial distortion of the diffraction pattern. This may be measured with a suitable standard specimen.

2.4.1.3. *Preferred orientations*

The techniques of specimen preparation may result in a strong preferred orientation of the crystallites, resulting in strong arcing of powder-pattern rings, the absence of some rings, and perturbations of relative intensities.

For example, small crystals of flaky habit deposited on a flat supporting film may be oriented with one reciprocal-lattice axis preferentially perpendicular to the plane of the support. A ring pattern obtained with the incident beam perpendicular to the support then shows only those rings for planes in the zone parallel to the preferred axis. Such orientation is detected by the appearance of arcing and additional reflections when the supporting film is tilted. Tilted specimens give the so-called oblique texture patterns which provide a rich source of three-dimensional diffraction information, used as a basis for crystal structure analysis.

A full discussion of the texture patterns resulting from preferred orientations is given in Section 2.5.3 of *IT* B (1993).

2.4.1.4. *Powder-pattern intensities*

In the kinematical approximation, the expression for intensities of electron diffraction follows that for X-ray diffraction with the exception that, because only small angles of diffraction are involved, no polarization factor is involved. Following Vainshtein (1964), the intensity per unit length of a powder line is

$$I(h) = J_0\lambda^2 \left| \frac{\Phi_h}{\Omega} \right|^2 V \frac{d_h^2 M}{4\pi L\lambda}, \qquad (2.4.1.3)$$

where J_0 is the incident-beam intensity, Φ_h is the structure factor, Ω is the unit-cell volume, V is the sample volume, and M is the multiplicity factor.

The kinematical approximation has limited validity. The deviations from this approximation are given to a first approximation by the two-beam approximation to the dynamical-scattering theory. Because an averaging over all orientations is involved, the many-beam dynamical-diffraction effects are less evident than for single-crystal patterns.

references