2.5. Energy-dispersive techniques

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2.5.1. Techniques for X-rays (By B. Buras and L. Gerward)

X-ray energy-dispersive diffraction, XED, invented in the late sixties (Giessen & Gordon, 1968; Buras, Chwaszczewska, Szarras & Szmid 1968), utilizes a primary X-ray beam of polychromatic ('white') radiation. XED is the analogue of white-beam and time-of-flight neutron diffraction (*cf.* Section 2.5.2). In the case of powdered crystals, the photon energy (or wavelength) spectrum of the X-rays scattered through a fixed optimized angle is measured using a semiconductor detector connected to a multichannel pulse-height analyser. Single-crystal methods have also been developed.

2.5.1.1. *Recording of powder diffraction spectra*

In XED powder work, the incident- and scattered-beam directions are determined by slits (Fig. 2.5.1.1). A powder spectrum is shown in Fig. 2.5.1.2. The Bragg equation is

$$2d\sin\theta_0 = \lambda = hc/E, \qquad (2.5.1.1a)$$

where d is the lattice-plane spacing, θ_0 the Bragg angle, λ and E the wavelength and the photon energy, respectively, associated with the Bragg reflection, h is Planck's constant and c the velocity of light. In practical units, equation (2.5.1.1*a*) can be written

$$E(\text{keV})\,d(\text{Å})\sin\theta_0 = 6.199. \qquad (2.5.1.1b)$$

The main features of the XED powder method where it differs from standard angle-dispersive methods can be summarized as follows:

(*a*) The incident beam is polychromatic.

(*b*) The scattering angle $2\theta_0$ is fixed during the measurement but can be optimized for each particular experiment. There is no mechanical movement during the recording.

(*c*) The whole energy spectrum of the diffracted photons is recorded simultaneously using an energy-dispersive detector.

The scattering angle is chosen to accommodate an appropriate number of Bragg reflections within the available photon-energy range and to avoid overlapping with fluorescence lines from the sample and, when using an X-ray tube, characteristic lines from the anode. Overlap can often be avoided because a change in the scattering angle shifts the diffraction lines to new energy positions, whereas the fluorescence lines always appear at the same energies. Severe overlap problems may be encountered when the sample contains several heavy elements.

The detector aperture usually collects only a small fraction of the Debye–Scherrer cone of diffracted X-rays. The collection of an entire cone of radiation greatly increases the intensities. Also, it makes it possible to overcome crystallite stratistics problems and preferred orientations in very small samples (Holzapfel & May, 1982; Häusermann, 1992).

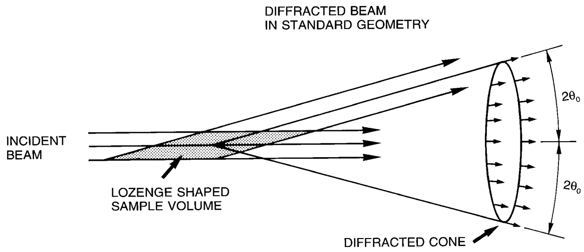

Fig. 2.5.1.1. Standard and conical diffraction geometries: $2\theta_0$ = fixed scattering angle. At low scattering angles, the lozenge-shaped sample volume is very long compared with the beam cross sections (after Häusermann, 1992).

2.5.1.2. *Incident X-ray beam*

(*a*) *Bremsstrahlung from an X-ray tube*

Bremsstrahlung from an X-ray diffraction tube provides a useful continuous spectrum for XED in the photon-energy range 2–60 keV. However, one has to avoid spectral regions close to the characteristic lines of the anode material. A tungsten anode is suitable because of its high output of white radiation having no characteristic lines in the 12–58 keV range.

A drawback of *Bremsstrahlung* is that its spectral distribution is difficult to measure or calculate with accuracy, which is necessary for a structure determination using integrated intensities [see equation (2.5.1.7)]. *Bremsstrahlung* is strongly polarized for photon energies near the high-energy limit, while the low-energy region has a weak polarization. The direction of polarization is parallel to the direction of the electron beam from the filament to the anode in the X-ray tube. Also, the polarization is difficult to measure or calculate.

(*b*) *Synchrotron radiation*

Synchrotron radiation emitted by electrons or positrons, when passing the bending magnets or insertion devices, such as wigglers, of a storage ring, provides an intense smooth spectrum for XED.

Both the spectral distribution and the polarization of the synchrotron radiation can be calculated from the parameters of the storage ring. Synchrotron radiation is almost fully polarized in the electron or positron orbit plane, *i.e.* the horizontal plane, and inherently collimated in the vertical plane. Full advantage of these features can be obtained using a vertical scattering plane. However, the mechanical construction of the diffractometer, the placing of furnaces, cryogenic equipment, *etc.* are easier to handle when the X-ray scattering is recorded in the horizontal plane. Recent XED facilities at synchrotron-radiation sources have been described by Besson & Weill (1992), Clark (1992), Häusermann (1992), Olsen (1992), and Otto (1997).

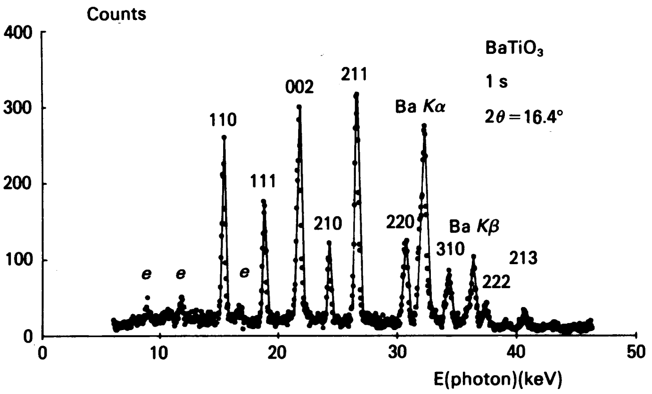

Fig. 2.5.1.2. XED powder spectrum of BaTiO$_3$ recorded with synchrotron radiation from the electron storage ring DORIS at DESY-HASYLAB in Hamburg, Germany. Counting time 1 s. Escape peaks due to the Ge detector are denoted by *e* (from Buras, Gerward, Glazer, Hidaka & Olsen, 1979).