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The easy wavelength selection makes it possible to avoid specimen fluorescence, to record data on both sides of an absorption edge for anomalous-scattering studies, to select optimum angles and wavelengths for lattice-parameter measurements, and to vary the dispersion. Short-wavelength radiation can be used for uncomplicated patterns without the background occurring in X-ray tube spectra. Fig. 2.3.2.2 shows a silicon pattern obtained with 1.0 Å X-rays in which there are twice as many reflections as can be recorded with Cu $K\alpha$, and the background remains very low out to the highest 2θ angles. The short wavelengths (~ 0.7 Å) are especially useful for samples mounted in cryostats, furnaces, and pressure cells.

Using an incident-beam tunable monochromator, no continuous radiation reaches the specimen and a wavelength can be selected that gives a high peak-to-background ratio and no specimen fluorescence. If the specimen contains different chemical phases, patterns can be recorded using wavelengths on both sides of the absorption edge to enhance one of the patterns as an aid in identification. This is illustrated in Fig. 2.3.2.3 for a mixture of Ni and ZnO powders. A pattern (*a*) with maximum peak-to-background ratio is obtained with a wavelength slightly longer than the Ni *K*-absorption edge but using a wavelength shorter than the edge (*b*) causes high Ni *K* fluorescence background. The relative intensities of the peaks in each compound are the same with both wavelengths. However, the large change in the Ni absorption across the edge caused a large difference in the ratio of Ni/ZnO intensities. The Ni(111) decreased by 85% and the intensity ratio Ni(111)/ZnO(102) dropped from 4.2 to 1.3.

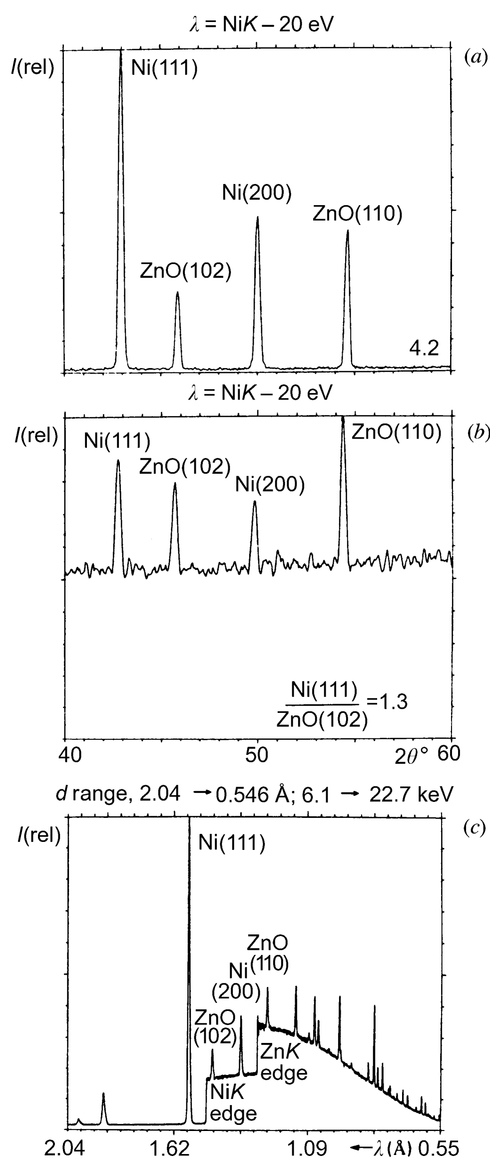

Fig. 2.3.2.3. Synchrotron-radiation patterns of a mixture of Ni and ZnO powders. Diffraction pattern using a wavelength (*a*) slightly longer than the Ni *K*-absorption edge and (*b*) slightly shorter. (*c*) High-resolution energy-dispersive diffraction (EDD) pattern.

Modified conventional vertical-scanning diffractometers are used to avoid intensity losses from the strong polarization in the horizontal plane. The six basic powder diffraction methods that have been used are:

(*a*) Monochromatic X-rays with θ–2θ scanning and flat specimen as in conventional X-ray tube methods but using parallel-beam X-ray optics. This is the most widely applicable method for polycrystalline materials.

(*b*) Monochromatic X-rays with fixed specimen and 2θ detector scan, used for analysing texture, preferred orientation, and grazing-incidence diffraction.

(*c*) Monochromatic X-rays with a capillary specimen and scanning receiving slit or position-sensitive detector.

(*d*) Energy-dispersive diffraction using a step-scanned channel monochromator, selectable fixed θ–2θ positions, and conventional scintillation counter and electronics. The instrumentation is the same as (*a*) and may be used in methods that require a stationary specimen.

(*e*) Energy-dispersive diffraction using the white beam, solid-state detector and multichannel analyser, and selected fixed θ–2θ. This is the method frequently used with synchrotron and X-ray tube sources but it has low pattern resolution (Giessen & Gordon, 1968).

(*f*) Angle-dispersive or energy-dispersive experiments with an imaging-plate detector, whereby complete Debye–Scherrer rings are recorded simultaneously, as in some film methods (Subsection 2.3.4.1) (*e.g.* Piltz *et al.*, 1992). This is a particularly useful technique for studies under non-ambient conditions, such as experiments at ultra-high pressure (*e.g.* McMahon & Nelmes, 1993).

2.3.2.1. *Monochromatic radiation, θ–2θ scan*

The X-ray optics of a plane-wave parallel-beam diffractometer is shown schematically in Fig. 2.3.2.4(*a*). The primary white beam is limited by slits at *C*1. A channel monochromator CM is used because it has the important property of maintaining the same direction and position for a wide range of wavelengths. It may be used in the dispersive setting with respect to the specimen or in the parallel setting [Fig. 2.3.2.4(*b*)]. The monochromatic beam is larger than the entrance slit ES and it is unnecessary to realign the powder diffractometer when changing wavelengths. The monochromator can be mounted on a stripped diffractometer for easy alignment and step scanning.

There are no characteristic spectral lines and the wavelength calibration of the monochromator is made by step scanning the monochromator across absorption edges of elements in a specimen or pure element foils placed in the beam. The wavelength accuracy is limited by the uncertainty as to what feature of the edge should be measured and which one was used for the wavelength tables. A standard powder sample such as NIST silicon 640b whose lattice parameter is known with moderately high precision can also be used. An alternative method is to measure the reflection angle of a single-crystal plate of float-zones oxygen-free silicon whose lattice parameter is known to 1 part in 10^{-7} and to determine the wavelength from

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the Bragg equation (Hart, 1981). The accuracy is then limited by the angular accuracy of the diffractometer and the orientation setting.

It is necessary to monitor the monochromatic beam intensity I_0, which changes during the recording due to decreasing storage-ring current, orbital shifts or other factors. This can be done by inserting a low-absorbing ionization chamber in the beam or by using a scintillation counter to measure scattering from an inclined thin beryllium foil, kapton or other low-absorbing material. The data are recorded and used to correct the observed intensities. The monitored counts can also be used as a timer for step scanning if a sufficient number are recorded for good counting statistics.

The entrance slit ES determines the irradiated specimen length, which is equal to ES/sin θ_s. Vertical parallel slits VPS with $\delta \simeq 2^\circ$ are used to limit the axial divergence. The longer the distance between the specimen and detector, the smaller the asymmetry, and a vacuum path should be used to avoid air-absorption losses. The specimen may be used in either reflection or transmission simply by rotating it 90° around the diffractometer axis from its previous position.

The diffracted beam can be defined by a receiving slit (Parrish, Hart & Huang, 1986), horizontal parallel slits HPS [Fig. 2.3.2.4(*a*)] (Parrish & Hart, 1985) or a high-quality single-crystal plate which acts as a very narrow receiving slit [Fig. 2.3.2.4(*b*)] (Cox, Hastings, Thomlinson & Prewitt, 1983; Hastings *et al.*, 1984). If a receiving slit is used, the intensity, profile width and shape are determined by the widths of both ES and RS. If either one is much wider than the other, the profile has a flat top. Increasing the RS width and keeping ES constant causes symmetrical profile broadening and increases the intensity as in conventional focusing diffractometry. There are disadvantages in using a receiving slit because the intensities are low and

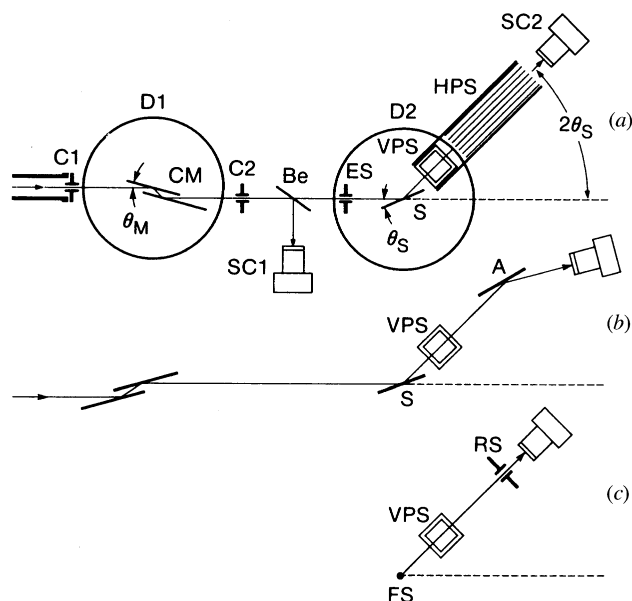

Fig. 2.3.2.4. (*a*) Optics of dispersive parallel-beam method for synchrotron X-rays. *C*1 primary-beam collimator, *D*1 diffractometer for channel monochromator CM, *C*2 antiscatter shield, Be beryllium foil for monitor, SC1 and SC2 scintillation counters, ES entrance slit on powder diffractometer *D*2, VPS vertical parallel slits to limit axial divergence, HPS horizontal parallel slits, which determine the resolution. (*b*) CM in nondispersive setting and crystal analyser *A* used as a narrow receiving slit. (*c*) Fibre specimen FS with receiving slit RS or with position-sensitive detector (not shown) with RS removed.

it causes the same specimen-surface-displacement and transparency errors as the focusing geometries.

A set of horizontal parallel (Soller) slits is advantageous because of the much higher intensity and it eliminates the displacement errors. The profiles of specimens without broadening effects have the same FWHM as the aperture of the slits, equation (2.3.1.7). The FWHM increases as $\tan\theta$ due to wavelength dispersion. By increasing the length of the foils and keeping the same spacing, the aperture can be reduced to increase the resolution without large loss of intensity. A set of 365 mm long slits with 0.05° aperture has been used and even smaller apertures are feasible. Longer slits decrease the fluorescence intensity (if any) reaching the detector. They must be carefully made and aligned to avoid loss of intensity and should be evacuated or filled with He to avoid air-absorption losses.

The use of a crystal analyser eliminates fluorescence and gives the highest resolution powder profiles with FWHM $= 0.02$ to $0.05^\circ 2\theta$, depending on the quality of the crystal (Hastings *et al.*, 1984). The alignment of the crystal is critical and must be done with remote automated control every time the wavelength is changed. Displacement aberrations are eliminated but the intensity is much lower than the HPS because of the small rocking angle and low integrated reflectivity of the crystal.

The correct orientation of crystalline powder particles for reflection is far more restrictive for the parallel beam than the X-ray tube divergent beam. A much smaller number of particles will have the exact orientation for reflection, and thus the recorded intensity will be lower and relative intensities less accurate. If the specimen is stationary, the standard deviations of the intensities due to particle size are six to nine times higher than in focusing methods (Parrish, Hart & Huang, 1986). It also becomes more difficult to achieve the completely randomly oriented specimens required for structure determination and quantitative analysis and, as in X-ray tube data, a preferred-orientation term is included in the structure refinement. It is, therefore, essential to use small particles $< 10\,\mu$m and to rotate the specimen. Some investigators prefer to oscillate the specimen over a small angle but this is not as effective as rotation.

The profiles are virtually symmetrical except at small angles where axial divergence causes asymmetry. The profiles in Fig. 2.3.2.5 show the differences in the shape and resolution obtained with conventional focusing (*a*) and parallel-beam synchrotron methods (*b*). The effect of the higher resolution on a mixture of nearly equal volumes of quartz, orthoclase, and feldspar recorded with X-ray tube focusing methods is shown in Fig. 2.3.2.5(*c*) and with synchrotron radiation in Fig. 2.3.2.5(*d*). The symmetry and nearly constant simple instrument function make it easier to separate overlapping reflections and simplify the profile-fitting procedures and the interpretation of specimen-broadening effects.

The early crystal-structure studies using Rietveld refinement were not as successful with X-ray tube focusing methods as they were with neutron diffraction because the complicated instrument function made profile fitting difficult and inaccurate. The development of synchrotron powder methods with simple symmetrical instrument function, high resolution, and the use of longer wavelengths to increase the dispersion have made structural studies as successful as with neutrons, and have the advantage of orders-of-magnitude higher intensity. Some examples are described by Attfield, Cheetham, Cox & Sleight (1988), Lehmann, Christensen, Fjellvåg, Feidenhans'l & Nielsen (1987), and *ab initio* structure determinations by

McCusker (1988), Cernik *et al.* (1991), Morris, Harrison, Nicol, Wilkinson & Cheetham (1992), and others.

Structures have also been solved using a two-stage method in which the integrated intensities are determined by profile fitting the individual reflections and used in a powder least-squares refinement method (*POWLS*) (Will, Bellotto, Parrish & Hart, 1988). The method was tested with silicon, which gave R(Bragg) 0.7%, and quartz, which gave 1.6%, which is a good test of the high quality of the experimental data and the profile-fitting procedure. Fig. 2.3.2.6 shows Fourier maps of orthorhombic Mg_2GeO_4 calculated using Fourier coefficients taken directly from the profile-fitting intensities.

Other types of powder studies have been carried out successfully. For example, these have been used in anomalous-scattering studies (Will, Masciocchi, Hart & Parrish, 1987; Will, Masciocchi, Parrish & Hart, 1987), Warren–Averbach profile-broadening analysis (Huang, Hart, Parrish & Masciocchi, 1987), studies of texture in thin films (Hart, Parrish & Masciocchi, 1987), and precision lattice-parameter determination (Hart, Cernik, Parrish & Toraya, 1990).

2.3.2.2. *Cylindrical specimen, 2θ scan*

The flat specimen can be replaced by a thin cylindrical [Fig. 2.3.2.4(*c*)] specimen as used in powder cameras. The powder can be coated on a thin fibre or reactive materials can be forced into a capillary to avoid contact with air. The intensity is lower than for flat specimens because of the smaller beam, and less powder is required. Thompson, Cox & Hastings (1987) used the method to determine the structure of Al_2O_3 by Rietveld refinement. They used a two-crystal incident-beam Si(111) monochromator; the first crystal was flat and the second a cylindrically bent triangular plate for sagittal focusing to form a 4×2 mm beam with spectral bandwidth $\Delta\lambda/\lambda \simeq 10^{-3}$.

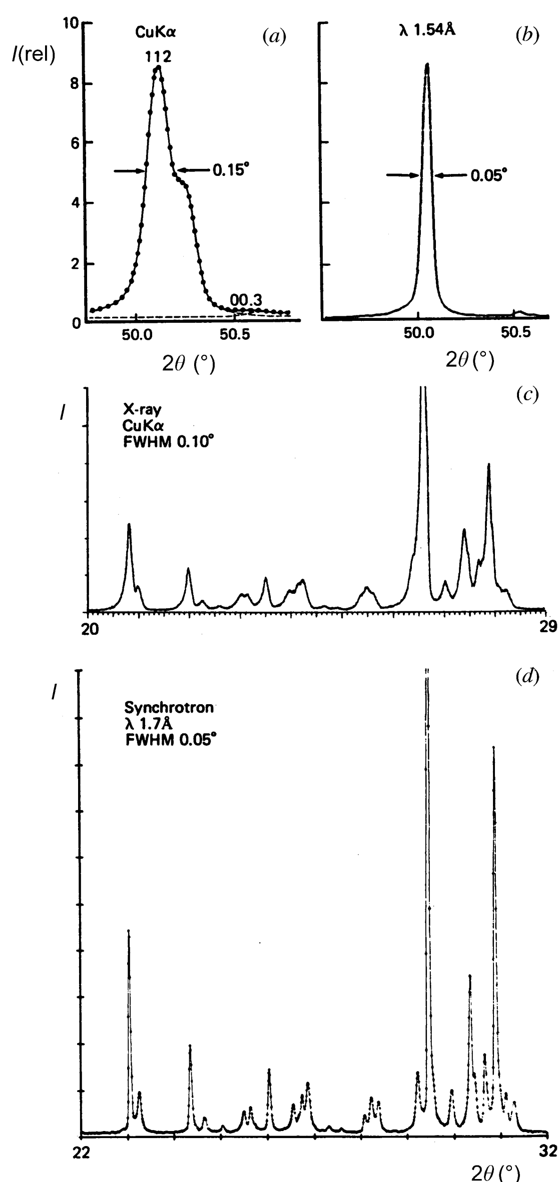

Fig. 2.3.2.5. Comparison of patterns obtained with a conventional focusing diffractometer (*a*) and (*c*), and synchrotron parallel-beam method (*b*) and (*d*). (*a*) and (*b*) quartz powder profiles; (*c*) and (*d*) mixture of equal amounts of quartz, orthoclase, and feldspar.

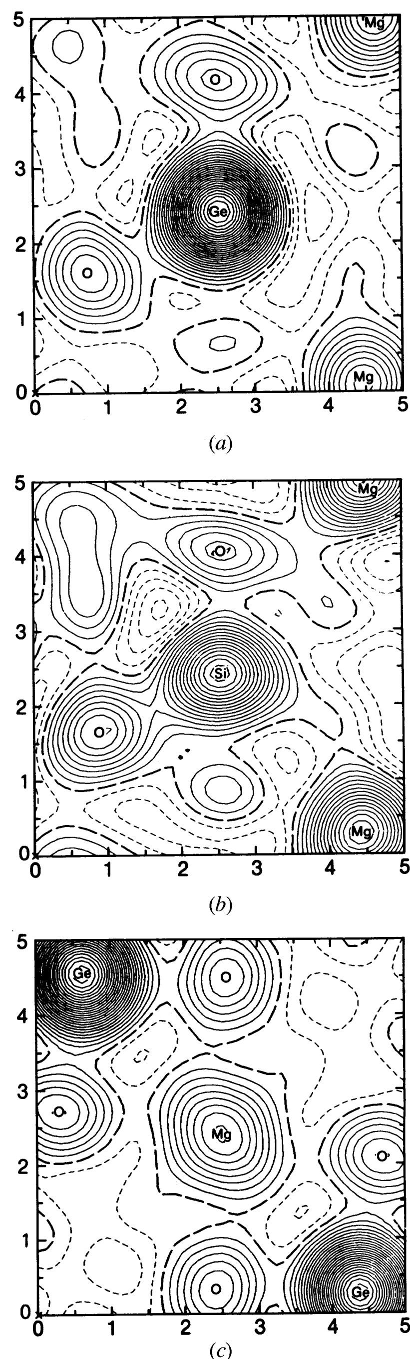

Fig. 2.3.2.6. (*a*) and (*c*) Fourier maps of orthorhombic Mg_2GeO_4 calculated directly from profile-fitted synchrotron powder data. (*b*) Fourier section of isostructural Mg_2SiO_4 calculated from single-crystal data for comparison with (*a*).

references