

Guest Comment

The papers in this special issue of the *Australian Journal of Physics* were presented at an International Symposium on X-ray Powder Diffractometry in Fremantle, Western Australia, in August 1987. The Symposium, with 160 participants, followed the Fourteenth Congress of the International Union of Crystallography in Perth.

A sense of urgency and excitement has been injected into the field of X-ray powder diffractometry, even though it is such a routinely used technique for characterising materials, by a few recent advances in technology. These are the advent of full-profile analysis, energy-dispersive and area detectors, and synchrotron sources, coupled with the automatic collection and analysis of data.

A measure of the importance of powder diffractometry in current thinking is the fact that a new Commission on Powder Diffraction came into being at the XIVth IUCr Congress; powder diffractometry featured in a microsymposium, and there were 27 poster papers.

The Fremantle meeting followed immediately and included a further 27 keynote and invited papers, together with 32 contributed poster papers. Two special events on the program gave a historical perspective; the second Hanawalt Award of the Joint Committee for Powder Diffraction Standards, International Centre for Diffraction Data, awarded to Dr William Parrish, and the opening address giving a short history of the Rietveld profile analysis method by its originator, Dr Hugo Rietveld. Written versions of the Hanawalt Oration and of the Rietveld address are presented in this volume, but the human touches are missing. In a way, the meeting served as a memorial to Dan Hanawalt, who passed away in June 1987 at the age of 84.

Hanawalt is remembered for pioneering the system of identification of crystalline substances which bears his name and which is still the most powerful method of approach; the first 1000 substances examined in his Dow Chemical laboratory provided the basis for set 1 of the Powder Diffraction File. Although he went on to study magnesium and its alloys, and received two gold medals for scientific and technological achievements in this field, he continued to be interested in X-ray identification, and from 1974–78 he was chairman of JCPDS.

William Parrish, to whom the award was made, is himself a legend in the field. He is the 'father' of the 12–15 000 Bragg–Brentano diffractometers in use around the world, and the Fremantle meeting marked the 40th anniversary of their 'birth'. Trained in crystallography at MIT, Dr Parrish developed methods of cutting oriented slices of quartz crystals for war-time use, and then spent many years in inventing and improving X-ray diffraction techniques, the results of his work being incorporated in Philips X-ray equipment distributed worldwide. After a short interval with NASA, Dr Parrish joined the IBM Research Division in San Jose, where exacting demands for structural and chemical characterisation of materials including thin films again taxed his ingenuity and resulted in a series of IBM X-ray products. His new environment also brought to life an interest in automation methods and line profile analysis, which re-opened the application of X-ray



The Chairman of JCPDS-ICDD Professor Deane K. Smith (left) presenting Dr William Parrish with the citation and prize for the 1987 Hanawalt Award.

diffraction to particle size and stress analysis. The methods involved removal of the instrumental contribution to the observed diffraction pattern, the basis for current research by JCPDS intended to make the powder data file a truly universal standard for full profile analysis.

At an age when most people are considering retiring, Dr Parrish became interested, with Professor Michael Hart of the University of Manchester, in synchrotron radiation, using facilities at Stanford. Innovative techniques again resulted in remarkable results. Before concentrating on powder diffraction applications, he showed that topographic and crystallographic detail could be obtained from a magnetic surface film of garnet and its single crystal garnet substrate. Using parallel beam X-ray optics and a very versatile powder diffractometer, Parrish has successfully experimented with crystal structure refinement, anomalous scattering, texture determination, determination of precision lattice parameters, complex qualitative analyses, and the use of grazing incidence diffraction for depth profiling of thin films. These are growth areas in powder diffraction, and papers at this conference show that interest is not abating.

Parrish accepted the challenge presented by Dan Hanawalt, and although he was born only twelve years after him, is still carrying the discipline into the future.

This volume contains most of the invited papers presented at the Symposium, the exceptions being withheld by the authors for a variety of reasons. This is particularly unfortunate in the case of the Keynote Address by Michael Hart on 'Future directions in X-ray powder diffractometry'. His crystal-ball-gazing oration gave promise of continuing development of instrumentation to utilise the improving sources and monochromators, including the effects of anomalous dispersion; of powder data limited by the perfection of the specimen rather than the diffractometer resolution; of new information from line profile analysis; and of the ability to investigate smaller samples under more extreme conditions. Hart emphasised that nearly all the identification and analytical work will continue to be done by standard techniques using laboratory sources, but that there will be new developments restricted to those with access to modern high-cost high-intensity sources. He suggested that the use of linear and area detectors could increase the efficiency of use of laboratory sources so that they will be able to match the time-resolution ability of present synchrotron sources. He also pointed out that the ability to analyse single crystals is developing in parallel with the powder techniques, so that it may soon be possible to collect a full data set from a 1 cubic micrometre crystal. Would we still want powder data?

The Poster Session at the Symposium was a somewhat mixed bag and included a few papers using unsophisticated traditional techniques. One paper described a rapid automatic data collection and search/match system dedicated to the identification of renal calculi. Several posters used measurement of line-shapes to investigate particle size, strain, defects and inter-diffusion, but there did not seem to be unanimity over the best shape model to use. The same problem arose in many papers using the Rietvelt method for structure refinement or for quantitative analysis. Where phase transitions were studied on a short time-scale, synchrotron sources were used. Some papers acknowledged that X-ray and neutron diffractometry could be complementary, especially in the final stages of refinement. Two papers dealt with quantitative thin film diffractometry, while a few dealt with equipment: X-ray powder diffractometry at Daresbury; new solid state (position) detectors; and the use of energy dispersive diffraction equipment at the Photon Factory.

A popular display at both the Congress and the Symposium was the JCPDS-ICDD search-match system based on a CD-ROM data storage system. The speed and flexibility of this approach is quite exciting, involving visual matching of patterns if required. The International Centre is seriously considering storing standard full-profile data instead of the diffraction line/intensity data currently used; CD-ROM systems which could cope with this mass of data are just around the corner, so speed of retrieval could be adequate.

The selection of papers presented here is representative of current effort in the field, and will provide a reasonable overview for those wishing to update their knowledge. The references are prolific enough to give a basis for up-to-date work.

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Advances in Synchrotron X-ray Polycrystalline Diffraction*

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Abstract

The advantages of synchrotron radiation for X-ray polycrystalline diffraction are illustrated by a number of examples. The plane wave parallel-beam X-ray optics uses a Si(111) channel monochromator for easy wavelength selection and a set of long parallel slits to define the diffracted beam. The constant simple instrument function and the high resolution symmetrical profiles (FWHM 0.05°) greatly simplify the data analysis and add a new dimension to profile broadening studies. The geometry permits uncoupling the θ - 2θ sample-detector relationship without changing the profile shape and makes possible new applications such as grazing angle incidence depth analysis of thin films. The same instrumentation is used for high resolution energy dispersive diffraction (EDD) by step-scanning the monochromator. The resolution is two orders of magnitude better than conventional EDD and can be used at high count rates. The easy wavelength selection yields diffraction patterns with the highest P/B and permits anomalous scattering studies.

1. Introduction

Three major advances in the last decade have revolutionised powder diffraction: computer automation and data analysis, profile fitting, and synchrotron radiation.

Powder diffraction is now based on the widespread use of computers. Most modern diffraction instruments are supplied with computers for instrument control and data collection. Retrofitting older equipment is relatively easy and inexpensive. The rapid advances in computer technology have made it practical to do an increasing amount of data reduction and analysis on small computers. Profile fitting has emerged as the most important method to determine the reflection shapes, intensities and scattering angles. The essential role of computers and profile fitting for synchrotron radiation powder diffraction will become apparent in this paper.

The advantages of synchrotron radiation for powder diffraction are the high intensity, the easy wavelength selection from the broad continuous radiation, and the virtually parallel beam. They make it possible to use a menu of experiments and methods that are difficult or impossible with X-ray tubes. Conventional X-ray tube diffractometry uses a narrow line source and focusing optics. Synchrotron radiation diffractometry uses a wide source and the plane wave parallel-beam diffraction

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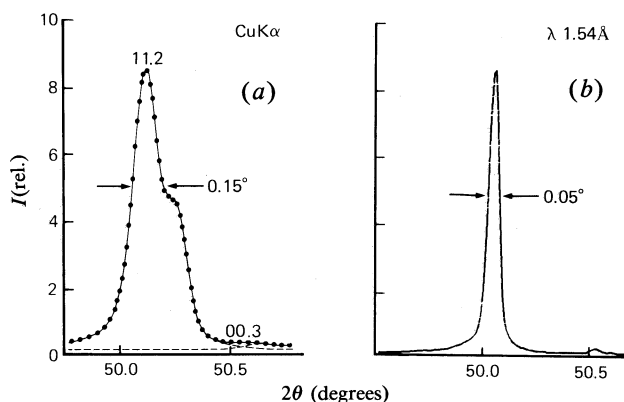


Fig. 1. Profiles of quartz (11.2) and (00.3) reflections recorded using (a) the conventional X-ray tube focusing method and (b) the synchrotron radiation parallel-beam method.

geometry requires different X-ray optics. Consequently, new instrumentation and methods were required to use the new radiation in the most effective way.

The two methods have markedly different profile shapes as shown in Fig. 1 for a pair of quartz powder reflections. In the X-ray tube case in Fig. 1a the $\text{CuK}\alpha_{1,2}$ doublet causes asymmetric broadening on the high-angle side, and the geometrical aberrations cause asymmetry on the low-angle side. Both asymmetries vary differently with scattering angle. The profile shape can be formulated as a sum of seven Lorentzian curves (Parrish and Huang 1980). The long tails extend to adjacent reflections; the weak (00.3) peak is difficult to measure because of the (11.2) tail. The parallel-beam profiles in Fig. 1b are single symmetrical peaks with three times better resolution and several times higher intensity. The shape is constant across the entire scanning range, and only the width increases with $\tan\theta$ due to wavelength dispersion. A pseudo-Voigt profile fitting function using the sum of 75% Gauss and 25% Lorentz components closely fits the experimental data (Parrish and Hart 1988b). This simple instrument function is an important advantage in determining the intensities and scattering angles, and in analysing profile broadening caused by the properties of the sample.

Synchrotron X-ray diffraction methods and applications used at the Photon Facility (Japan) have been described by Hosoya *et al.* (1986), at Brookhaven by Cox (1987) and at Stanford by Parrish and Hart (1985, 1988a). The instrumentation and methods described below evolved from developments made in four runs over a three-year period at the Stanford Synchrotron Radiation Laboratory.

2. X-ray Optics and Instrumentation

A schematic of the instrumentation presently used is shown in Fig. 2. The objective was to develop a design which matches the properties of the monochromator to the source and standard sample geometries in order to take maximum advantage of their characteristics. The total X-ray path was 114.3 cm; 43 cm was in air (due to a pipe obstruction) and 71.3 cm in vacuum (including the 52.5 cm collimator and a 18.7 cm vacuum pipe). The white beam, approximately 22 mm wide by 5 mm high,

enters the hutch through a pipe at the left, and is limited by adjustable slits C1. Two powder diffractometers are used in line, D1 for the monochromator and D2 for sample analysis (Parrish 1965). Scanning is in the vertical plane to avoid problems from the high degree of polarisation in the horizontal plane. The maximum scanning angle is about 145° – 150° . The diffractometers are operated by Compumotor stepping motors controlled by an IBM Personal Computer, which was also used for data collection and graphic displays. Data reduction was done off-line on a host computer.

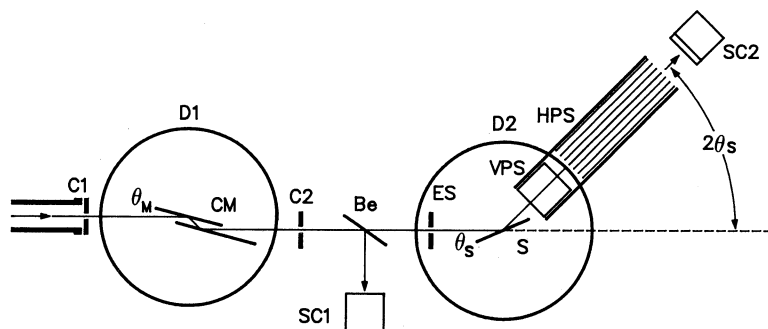


Fig. 2. Schematic of the parallel-beam X-ray optics developed for synchrotron radiation. Symbols are described in Section 2.

The channel monochromator C1 was cut from a dislocation-free silicon ingot with (111) orientation and 5 mm separation between the plates. It was designed to eliminate mounting strains. The crystal was thermally stable without cooling even at the highest beam currents of the bending-magnet source (the thermal conductivity of Si is 42% of Cu). The monochromator had high intensity and practically no harmonic content when used with a single channel pulse height analyser. Its resolution is determined by the energy spread of the perfect crystal bandpass, 1.33×10^{-4} for this orientation, and the wavelength dispersion which is very small at small $2\theta_s$ and increases with $\tan\theta$ (Beaumont and Hart 1974). The useful wavelength range is approximately 0.5 to 2 Å, limited by the storage ring energy at short wavelengths and by the window and air-path transmission at long wavelengths.

The incident white beam also produces Laue spots which must be prevented from striking the specimen. A pair of steel blocks at C2 limits the size of the monochromatic beam and together with additional shielding (not shown) prevents the intense white beam scattering from entering the system. Proper shielding is very important to avoid large background counts. To achieve maximum precision in setting the Bragg angle of the monochromator θ_M , the D1 diffractometer was modified to rotate the crystal directly from the large worm gear rather than through the 2:1 gears.

An important property of the channel monochromator is that the position and direction of the beam remain fixed for the wavelength range used. The beam is larger than the entrance slit ES of D2 so that small movements of the beam in changing wavelengths do not require repositioning or recalibrating the powder diffractometer.

It is necessary to continually monitor the intensity of the monochromatic beam to allow for the gradually decreasing ring current and to detect orbital shifts which may cause large intensity changes. The scattering from a thin (25 μm) beryllium foil (Be) inclined to the beam was recorded with scintillation counter SC1. The intensities must be high enough for good counting statistical accuracy and we used high speed

Rigaku scintillation counters and single channel analysers which have about 1% loss in the 10^5 to 10^6 counts per second range. With stable storage ring operation the decrease of intensity is slow and the average monitor counts of a number of steps can be used. The counts at each step from SC2 are divided by the SC1 monitor counts to make the correction.

The entrance slit width (ES) is selected to limit the beam to the illuminated specimen length l at the smallest angle to be scanned, $l = ES/\sin\theta_{\min}$. The intensity is proportional to ES and the peak positions and profile shapes remain constant at all widths. The specimens are the same size used in conventional diffractometry. The powders are packed in a cylindrical aluminium holder with 22 mm diameter powder area and rotated about 70 r.p.m. around the axis normal to the specimen surface to improve the precision of the intensity measurements; the important role of specimen preparation has been described (Parrish and Hart 1988*b*).

If an X-ray transparent specimen mount is used the specimen can be studied in transmission geometry simply by rotating the holder 90° ; no other instrument changes are required. Comparisons of the transmission and reflection patterns are useful in determining gross preferred orientation effects.

The diffracted beam is defined by vertical parallel slits (VPS) and horizontal parallel slits (HPS) mounted together in a vacuum housing with thin Mylar windows on the detector arm. The former are 7.6 cm long with 1.9° full aperture and greatly reduce the asymmetry in peak shape caused by axial divergence. The HPS determine the resolution and shape of the profiles and are 35.6 cm long with 0.064° full aperture. Both were made with 0.005 cm thin stainless steel flat foils. Using the same foil thickness and spacing, the intensity is independent of the length; we obtained the same intensity with a 10.1 cm long collimator with the same foil thickness and spacing. The collimator was aligned at 0° with an accurate bubble level. The long distance between specimen and detector (59.1 cm) reduces the fluorescence background without the loss of intensity caused by a diffracted beam monochromator.

3. Wavelength Selection

The easy wavelength selection made it possible to use a wavelength best suited to the analysis. A wavelength slightly longer than the absorption edge of the lowest atomic number element in the specimen avoids fluorescence. (We can neglect the very low atomic number elements whose soft X-rays are absorbed in the windows or air path.) The pattern can then be recorded with the highest possible peak-to-background ratio. Short wavelengths can now be used without the problems associated with X-ray tube $\text{Mo K}\alpha$ radiation. It has the advantage of a shorter recording time for the same range of d_s , and very small d_s (to about $0.35 \text{ \AA}$) can be recorded with low background at the highest $2\theta_s$. Long wavelengths are used to increase the peak separations which is important in resolving overlapping reflections.

The selected wavelength can be determined with respect to an absorption edge of an element in the specimen or a thin foil placed in the beam. The spectrum near the edge is recorded by step scanning the monochromator using the energy dispersive diffraction mode. Another method is to use θ - 2θ step-scanning to record the pattern of a silicon powder standard, or a float-zoned oxygen-free single crystal plate, whose lattice parameters are known to $\pm 1 \times 10^{-5}$ and $\pm 1 \times 10^{-7}$ respectively. The least squares refined values of the lattice parameter a_0/λ_{obs} , where λ_{obs} is calculated from θ_M , can be related to the standard.

The wavelength range provides a unique opportunity to do anomalous scattering studies. Recently, powder diffraction data were used to determine f' , the real part of the scattering factor of Yb (Will *et al.* 1987). The crystal structure of a Yb_2O_3 powder sample was refined from data collected at four wavelengths slightly longer than the Yb L_{III} absorption edge and the values of f' determined by least squares refinement with a precision of ± 0.2 electron units.

4. Energy Dispersion Diffraction

The instrumentation shown in Fig. 2 can be used without modification to do high resolution energy dispersion diffraction (EDD) (Parrish and Hart 1985). The channel monochromator is step-scanned producing a continually varying set of monochromatic wavelengths, and the sample and detector are set at a selected θ - 2θ position. The

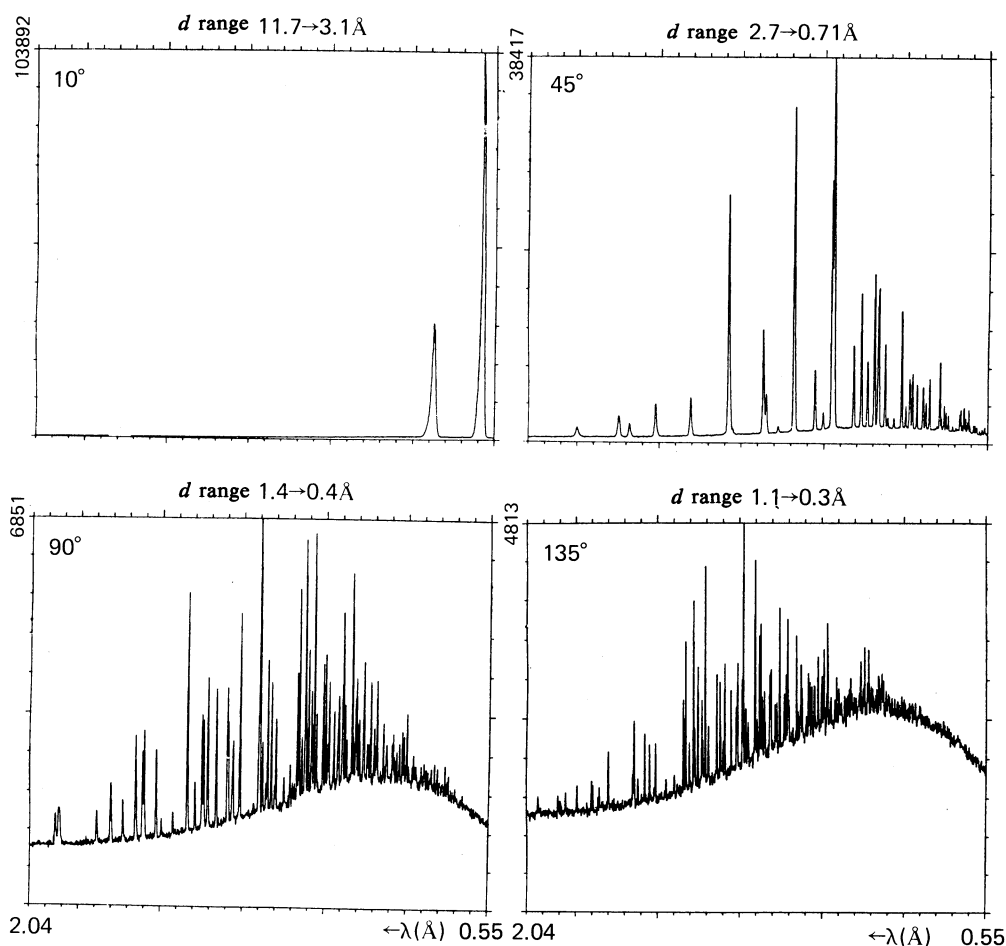


Fig. 3. High resolution energy dispersion diffraction patterns of quartz using 0.55 to 2.04 Å incident X-rays. The lattice spacing d range recorded depends on the 2θ setting (upper left corner) of the detector.

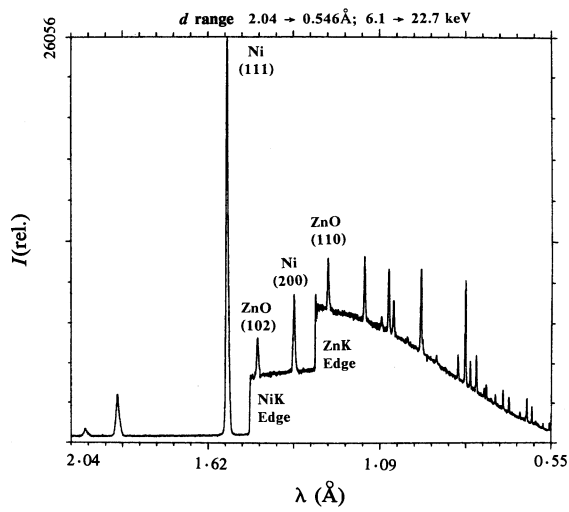


Fig. 4. EDD pattern of a mixture of ZnO and Ni powders showing the K-absorption edges.

resolution is determined by the parallel slit collimator and is about two orders of magnitude better than the conventional method where the resolution is determined by the solid state detector. The scintillation counter can also be used at far higher count rates without dead-time corrections.

The range of d spacings that can be recorded is determined by the 2θ setting of the detector and the input wavelength range as shown in Fig. 3. The monochromator

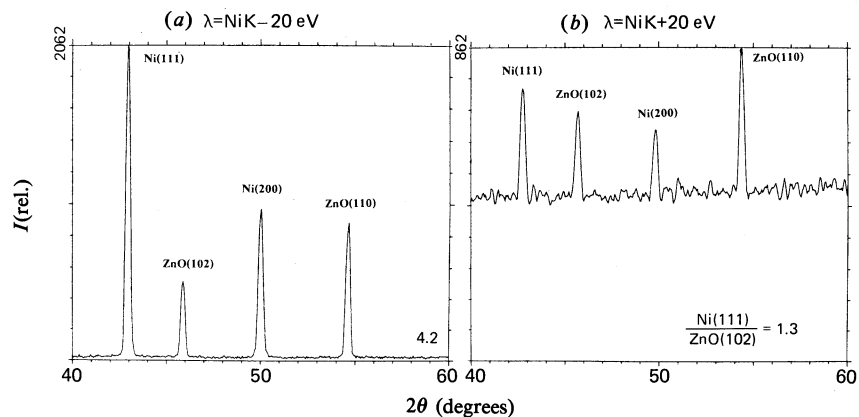


Fig. 5. θ - 2θ patterns of ZnO and Ni powders recorded with a wavelength (a) slightly longer than the Ni K edge and (b) slightly shorter than the edge.

was stepped at 0.01° increments and the number of points per peak and the peak separations were small at the short wavelengths, and increased with λ . Computer graphics are used to expand the scales and simplify the interpretation. An example of the use of EDD for determining the spectral distribution around absorption edges is shown in Fig. 4 for a sample containing a mixture of ZnO and Ni powders. Starting from $0.55 \text{ \AA}$ the Zn K and Ni K fluorescence background increases as the incident wavelengths approach the absorption edges. There are sharp drops in the background when the absorption edges are crossed. Enlarged diagrams of this type can be used to select wavelengths for anomalous scattering studies.

An example of the use of wavelengths on both sides of the absorption edge with θ - 2θ scanning is shown in Fig. 5 for the same sample used in Fig. 4. The wavelength slightly longer than the Ni K-absorption edge produced the high intensity and low background pattern (Fig. 5a). The slightly shorter wavelength below the edge (Fig. 5b) caused a large Ni K fluorescent background and lower peak intensities. In crossing the edge the P/B of Ni(111) decreased from 64 to 0.6 and the peak intensity ratio of Ni/ZnO changed by more than a factor of three. The ZnO absorption remains

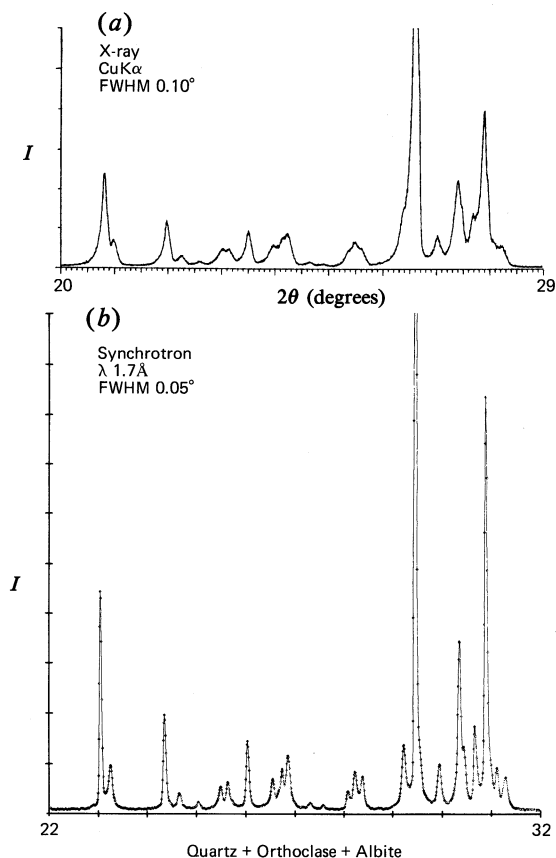


Fig. 6. Comparison of the complex pattern of a mixture of low symmetry minerals obtained with (a) the highest resolution X-ray tube focusing method and (b) the parallel-beam method.

virtually unchanged in crossing the edge but the Ni absorption increases an order of magnitude. This type of experiment may be useful in phase identification of mixtures and for other studies but the poor P/B limits the quality of the data below the absorption edge.

5. Applications

An example of high resolution θ - 2θ scanning is shown in Fig. 6 for a mixture of three low symmetry minerals of interest to petrologists. The upper recording was made with state-of-the-art X-ray tube focusing diffractometry using the highest resolution and best recording conditions. The lower pattern of the same sample was made with high resolution and longer wavelength synchrotron radiation. All the peaks in this range were resolved and can be used for qualitative and quantitative analysis of the mixture.

The high quality and simple instrumentation function of the synchrotron radiation data has stimulated renewed interest in crystal structure determination using X-ray powder diffraction. Difficulties had been encountered with conventional X-ray tube data because of the complex profile shapes, and this problem has been eliminated by the new methods. Moderately complicated structures of materials not available as single crystals have been solved (see, for example, Attfield *et al.* 1986; Lehmann *et al.* 1987). Fourier maps showing the electron density of orthorhombic Mg_2GeO_4 have recently been made (Will *et al.* 1988).

The absence of systematic errors caused by the flat specimen, specimen surface displacement and other aberrations inherent in conventional focusing methods, makes it possible to increase the precision and confidence of lattice parameter determination (Parrish *et al.* 1987). Profile fitting has been used to determine $2\theta_s$ to $\pm 0.0001^\circ$, and least squares refinement to determine the zero-angle calibration correction and lattice parameters. The precision in the lattice parameter estimated from the standard deviation of the mean was in the 10^{-6} range for the NBS silicon standard. A remaining problem is the determination of the wavelengths to the same precision.

Synchrotron radiation diffraction patterns have major advantages in line-broadening profile analysis for microstructure studies using the Warren-Averbach method (Warren 1969). The elimination of the $K\alpha$ doublet correction, the symmetrical fixed profile shape, the constant instrumentation function and the use of short wavelength X-rays, now make it possible to do three-dimensional analyses of metal and powder samples with greater reliability and precision. Peak shifts and broadening can be detected more easily and with more certainty than by conventional methods.

An analysis of palladium powder in the as-received and after annealing conditions was made using 1 Å X-rays (Huang *et al.* 1987). The higher order (333), (444), and (440) reflections, not observable with $\text{Cu K}\alpha$ radiation, could be recorded, making available three sets of $n(111)$, a set of $n(220)$ and $n(200)$ reflections for the Fourier analysis. A marked crystallite size anisotropy was found along the three major crystallographic axes. The root-mean-square microstrains could also be determined for the three axial directions. The deformation faults were derived from the peak shifts between (111) and (200), and the twin fault probability from differences between the peak maximum and center-of-gravity. Both were very small and could not have been precisely measured without a symmetric instrument function.

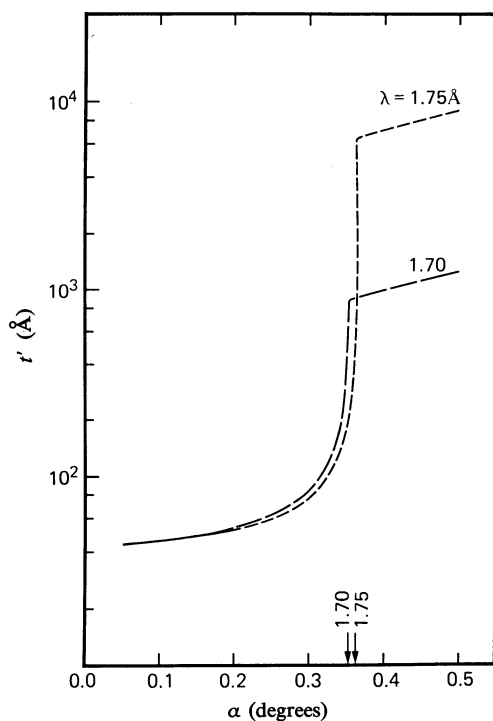


Fig. 7. Penetration depth t' as a function of the grazing angle of incidence α of an iron oxide film for two wavelengths straddling the Fe K absorption edge at 1.74 Å.

6. Thin Film Studies

Another important advantage of the parallel-beam method is that the specimen-detector θ - 2θ relationship can be uncoupled without changing the profile shapes (it would cause severe defocusing in conventional methods). This feature makes possible several new methods which are particularly useful for the structural characterisation of thin films.

The sample can be fixed at any selected θ angle and only the detector arm scanned. This is equivalent to the Seemann-Bohlin (SB) focusing geometry (Parrish and Mack 1967). The advantages of the parallel-beam method are: (1) the diffractometer does not have to be realigned and recalibrated when changing the specimen angle; (2) much smaller incidence angles can be used; (3) the relative intensities do not require corrections for receiving slit aperture variations with 2θ ; and (4) the profile widths (except for wavelength dispersion) do not change with 2θ .

When conventional θ - 2θ or SB methods are used the X-ray beam usually penetrates the entire film thickness. Since thin films are often prepared with properties that vary with depth, it is necessary to follow structural changes as a function of film depth for thin film characterisation. The method developed uses incidence angles α smaller than the critical angle for total reflection α_c to obtain diffraction patterns from the upper tens of Angstroms, and by increasing the angle to nearly α_c to include the top several hundred Angstroms (Lim *et al.* 1987). The penetration depth abruptly increases to thousands of Angstroms above α_c as shown in Fig. 7. Longer wavelengths have the advantage that the depth of penetration with increasing α is more gradual.

The method can be used to determine phases, lattice parameters, strain and other properties. It has a different geometry from the surface scanning method of Marra *et al.* (1982).

The incidence angle of the sample is set by a stepping motor with 0.01° smallest increment. The $\alpha = 0^\circ$ sample position is taken to be the horizontal plane. This position can also be determined with a third scintillation counter mounted in a stationary position above the sample so as not to interfere with the scattering measurements. The specimen is step-scanned and the step at which fluorescence counts from the specimen appear is taken as the $\alpha = 0^\circ$ position. The fluorescence intensity increases with α .

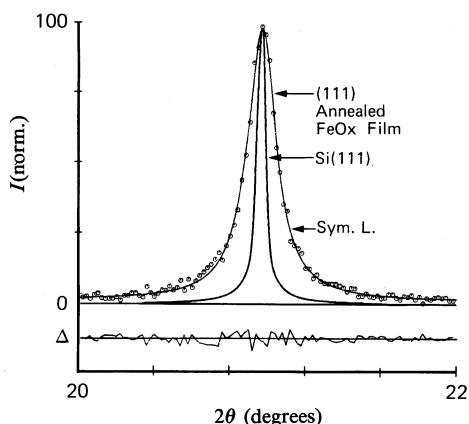


Fig. 8. Comparison of symmetrical profile shapes observed with grazing incidence ($\alpha = 0.25^\circ$) diffraction. The inner Si(111) powder profile has a narrow pseudo-Voigt shape. The broadened profile from 300–400 Å crystallites in a $\gamma\text{-Fe}_2\text{O}_3$ thin film has a Lorentzian shape with the calculated differences Δ shown below ($\lambda = 1.75 \text{ \AA}$).

The diffraction pattern is recorded by 2θ scanning of the detector arm. The grazing incidence profile shapes are the same as in θ - 2θ scanning. The profiles will be broadened by small particle sizes as in normal scanning. Fig. 8 compares the unbroadened pseudo-Voigt silicon (111) profile with the Lorentzian iron oxide (111) profile broadened by the 300–400 Å crystallite sizes. However, the intensities are about an order of magnitude lower because of the smaller diffracting volume and the high source intensity is essential in obtaining useful data.

An example of the method is shown in Fig. 9 for a 5000 Å thick iron oxide film. The θ - 2θ scan (Fig. 9a) penetrates the full film thickness and contains scattering from the amorphous glass substrate. The $\alpha = 0.25^\circ$ grazing incidence scan (Fig. 9b) has the same Miller indices but they are from planes inclined 11° to 37° instead of parallel to the surface. Only the top 60 Å contributed to the pattern and substrate scattering is absent. The film has (111) preferred orientation as shown by comparing the peak intensities with the random powder intensities given by the numbers above the peaks in Fig. 9a.

The films as deposited by sputtering were Fe_3O_4 and were converted to $\gamma\text{-Fe}_2\text{O}_3$ by annealing. They have similar crystal structures but different magnetic properties. Both have the same fundamental X-ray reflections but $\gamma\text{-Fe}_2\text{O}_3$ has smaller lattice spacings and one or more weak superstructure peaks. The peak positions of the grazing incidence patterns must be corrected for the index of refraction which causes shifts of the order of 0.2° (2θ) at small angles (Lim *et al.* 1987). The grazing incidence pattern of the annealed films also had weak $\alpha\text{-Fe}_2\text{O}_3$ peaks in about 1–2% concentration, which could be identified by profile fitting, and indicate the higher oxidation state in the top surface.

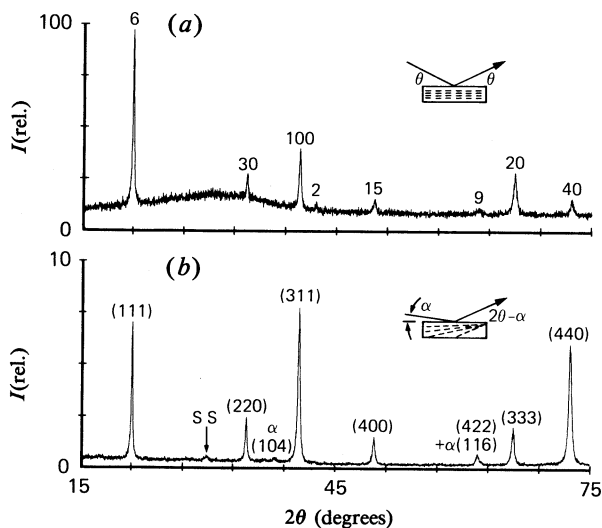


Fig. 9. (a) The θ - 2θ diffraction pattern of annealed 5000 Å γ - Fe_2O_3 film with (111) preferred orientation. The numbers above the peaks are relative intensities of a random powder sample. (b) A 0.25° incidence angle with a 2θ scan of the top 60 Å of the same film (SS marks the superstructure peak and α preceding the Miller indices marks the α - Fe_2O_3 peaks).

The decoupling of the specimen and detector also makes possible the study of preferred orientation in thin films with the EDD mode (Hart *et al.* 1987). The selected scattering angle 2θ determines the separation of the Bragg reflections and the α -range that can be recorded with the incident range of wavelengths. A set of lattice planes oriented parallel to the surface of the film has its highest intensity when the sample is in the normal symmetric position (θ - 2θ relation). Rotating the sample counterclockwise around the diffractometer θ -axis, while keeping 2θ fixed, reduces the intensity and brings another set of planes inclined to the surface to its symmetric reflecting position. The amount of rotation required is the interplanar angle between the two sets of planes. This can be repeated for all lattice planes of interest. By using small rotation steps around the symmetrical positions the angular distribution of the planes can be related to the inclinations to the film surface.

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