

12.X-3 OPTIMIZATION OF POWDER DIFFRACTION GEOMETRY FOR CONVENTIONAL AND SYNCHROTRON RADIATION SOURCES. By P. Suortti, Department of Physics, University of Helsinki, Finland.

The propagation of the x-ray beam in the optical system of the source, monochromators, mirrors, slits, sample, analyzer and detector is studied using 3-dimensional phase space diagrams. The variables are the width and divergence in the plane of diffraction and the wavelength. Various geometries currently employed in the synchrotron radiation studies are analyzed and the optimization of the angular resolution and the peak-to-background ratio is discussed. Reflection profile studies on a series of nickel samples at the X13A beam line of the NSLS (Brookhaven) serve as examples. A conventional high-resolution powder instrument is described (Ahtee & Suortti, this congress). The resolution is analyzed using the phase space diagrams including the effects of geometrical aberrations, and it is demonstrated that at large scattering angles the resolution can be even better than that of the synchrotron radiation instruments. This is primarily due to the small band-width of the characteristic radiation from an x-ray tube.

12.X-4 THE USE OF POSITION SENSITIVE DETECTORS IN POWDER DIFFRACTOMETRY. By H. Hashizume, Research Laboratory of Engineering Materials, Tokyo Institute of Technology, Nagatsuta, Midori, Yokohama, 227 Japan.

An ideal position sensitive detector (PSD) in X-ray powder diffractometry should cover 180° in 2θ with an overall angular resolution better than 0.05° . Development of such a detector using gas ionization requires a means to support the detector anode in a circular arc centered on the specimen. Several cylindrical position sensitive proportional detectors have been successfully operated, which conform a thin or medium-diameter anode wire by electromagnetic or elastic means. This technique allows an anode length not much longer than 200mm, which limits the detector 2θ coverage to ca. 90° at a radius of 135mm. A good resolution of $\Delta 2\theta = 0.06^\circ$ is achieved with the use of pressurized xenon-based gas and the delay line technique to readout the signal. Wolfel (J. Appl. Crystallogr., 1983, 16, 341-348) has incorporated a PSD of this class to a curved-crystal optics to determine the peak positions from a powder specimen in a capillary or in transmission geometry to an accuracy of $\Delta 2\theta = \pm 0.02^\circ$. The use of specimen environment chambers often requires a more extended detector. Shishiguchi et al. (*ibid.*, 1986, 19, 420-426) describes a cylindrical PSD having a 250mm radius and an 120° angular span. Here a thin metal blade forming a hollow cylinder serves as anode. The signal-to-noise ratio problem, arising from the large electrostatic capacitance of the chamber, is circumvented by using a special gas filling to work the detector in the self-quenching streamer mode. This latter mode of gas ionization provides for each absorbed photon a signal charge an order of magnitude greater than the proportional mode. A resolution of $\Delta 2\theta = 0.06^\circ$ has been observed over the entire 120° range at the detector output. Many PSDs show non-linear spatial response needing cor-

rections in powder works. Differential non-linearity in position determination can affect the peak positions as well as their intensity profile. This is most difficult to adequately correct for. Typical integral and differential non-linearities in the current detectors are $\pm 0.2\%$ and $\pm 3\%$, respectively. Mechanical imprecisions in the chamber, the scheme of signal readout and the properties of the employed electronics can be the causes for the non-linearities.

The unique feature of the wide-angle PSD is the ability to record a powder pattern simultaneously without any mechanical scan. This advantage is best exploited in rapid data collection from a small-volume specimen and in the real-time study of structure changes occurring in the specimen crystal. Although up to now the PSD data have been used to extract information on the peak positions and integrated intensities, attempts are being made to analyze the data with the pattern fitting techniques. This will open a new possibility in powder diffractometry to refine unstable crystal structures.

12.X-5 PROBLEMS IN PROFILE REFINEMENT OF POWDER DIFFRACTION DATA. By J.I. Langford, Department of Physics, University of Birmingham, Birmingham B15 2TT, UK.

The principal ways in which profile refinement is applied to the total diffraction pattern from a powder sample are (a) *Rietveld method* for structure refinement, in which a comparison is made between the observed pattern and that calculated from a suitable structural model (H.M. Rietveld, *Acta Cryst.*, 1967, 22, 151) and (b) *pattern decomposition*, whereby the pattern is divided into its component Bragg reflections without the use of structural information (eg W. Parrish et al., *Trans Am Cryst Assoc.*, 1980, 12, 55 and E.J. Sonneveld & J.W. Visser, *J Appl Cryst.*, 1975, 8, 1). In broad terms the problems associated with either approach fall into three categories. Some are instrumental in origin, others arise from the nature of the sample, and the third group originates in the analysis and interpretation of the data.

The four main sources of radiation used to obtain data for profile refinement are 'conventional' and synchrotron X-rays and continuous and pulsed neutrons. Each has its advantages and limitations and employs different experimental techniques (J.I. Langford, *Prog Cryst Growth & Charac.*, 1987, 19, in press and A.W. Hewat, *Chemica Scripta*, 1968, 26A, 119). Factors which influence profile refinement include stability, available intensity reliability and precision of wavelength determination. Instrumentation has improved considerably in recent years and few problems remain in this area, though in some applications resolution and the effect of diffractometer geometry on line shape may be a consideration (W. Parrish et al., *Adv X-ray Anal.*, 1986, 29, 243).

The sample itself can be the source of several aberrations and uncertainties. These include preferred orientation,

extinction (T.M. Sabine, *Aust J Phys*, 1985,38,507), thermal diffuse scattering, transparency, structural defects (eg A.J.C. Wilson, *Mathematical Theory of X-ray Powder Diffractometry*, 1963, Eindhoven: Centrex), partial crystallinity, such as can occur in polymers and glassy materials (J.N. Hay *et al*, *Polymer Commun*, 1984,25,175), and contamination of the diffraction pattern by impurities (P.J. Bendall *et al*, *J Appl Cryst*, 1983,16, 164).

Limitations on an analysis of the data can be imposed by the nature of the diffraction pattern; background determination and the separation of peaks with severe overlap in complex patterns (J.I. Langford *et al*, *Powder Diff*, 1986,1,211) and a paucity of lines all affect the results of profile refinement. Inadequacy of the function used to model peak shapes is often a source of systematic error (R.A. Young & D.B. Wiles, *J Appl Cryst*, 1982,15,430), as is the model used in any size-strain analysis.

The significance of these factors depends on what information is to be extracted from pattern fitting. In general, requirements of the Rietveld method are less stringent than for size-strain analysis, for example, and for *ab initio* indexing of powder data precise peak positions are more important than other profile parameters. Some problems in profile analysis can be avoided, or at least minimised, by a suitable design of the experiment and by systematic sample preparation (G. Will *et al*, *J Appl Cryst*, 1983,16,611). Others can be treated analytically, but there can also be residual problems, often originating in the sample, for which there is no remedy; these must be taken into account when presenting the results of profile refinement.

12.X-6 NEW TECHNOLOGIES IN SEARCH-MATCH PROCEDURES. By R. Jenkins, International Centre for Diffraction data, U.S.A.

First systematic attempts to identify mixtures of polycrystalline phases by unscrambling their composite x-ray powder patterns dates back to the mid-1950's, and the original idea of searching small subsets of the d/I lists (the search), and then comparing potential candidates with the full pattern (the match), is still used today. In the mid-1960's, the first attempts to automate the search-match process were made using large, main-frame computers. More recently, the advent of fully automated powder diffractometers and the increasing use of personal computers have led to widespread interest in computer search-matching.

Earlier search algorithms required some judgment on the part of the operator in the estimation of data quality, and problems arose due to uncertain quality of "d" spacings, and/or to the effects of solid solution. More recently, this situation has improved due to a better knowledge of the accuracy of measured and standard "d" values, combined with matching techniques based on statistical probabilities. A second problem is that of unreliable intensities due mainly to preferred orientation of the specimen. Where subtractive techniques are used to remove an "identified phase" from the composite pattern, too much or too little intensity may be removed. A recently employed alternative is the use of an additive method, in which a comparison is made with a composite pattern comprising each identified phase.

Other problem areas include the method of handling the polychromaticity of the source, use of elemental data before or after the d-spacing search, and the allocation of "figures of merit" for "hits" based on a given search strategy. This paper reviews, with practical examples, recent advancement in the treatment of these problems.

12.X-7 USE OF THE RIETVELD METHOD FOR DETERMINING COMPONENT PHASE ABUNDANCE AND PARTICLE SIZE/STRAIN CHARACTERISTICS: APPLICATIONS TO CERAMICS AND BATTERIES. By R.J. Hill, CSIRO Mineral Chemistry, PO Box 124, Port Melbourne, Vic 3207 Australia, and C.J. Howard, AEC Applied Physics, Lucas Heights Res Labs, Locked Bag No. 1, Menai, NSW 2234 Australia.

The Rietveld method was developed to refine crystal structures from neutron and X-ray powder diffraction patterns and has been extensively used for this purpose (Hewat, *Chemica Scripta*, 26A, 119, 1986). While most applications continue to be in structure refinement, it is now recognized that the method can also be used to obtain information on phase abundance in mixtures and on particle size, shape and strain.

Codes for multiphase Rietveld analysis were first developed to deal with impurity phases in otherwise standard crystal-structure refinement studies. However, the scale factors obtained in a multiphase analysis are directly related to the masses of the crystalline phases in the mixture. This relationship is the basis of a method for obtaining an accurate phase analysis without the need for standards or laborious experimental calibration; it is particularly powerful in the case of neutron diffraction.

Improvements in the description of peak shapes have been devised to provide better fits to the recorded diffraction patterns and thereby increase confidence in the derived crystal-structure parameters. In so doing, the analysis provides information on crystallite size and strain, which can also be of considerable interest.

In this presentation, we outline how the nonstructural parameters derived as a byproduct of Rietveld analysis are related to the physical state of the material. We also outline some current and potential applications, with particular emphasis on ceramics and batteries.

12.X-8 THE APPLICATION OF NEUTRON DIFFRACTION TECHNIQUES TO INDUSTRY. B.M. Powell, Chalk River Nuclear Laboratories, Chalk River, Ontario, KOJ 1J0, Canada.

Neutron diffraction is utilized increasingly as a commercial examination technique. Its advantage lies in the great penetration depth of neutrons in materials of common industrial use. Consequently, neutron diffraction can probe the interior of large industrial components or can investigate the bulk properties of a complete component. An application of fundamental industrial importance is the ability to measure the residual strain in the interior of a structural component. By masking the neutron beams appropriately, the spatial distribution of strain within a specified region or the average strain within the region can be measured. Welds, rolled joints, bent tubes and components as large as pipelines have been examined. Components produced in industrial processes often show pronounced texture, which can have a drastic effect on performance. Neutron diffraction can measure texture in large samples, thus minimizing inaccuracies due to grain size. The complete texture can be specified by construction of the orientation distribution function from measured pole figures. For industrial materials which contain secondary phases or develop them in use, neutron diffraction can investigate the volume fractions of these minority phases. High resolution neutron diffraction measurements analyzed with multicomponent refinement methods are more sensitive to the presence of such phases than most other detection methods. Certain industrial applications require large single crystal components e.g. semiconductor wafers, turbine blades. The quality of these crystals can be examined by neutron Bragg reflection. Various neutron techniques and their utilization will be discussed.