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 $\Delta 2\theta \approx 0.06°$ 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 $\Delta 2\theta = \pm 0.02°$. 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 $\Delta 2\theta = 0.06°$ has been observed over the entire 120° range at the detector output.

Many PSDs show non-linear spatial response needing corrections 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 ±0.2% and ±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,