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NEW TECHNIQUES FOR SYNCHROTRON POWDER DIFFRACTION STUDIES*

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NEW TECHNIQUES FOR SYNCHROTRON POWDER DIFFRACTION STUDIES

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ABSTRACT

This manuscript discusses two different powder diffraction methods which possess high resolution, low background and very high counting rates. Both methods utilize analyzer crystals in combination with position sensitive detectors. The first method uses a curved perfect crystal analyzer diffracting in the scattering plane to diffract a range of angles into the position sensitive detector. The second method is somewhat simpler, it uses a graphite analyzer crystal diffracting out of the scattering plane. Applications of these methods to anomalous scattering from both powder and amorphous materials are also discussed. One of the techniques should also be very useful for small angle scattering.

INTRODUCTION

Powder diffraction is a common analytical technique which is useful for the study of both crystalline and amorphous materials. World wide, there are thousands of powder diffraction units for basic studies of materials, analytical testing and process control. Powder diffraction techniques using synchrotron radiation have been successfully applied to numerous materials science problems[1]. The advantages of using synchrotron radiation for powder diffraction are many, but we wish to focus on the very high resolution and low background attainable with a synchrotron source. The standard methods of taking high resolution, low background powder data result in quite low count rates so that many hours are required to take data at high statistical accuracy, particularly if only capillary samples are available[1]. High count rates are particularly important to anomalous scattering studies and time resolved experiments. We have developed two new methods for the collection of high resolution, low background powder spectra with data rates many times faster than with existing methods. The focusing crystal-position sensitive detector method[2,3] which we will describe below, achieves very high resolution and high count rates since 4° of data can be acquired simultaneously. To date, the resolution achievable with this method has been limited by detector resolution to about 0.03° in two-theta. The out of plane analyzer crystal-position sensitive detector technique[4] also achieves high resolution and is considerably simpler to use . Both methods give signal to background ratios of better than 1000 to 1 for both Al_2O_3 and CeO_2 (the latter material exhibits large fluorescence but the analyzer crystal completely rejects this radiation). The methods are also extremely useful for laboratory based instruments, the out of plane version[4,5] is at least five times more efficient than the best commercial instruments. The focusing crystal

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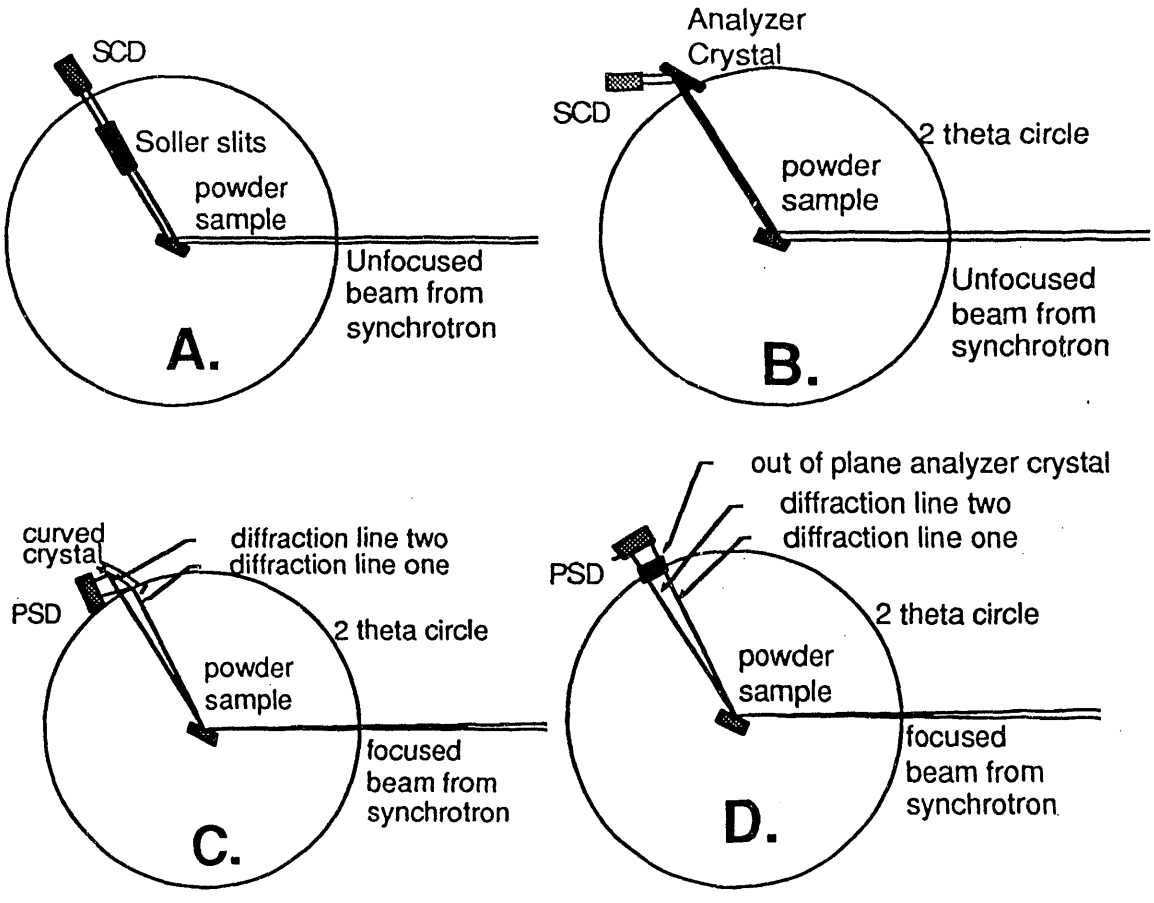
method should also be extremely valuable for small angle scattering since the method requires minimal slit and beam stop and also minimizes air scattering.

DESCRIPTION OF THE METHODS

In figure 1 we show schematic diagrams of our new methods and compare these methods to some existing techniques.



B. Standard Flat Analyzer single channel detector

Figure 1. Schematic Diagrams of;

A. Soller slit method.

B. Flat perfect crystal analyzer method

C. Focusing crystal position sensitive detector (PSD)method.

D. Out of plane analyzer crystal, position sensitive detector method

In figure 1A. we show the Soller slit method developed by Parrish *et. al*[6]. In this method the resolution will depend on the width of the Soller slits. In figure 1B we show the widely used method of Cox[1] for collecting high resolution powder diffraction data. In this technique the analyzer crystal acts both as an energy and angular filter, it only accepts rays coming from the sample which fall within its

Darwin width. The resolution depends on both the analyzer and beam monochromator crystals.The two new methods are shown in Fig. 1C and 1D. The method shown in figure 1C uses focusing perfect crystal analyzer to cut out background and determine the resolution of the instrument. The crystal is curved with a special 4 point bender so that its surface makes the analyzer Bragg angle with rays coming from the focal spot of the mirror on the sample over a wide range of two theta angles. Currently we are able to bend the crystal perfectly enough so that the Bragg condition is satisfied to within the Si **220** analyzer crystal Darwin width over a range of 4° in two theta. The crystal reflects any diffraction lines that fall within the 4° into the position sensitive detector (PSD) so that the data are recorded in parallel. In Figure 1D. we use a flat analyzer crystal (graphite) oriented so that the diffraction plane of the analyzer crystal is turned 90° with respect to the diffraction plane of the sample. The crystal will satisfy its Bragg condition to within its mosaic spread in its plane of diffraction and will have a wide acceptance in its chi direction which is the two theta direction for the sample. This arrangement will act as an energy filter to cut out sample fluorescence and resonant Raman scattering. In this case, the angular resolution is determined by the energy bandwidth of the beam from the focusing mirror- monochromator. The new methods are so much more efficient since 2-5° are taken simultaneously instead the 0.004° for the method shown in figure 1A and the typically 0.01°-02° for 1B.

We have used these new methods extensively and have done many Reitveld refinements on data taken in the laboratory[7]. For a laboratory instrument the resolution is 0.07° instead of the 0.03° observed in synchrotron experiments. When used with a rotating anode x-ray source, data collection is very fast. Very high signal to noise data can be obtained in 30 minutes or less, very high signal to noise data on Fe_2O_3 has been acquired in 5 minutes. In this report we will present synchrotron data taken with both of the methods on a number of different samples to illustrate the count rate, intensity, resolution and low background attainable.

EFFICIENCY AND RESOLUTION

Both methods are very efficient and offer quite high resolution. For the out of plane method the resolution depends on both the two-theta angle and amount of energy spread in the beam. The latter factor is governed by the energy resolution of the double crystal monochromator and vertical acceptance of the optical system (monochromator-mirror combination)[8]. With the in plane method the resolution of the data presented here is governed largely by the detector resolution[9] and seems to vary only slightly with angle. Both methods are very efficient and data suitable for Rietveld refinement can be taken in about 30 minutes.

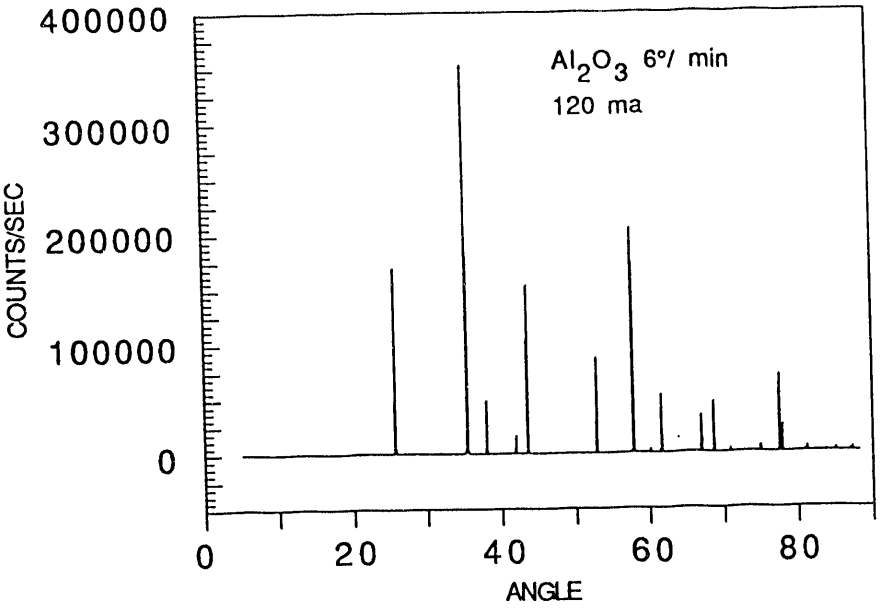
METHOD OF DATA TAKING AND ANGLE AVERAGING

As we have shown above, data are taken simultaneously, 1° to 4° in two-theta at a time. However, as a general rule one does not step the spectrometer in steps this large, one generally steps the angles 0.1° to 0.2° and, at each angle records the data. In this way every line is recorded many times at successively different positions on

the detector. The actual angular position of each can then be determined from the angle of the spectrometer and the position of the detector. A non-linear algorithm is used to merge the data from the different angles and to produce a conventional intensity versus angle plot. This procedure inevitably produces some line broadening but this effect is less than 0.005°. This data taking method has an additional advantage since data is taken at a large number of theta values so that problems of preferred orientation are somewhat minimized. This method also largely cancels out variations in detector response and crystal reflection non uniformity.

EXPERIMENTAL RESULTS

We have used the NSLS beamline X6B which is equipped with a double crystal Si(111) monochromator and a doubly focusing Rh coated mirror. All data were taken at 8.0 KeV and the full opening angle of the synchrotron was focused on the sample. Most of the experiments were carried out using 1 mrad of the horizontal spread of the beam. Let us first consider data taken on Al_2O_3[10] using both methods. In figure 2, we show the data taken with the focusing crystal method where we have plotted the data on both linear and log scales. The data took 15 minutes of counting time at a beam current of ~120 ma. The resolution was approximately independent of angle and was less than 0.03° which was also approximately the detector resolution (see fig.4). The background seen in the log plot reveals the amorphous component in the sample. Signal to background is about 1000 to 1 and signal to background noise is about 10,000 to 1 for the main peaks.



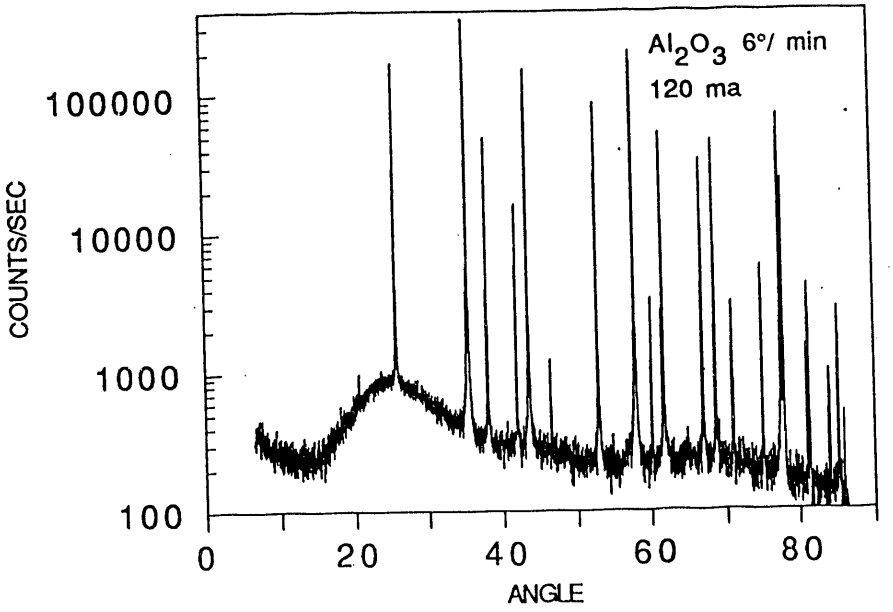


Figure 2 Al_2O_3 data shown on both linear and log scales under the conditions indicated.

In figure three we show the data for an individual line of Al_2O_3 to illustrate the resolution which can be obtained using this method.

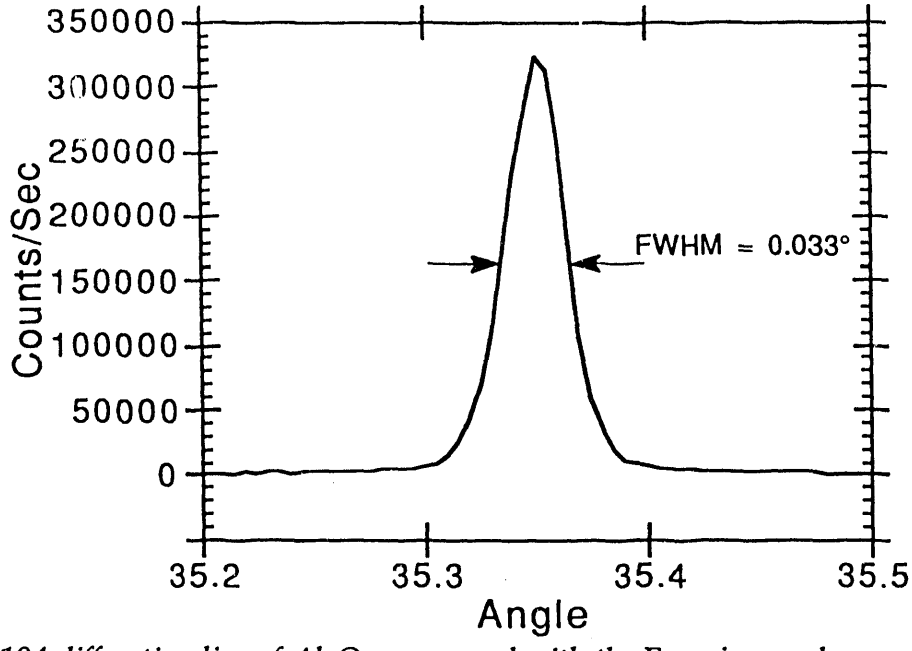


Fig 3 The 104 diffraction line of Al_2O_3 measured with the Focusing analyzer crystal -PSD method. The resolution in this case is largely determined by the detector resolution.

In figure 4 consider the data taken using the out of plane method. The count rate was about a factor of 10 times smaller. Some of this decrease can be explained by fact that we used approximately a 1 meter sample to detector distance so air absorption is a problem. In this case the resolution depends on angle and varies from 0.03° at low angles to about 0.1° at 100°. In order to improve this method we need a larger crystal, 50 mm wide instead of 25 mm, we should move closer (our detector resolution was only about 0.01° in this configuration so we could move closer without degrading the resolution much) and we should close down our vertical divergence in order to improve the resolution at high angles. With these changes this simple method will achieve both high count rates and resolution.

The background is also very low for materials which strongly fluoresce. Consider in fig. 5 the spectrum of CeO_2 run in 15 minutes of counting time using the graphite - out of plane technique. The signal to background ratio is again about 1000 to 1.

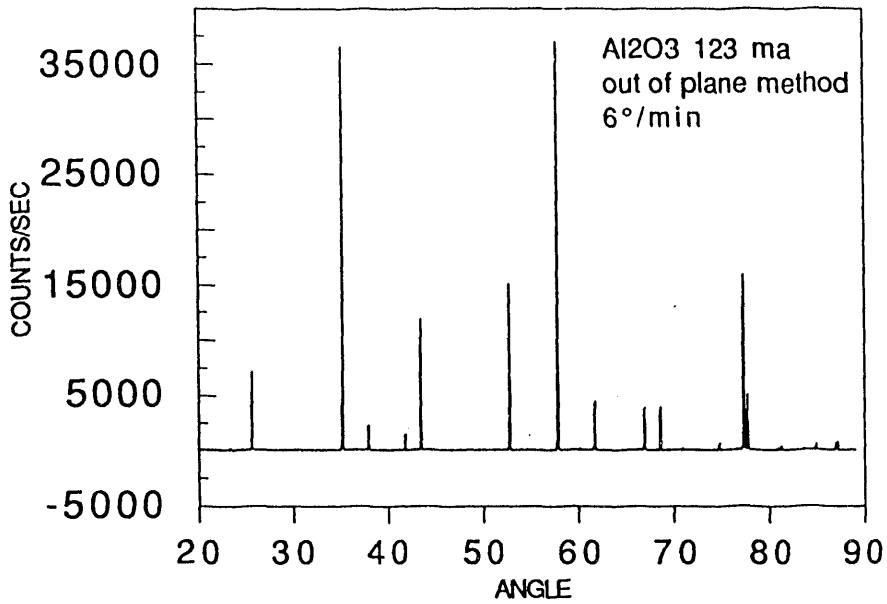
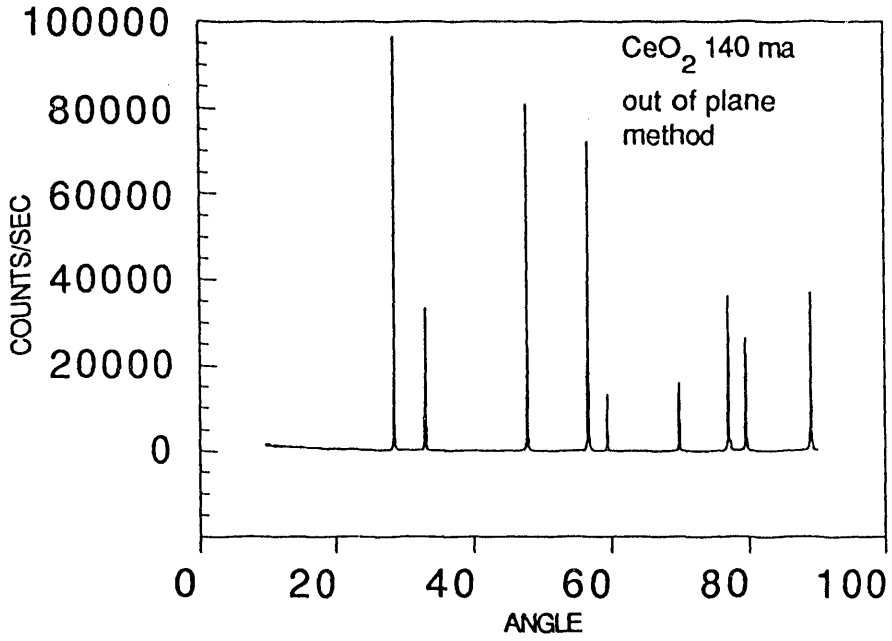


Figure 4 Al_2O_3 data taken using the out of plane method under the conditions indicated.



Fgure 5CeO_2 run with the out of plane method with graphite crystal.

Finally, in figure 6 we show the data taken on a sample of Fe_2O_3. This data took 30 minutes to run using the out of plane technique and has very good signal to background and signal to noise ratios.

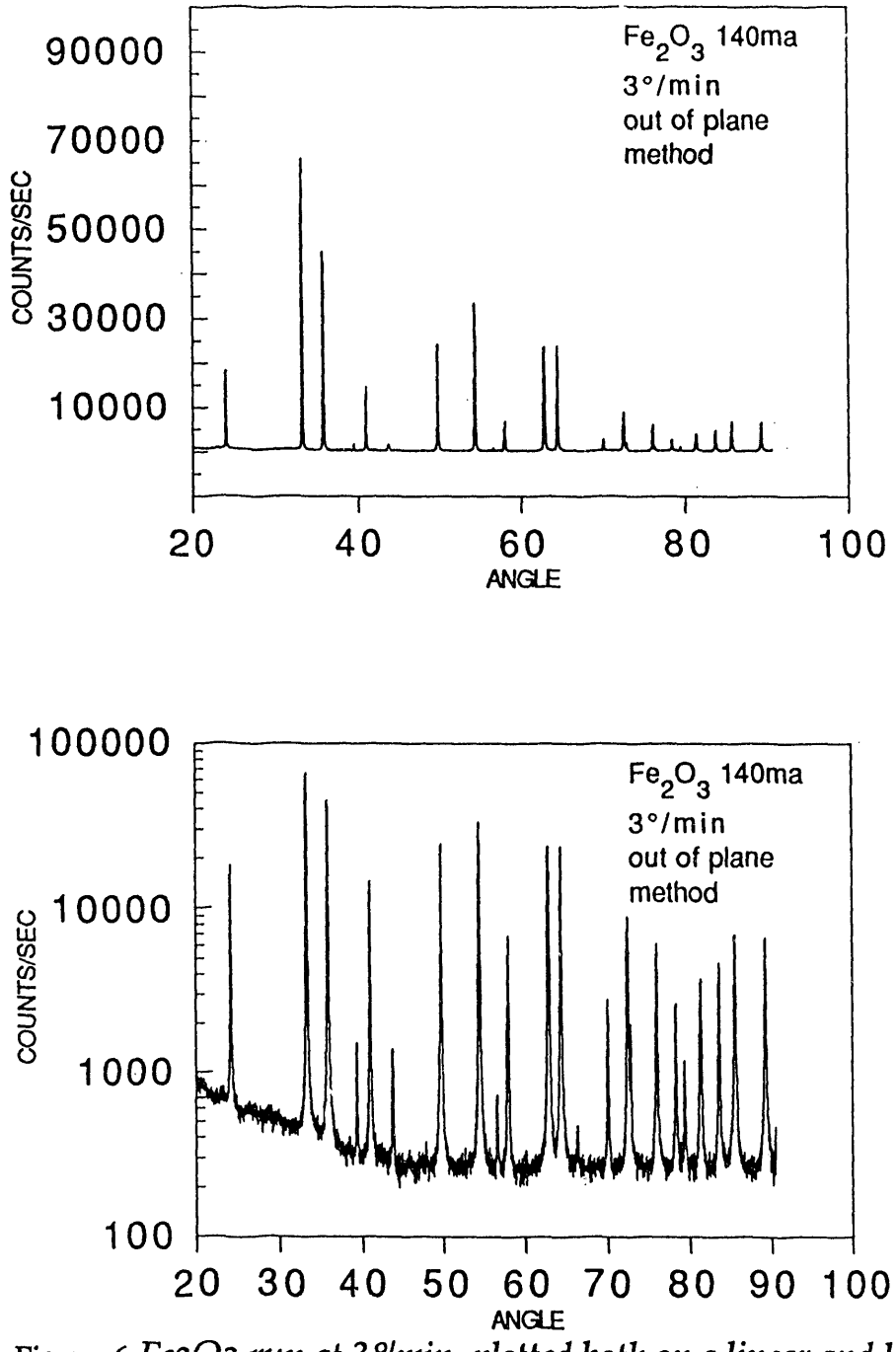


Figure 6. *Fe_2O_3 run at 3°/min. plotted both on a linear and log scale.*

One of the main advantages of our new techniques is that they should be very good for capillary samples. The focused beam puts high flux into a much smaller area than the flat analyzer- single channel technique (Fig. 1C). In figure 7 we show some data we took on a very small capillary of CeO_2 with the background caused by the capillary walls and the first few diffraction lines

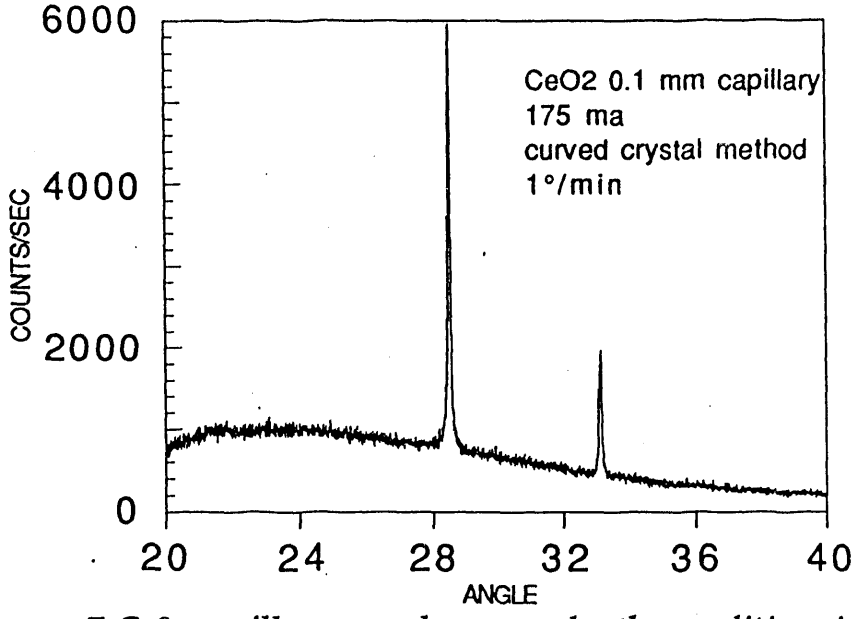


Figure 7.CeO_2 capillary sample run under the conditions indicated

FUTURE APPLICATIONS TO ANOMALOUS AND SMALL ANGLE SCATTERING

These new methods should be particularly good for anomalous scattering since high statistical accuracy and short data collection times are useful to minimizes problems of beam current changes and beam instability. With the out of plane method it may be possible to tune the beamline monochromator to the different energies for the anomalous scattering at each angle step (typically 0.2°). The band width of the graphite[11] should be enough so it would not have to be tuned at each energy. Since we can get very good data by accumulating data in 5 seconds at each angle, collecting 3 or 4 different energies at each angle we would still take less than 30 seconds per angle or less than 150 seconds per degree.

The in plane method should be particularly good for small angle scattering since the method has very good angular resolution and very good background rejection so one should be able to give data at very low angles. Since the curved crystal has a fairly wide acceptance in its out of plane direction, the use of an area detector would allow two dimensional data to be taken simultaneously.

ADVANTAGES AND DISADVANTAGES OF THE TWO METHODS

Each of the two methods has advantages and disadvantages. The curved crystal in plane method is better in terms of resolution and may be slightly better in terms of count rate. It is also better in terms of rejecting background. However, this method is complex in that a highly accurate , motor controlled 4 point bender must be used and must be carefully adjusted both for its shape and its angle. While this is not very difficult, it is somewhat time consuming. This method also requires that the two theta circle be very well aligned since the focusing crystal has a very small field of view and can easily become misaligned as the 2-theta angle is scanned. The graphite out of plane method is very easy to set up and use and it can give very good results. It does not require the 2-theta circle to be very well aligned and is simple to use if the energy must be scanned.

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8. G. S. Knapp, M. A. Beno, manuscript in preparation.
9. The linear detector we are using was manufactured by ORDELA, INC., Oak Ridge TN, USA.
10. Al_2O_3, NIST Standard Reference Material, 1976, XRD Flat-Plate Intensity Standard, U. S. Dept. of Commerce, National Institute of Standards & Technology, Gaithersburg, MD 20899.
11. ZYA Grade, Graphite purchased from Union Carbide Inc.

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