LA-10824-C
Conference

LA--10824-C

DE87 000848

UC-34
Issued: September 1986

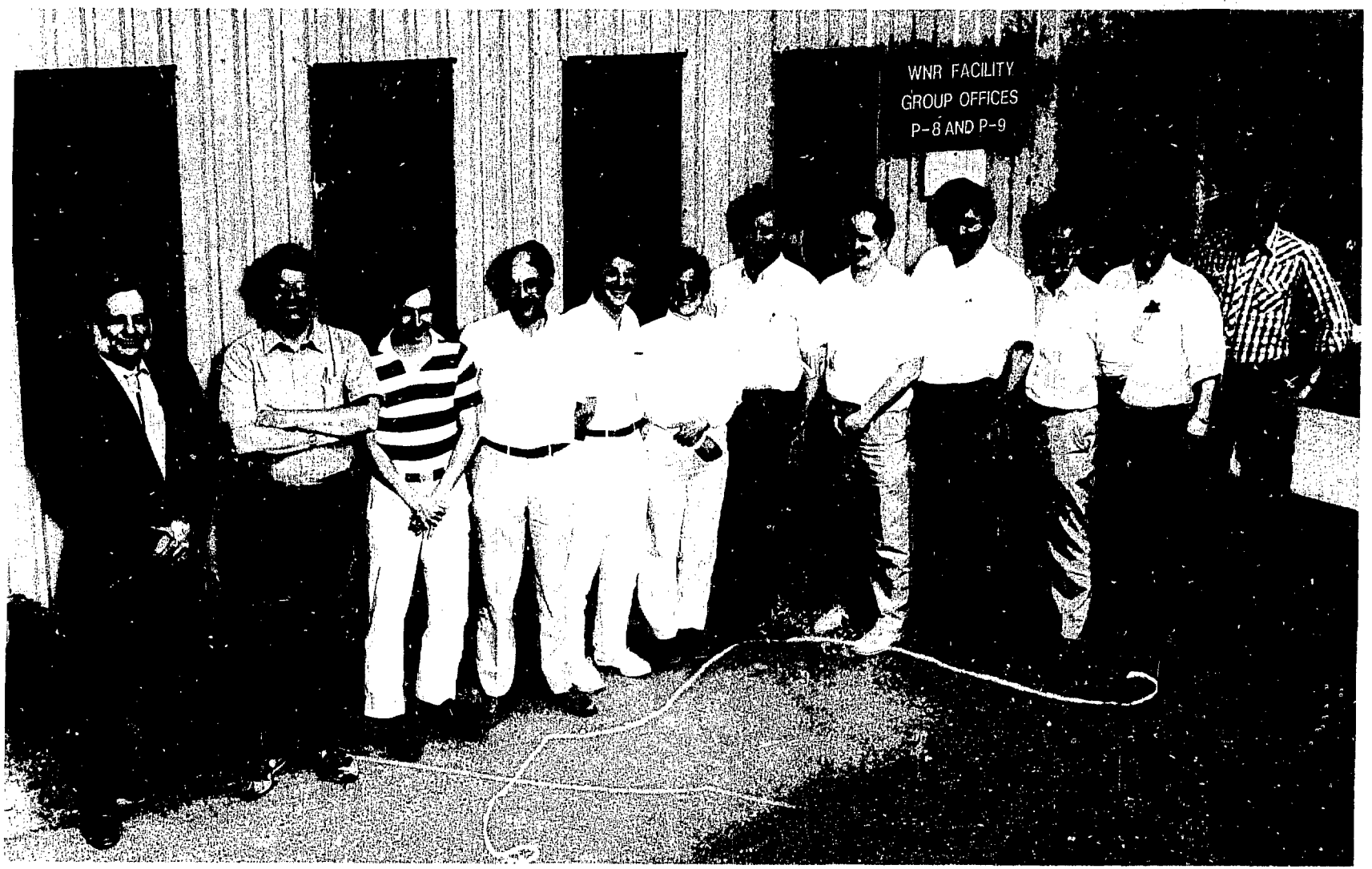
Proceedings of the 1986 Workshop on Advanced Time-of-Flight Neutron Powder Diffraction

Compiled by
A. C. Lawson
K. Smith

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

WORKSHOP ON ADVANCED NEUTRON POWDER DIFFRACTION

19-21 May 1986, Los Alamos, NM



The workshop participants from left to right: A. C. Larson, R. B. Von Dreele, M. Eddy, A. W. Hewat, J. Pannetier, J. A. Goldstone, J. D. Jorgensen, W. I. F. David, J. Faber, Jr., M. W. Johnson, A. C. Lawson, A. Williams

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PROCEEDINGS OF THE 1986 WORKSHOP ON ADVANCED TIME-OF-FLIGHT NEUTRON POWDER DIFFRACTION

Compiled by A. C. Lawson and K. Smith

Held at Los Alamos, New Mexico, May 19-21, 1986

This report contains abstracts of talks and summaries of discussions from a small workshop held to discuss the future of time-of-flight neutron powder diffraction and its implementation at the Los Alamos Neutron Scattering Center (LANSCE).

WORKSHOP OBJECTIVES AND SUMMARY

James D. Jorgensen, Program Chairman
Argonne National Laboratory
Argonne, IL 60439

The workshop on Advanced Neutron Powder Diffraction, held at Los Alamos National Laboratory, May 19-21, 1986, was organized to review the most recent advances in neutron powder diffraction at steady state and pulsed neutron sources and to consider the next generation of neutron powder diffraction instrumentation. The workshop included a small number of participants (~12) who presented formal invited talks and also participated in informal working sessions. Abstracts of the formal talks and written summaries of the informal working sessions are included in this report.

The focus of the workshop divided into four areas:

1. Formal reports of the latest neutron powder diffraction achievements (e.g., HRPD at ISIS and D2B at ILL).
2. Formal discussion of the major scientific uses of neutron powder diffraction and where these fields are expected to go in the next decade.
3. Formal presentations and informal discussion of new instrument concepts and of the best methods for designing and evaluating neutron powder diffractometers.
4. Discussion of what designs and methods still need to be developed and an attempt to organize the community to accomplish them.

Most notable among the recent achievements in neutron powder diffraction were the results from the initial operation of two new high-resolution neutron powder diffractometers, D2B at ILL and HRPD at ISIS. These instruments achieve resolution of $\Delta d/d = 5 \times 10^{-4}$ and also exhibit high count rates. Enough data has been collected to confirm the expected instrument performance. Rietveld refinement of the high resolution data has not yet been achieved but is expected to occur shortly. These two new instruments exhibit resolution which rivals that which is currently achieved on X-ray

powder diffractometers at synchrotron light sources and may, in fact, have reached the resolution limits imposed by sample-contributed line broadening. Clearly, these two instruments represent the current state of the art in neutron powder diffraction and are the basis for comparison with new instrument designs.

Structural refinement is now the most dominant use of neutron powder diffraction and is expected to remain so over the next decade. Initial results from the new instruments suggest that solution of unknown structures will also become possible with the high resolution that is now becoming available. High speed diffraction for kinetic studies and thermodiffractometry is now done on a time scale of approximately one minute per data set and is expected to reach the millisecond scale within a few years as new instruments are optimized for this work. Fine-beam diffraction, which utilizes the unique penetrating power of neutrons to examine the structure, composition, strain distribution, or texture of a small region of an extended sample, is expected to become an increasingly more important technique for materials properties studies. Judging from the science currently being done on neutron powder diffractometers, the majority of neutron powder diffraction experiments will be done in special sample environments such as low temperature, high temperature, high pressure, magnetic fields, controlled atmospheres, reaction vessels, etc., which, again, take advantage of the penetrating power of the neutron as compared to X-rays.

The LANSCE facility at Los Alamos will offer an opportunity to construct and operate a new generation of neutron powder diffractometers over the next few years. Using the proton storage ring to optimize proton flux and repetition rate, LANSCE is projected to produce 100 μA of 800 MeV protons at a repetition rate of 12 Hz in 1988 and may be extended to 200 μA at 24 Hz in 1989. Thus, LANSCE promises to be one of the most intense pulsed neutron sources in the world and will have a repetition rate nicely matched to the needs of high resolution powder diffraction.

One of the goals of the informal discussions was to set guidelines for the design of powder diffractometers at LANSCE. Concensus was reached in at least three important areas:

1. Three powder diffraction instruments will probably be needed to meet the powder diffraction needs at LANSCE.
   a. A high-resolution diffractometer for structure refinement and solution.
   b. A high-count-rate instrument for time-dependent studies, special sample environments and small samples.
   c. A liquids/amorphous diffractometer which provides elastic discrimination and emphasizes the use of high neutron energies and small scattering angles.
2. Special sample environments are now used for the majority of neutron powder diffraction experiments. The design and construction of such equipment should be given a high priority and included in the initial instrument package.
3. Analytical methods for evaluating and comparing the performance of neutron powder diffractometers are not well developed. Such methods are particularly troublesome when comparisons between time-of-flight and constant-wavelength diffractometers are attempted. Meaningful techniques for evaluating instrument performance will be expecially important for optimizing new time-of-flight diffractometer designs involving the use of multiple scattering angles.

Discussion of particular instrument designs focused on concepts for multiple-angle, time-of-flight diffractometers. It was the concensus that the design goal for a high-resolution powder diffractometer at LANSCE should be $\Delta d/d = 5 \times 10^{-4}$ at back scattering angles and $\Delta d/d = 1 \times 10^{-3}$ at $2\theta = 90^{\circ}$. This performance could be achieved with an incident flight path between 50 and 100 meters. The instrument should be designed to operate at the full repetition rate of 24 Hz, which is anticipated in 1989, by utilizing multiple scattering angles to collect a full data set. Particular attention should be paid to the design of the $2\theta = 90^{\circ}$ scattering bank so that the ability to work in special sample environments at high resolution is optimized. Such an instrument, operating on a pulsed source such as LANSCE, would undoubtedly provide world-class capability in neutron powder diffraction.

I wish to thank my colleagues who were willing to present their latest work, much of it unpublished, and to provide detailed input to the informal

discussion sessions in order to make this workshop a success. I am particularly grateful to those who traveled from foreign countries to attend and to Los Alamos National Laboratory and the staff at LANSCE for hosting the workshop.

Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

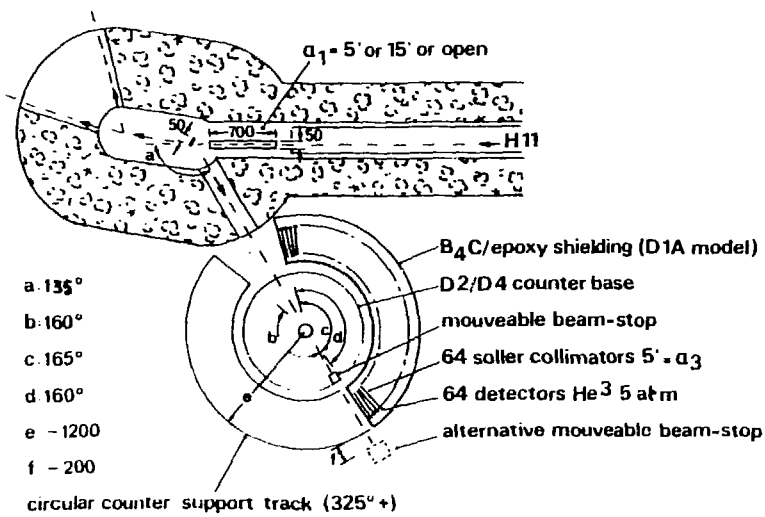
D2B, A NEW HIGH RESOLUTION NEUTRON POWDER DIFFRACTOMETER AT ILL GRENOBLE

(To be published in Materials Research Forum, 1986)

A. W. Hewat
Institut Max von Laue-Paul Langevin
BP 156X, 38042 Grenoble Cedex, FRANCE

ABSTRACT

Applications of high resolution neutron powder diffraction to materials science have grown rapidly in the past 10 years with the development of Rietveld methods of profile refinement [1] and new high resolution diffractometers and multidetectors [3-7]. Materials studied range from catalysts to zeolites and from battery electrodes to prestressed superconducting wires. Although the techniques have now been adapted for X-ray and synchrotron radiation, neutron powder diffraction retains unique advantages. In this paper we describe the design and first test measurements on the latest high resolution neutron powder diffractometer D2B at ILL Grenoble. A review of the applications is published elsewhere [8].

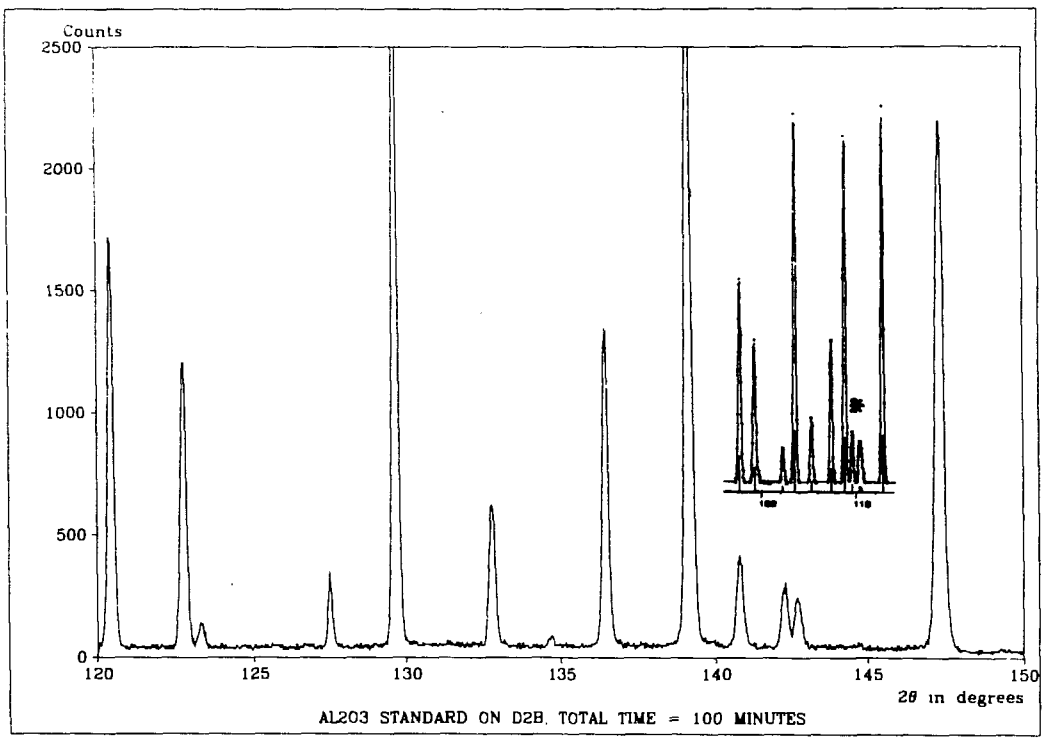


The ILL reactor beam tube M11 was enlarged to 200-mm diameter to illuminate a 300 mm-high composite squashed germanium monochromator, vertically focussing the beam onto a 40 mm-high sample. Wavelength focussing at the large take-off angle of 135° further increases the flux on the sample

to between 10^6 and 7 x 10^6 n $cm^{-2}sec^{-1}$. Soller collimators [9] of 5' divergence are used before each of the 64 detectors. Since the detectors are spaced at 2.5-degree intervals, the complete 160° scattering range can be scanned in only 100 steps of 0.025° in a total time of as little as 100 minutes for the Al_2O_3 standard sample.

The plot of the Al_2O_3 diffraction pattern shows that at 1.6 Å the resolution is better than 10^{-3} for a large scattering range between 2θ = 120° and 160°, with a minimum of 5.6 x 10^{-4}. This compares well with the nominal 5 x 10^{-4} resolution expected for a perfect sample. The insert shows for comparison D1A results at 1.38 Å [4] for the same section. Note that the three lines marked * on D1A are resolved as four lines on D2B, even though D1A is still one of the highest resolution neutron diffractometers. These same lines are resolved almost equally well on the new TOF HRPD on the ISIS pulsed neutron source.

0.105	0.095	0.11	0.16	$\Delta\theta$ degree
10.0	7.8	7.1	5.6	$\Delta d/d$ x 10^{-4}



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HIGH RESOLUTION POWDER DIFFRACTION AT ISIS

W. I. F. David, W. T. A. Harrison and M. W. Johnson
Rutherford Appleton Laboratory
Chilton, Didcot, Oxon OX11 0QX, UNITED KINGDOM

ABSTRACT

The initial commissioning of the high resolution powder diffractometer, HRPD, on the Spallation Neutron Source, ISIS, at the Rutherford Appleton Laboratory has now been completed. Preliminary results have confirmed both intensity and resolution predictions indicating the $\Delta d/d$ lies between 0.04% and 0.08% for all d-spacings. The scientific potential of this increased resolution over existing time-of-flight diffractometers has been demonstrated in the successful ab initio structure determination of an unknown inorganic material, $FeAsO_4$, and the detailed study of subtle symmetry changes in NiO. The true instrumental resolution, however, has been observed in only a small number of experiments: sample broadening is often seen to play a dominant role in the determination of peak shape, particularly at longer d-spacings. This leads to the possibility of extracting useful information about macroscopic properties, such as anisotropic crystallite size and strain distributions and sample homogeneity, but also results in a significant increase in complexity of peak-shape description and data-analysis strategy.

In order to achieve resolutions of ca 0.0005, an optimized moderator design and long primary flight path, of the order of 100 m, are of primary importance. A 95 K liquid methane moderator poisoned with gadolinium produces an acceptable $\Delta t(\lambda)$ distribution over the widest possible range, and a 95 m neutron guide tube, with a curvature radius of 18 km over the first 60 m eliminates γ-rays and fast neutrons whilst producing an excellent neutron flux between 0.5 Å and ~8 Å.

At present, a backscattering detector is installed for maximum resolution, with 90^0 and low angle banks under consideration.

The peak shape function is much more complex than the simple Gaussian for angle-dispersive neutron diffraction but is based on the correct physical modelling of broadening due to the moderator pulse shape distribution,

geometrical and sample effects. Convolution of a pseudo-Voigt function with the Ikeda-Carpenter moderator function has successfully modelled the peak shape for a wide variety of substances and enabled the extraction of physically reasonable values for particle size and strain distributions.

Initial scientific results show the advantages of high-resolution over a wide d-spacing range. The rhombohedral α angle in NiO has been refined to 90.06081(12)° and the lattice parameters of Al_2O_3 have been refined to similar standards of accuracy to previous single crystal studies.

The structure of ferric arsenate has been solved and refined from powder data, the high resolution allowing automatic indexing and extraction of individual peak intensities, leading to a direct-methods structure solution and, consequently, integrated intensities least-squares refinement.

However, the resolution of HRPD has revealed anisotropic, hkℓ-dependent sample broadening in a number of cases, precluding Rietveld refinement until this effect can be incorporated in our Cambridge Crystallographic Subroutine Library based refinement programs, and we are currently examining this problem.

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A DIFFRACTOMETER FOR LIQUID AND AMORPHOUS MATERIALS RESEARCH AT ISIS (LAD)

W. S. Howells
Neutron Division, Rutherford Appleton Laboratory
Chilton, Didcot OX11 OQX, UNITED KINGDOM

ABSTRACT

LAD, an instrument at the ISIS spallation neutron source at the Rutherford Appleton Laboratory, is a diffractometer, or total scattering spectrometer, for the study of liquid and amorphous materials.

The principle of a total scattering spectrometer is simple in concept. A pulsed white beam of neutrons is incident upon the sample and the neutrons are scattered at angles and energies which are subsequently measured by fixed detectors connected to a time-of-flight scaler. If the instrumental flight paths, scattering angles and the neutron energy distribution within the incident pulse are known, the differential scattering cross section can be determined. The instrument in its simplest form consists of a large shielding block of borated resin at a distance ℓ_1 from the moderator with the sample in the center. This sample is viewed by several collimated detectors which are embedded in the shielding block at a distance ℓ_2 from the sample.

Several instruments of this type have already been constructed and the present design benefits from the experience gained on these.

This report reviews the scientific case for the instrument and outlines the design chosen.

Published as RAL-80-017, RAL-86-038

REAL-TIME NEUTRON POWDER DIFFRACTION

J. Pannetier
Institut Laue-Langevin
38042 Grenoble Cedex, FRANCE

ABSTRACT

The use of a high-flux neutron source, together with large curved one-dimensional position sensitive detectors (PSD's), allows a complete powder diffraction pattern to be recorded simultaneously on a time scale of a few minutes or less so that transient phenomena such as chemical reactions in the solid state or first-order phase transitions can now be studied in real-time. Such measurements provide direct information on the progress of a reaction (kinetic law), but may also shed light on the transformations of structure and/or morphology which occur in the reactants during the course of a reaction.

The instrumental parameters relevant to perform time-dependent experiments are as follows:

- The PSD which is required to be stationary, wide, homogeneous and efficient.
- The flux at sample position which finally limits the temporal resolution.
- The data acquisition system (data storage and retrieval).

The angular resolution of the diffractometer is essentially determined by the sample diameter and the spatial resolution of the PSD. This compels longer wavelengths to be used to achieve a reasonable resolution.

Three major kinds of real-time powder diffraction experiments can be envisaged:

- Kinetic studies: the time scale is then imposed by the process under investigation. Time resolutions of a few minutes or less can now be achieved on D1B at the ILL and are being used to study chemical reactions (gas-solid, liquid-solid) and first order transformations.
- Thermo-diffractometric studies: used to investigate thermally stimulated processes in the solid state. A straightforward

application is the study of polymorphic transformations, but its most valuable use is the study of thermal decompositions. For instance, in studies of dehydration processes, this method affords the possibility of investigating simultaneously the composition (proton content) and structural characteristics of a sample.

- Stroboscopic diffraction: used to investigate periodic reversible phenomena stimulated by pulsed environments (temperature, stress, electric or magnetic fields). Resolution of about 2.5 msec with a dead-time of 30 μsec can be obtained on the new high-flux powder diffractometer D20 at the ILL.

WORKSHOP ON ADVANCED NEUTRON POWDER DIFFRACTION

Session 2: Quantitative Evaluation of Powder Diffractometer Performance

Chair: James D. Jorgensen

Reporter: John Faber, Jr.

The evaluation of powder diffractometers and their performance is useful both from an experimenter point of view and for machine designers. Figures of merit are useful for evaluating powder diffractometer performance. Several figures of merit are often desirable or necessary to define performance for the instrument. The relevant merit figures may depend on the specific goals and requirements of a specific experiment. Finally, these characteristic descriptors are of enormous value in the evaluation of plans to upgrade and enhance powder diffractometers.

One clear standard of comparison continues to emerge as a reference for diffractometer design: the D1A at the ILL. The emergence of D2B and D2O ensure that these standards will continue. A number of specialized figures of merit were discussed during this session:

A. Instrumental Resolution

The difficult aspects of this figure of merit are associated with the observation that steady state, constant wavelength diffractometry most closely achieves Gaussian peak shapes over the predominant portion of the data range. That the next generation machines will clearly not follow this rule and that the peculiarities of time-emination delay with neutrons that emerge from pulsed neutron sources make machine comparison difficult. We were able to resolve that full-width-at-half-maximum (fwhm) are still very useful, but resolution should be evaluated as a function of $1/d^2$ since the density of Bragg peaks increases proportionately to $Q^2 = (4\pi \sin\theta/\lambda)^2$.

B. Count Rate

We consider

$$CR \propto \phi_s V \Omega_d, \qquad (1)$$

where ϕ_s is the effective flux on sample, V is the sample volume, and Ω_d is the effective detector solid angle. This figure of merit expresses no explicit cross-section details of the sample. There appear to be significant discrepancies in this particular figure of merit when constant wavelength machines are compared with TOF ones. However, the discrepancies appeared most notable when patterns of Al_2O_3 were compared between HRPD at Rutherford and D2B at the ILL. Several elements of this problem were discussed. First, it is clear that ϕ_s is overestimated in the TOF instruments since various segments in the flux dependence on λ are counted in Eq. (1) but not effectively used. Speculation was advanced on the idea that the differential quantities implied by Eq. (1) must be specifically defined and a specific integration carried out. The implication of Eq. (1) is that this figure of merit relates to the time required to collect suitable data. It may be that weighting by specific details of resolution and information content is also important.

C. Peak to Background Ratio: P/B

Signal-to-noise values are very instructive indicators of machine performance. However, background dependence on 2θ or time-of-flight values leads us to conclude that P/B ratios should be specified over several values of d-spacing that span a representative range for the instrument.

D. Delayed Neutron Fraction

This quantity is particularly important for pulsed neutron sources. This fraction is assumed to be effectively time independent since no particular phasing relative to source pulses is assumed. However, if choppers are employed to reduce this fraction, the background will exhibit specific wavelength dependencies.

E. Standard Samples

For current and new-generation high resolution powder diffractometers, it appears that a wide range of standard samples is required. It was felt that Al_2O_3, while important as a standard, does not sufficiently tax the abilities of high resolution machines. The selection of a standard should take into account graded degrees of structural complexity. The following additional samples were suggested:

1. Ammonium sulfate - Tutton Salt
2. Mg_2SiO_4 - Forsterite
3. β-alumina - perhaps sodium β-alumina
4. Langbeinite
5. Oxalic acid dihydrate - water sensitivity? Containment?
6. $BiVO_4$ - refractory
7. α-Mn
8. $La_2Si_2O_7$

Further study of these materials is suggested. Significant criteria for choice as a standard material should include: repeatable synthesis, low symmetry and 20-30 fractional atom coordinates.

One major highlight of this session was Bill David's discussion of maximum entropy techniques applied to information content analysis of diffraction patterns. It is clear in the TOF case that lagging edge exponential decays associated with the Bragg profiles restrict the information content of TOF patterns at low d-spacing. In relative terms, the Gaussian peak shapes of constant wavelength diffractometers maximize information content.

A number of conclusions about diffractometer comparisons arose during this session:

1. Raw data diffraction patterns from standard samples should be presented.
2. R(exp), R(wp), R(p), R(I), data collection time, sample size, and incident beam flux related quantities should be defined (proton current, energy, moderate details, etc.), calibration standards and values should be given.
3. Instrumental resolution should be plotted in $1/d^2$ units. The analytic form of the peak shape function should be given.
4. A single figure of merit appears to be elusive. Further study of this question should continue.

Work supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

QUANTIFYING POWDER DIFFRACTOMETER PERFORMANCE. CAN WE AGREE ON AN ANALYTICAL METHOD FOR EVALUATING AND COMPARING INSTRUMENT PERFORMANCE?

James D. Jorgensen
Materials Science and Technology Division, Argonne National Laboratory
Argonne, IL 60439

ABSTRACT

As new powder diffractometers are designed for both steady-state and pulsed neutron sources, it is increasingly important to be able to evaluate the performance of these instruments. The goal of such an evaluation is to compare the performance of an instrument with that of another instrument or with the requirements of a particular experiment. In some cases, the instrument under evaluation already exists and is producing data. In other cases, we wish to evaluate a proposed instrument design. In both cases, in order to be of value, the method of evaluating performance must be quantitatively meaningful. Data from existing instruments provide a means of determining whether this criterion is satisfied.

The only previous attempt to compare the performance of a number of neutron powder diffractometers was a study organized by the Commission on Neutron Diffraction of the International Union of Crystallography. In this study, standard samples of sintered aluminum oxide were distributed to neutron centers around the world and data were collected on the existing powder diffractometers. The results for 21 different instruments were reported in a paper by Andresen and Sabine.[1] Quantities reported included resolution ($\Delta d/d$), flux at the sample position, peak intensity (cts/min) and peak/background ratio (for the 113 Al_2O_3 reflection). Ratios of these and other quantities were plotted to illustrate which instruments were operating near their potential capability. Undoubtedly, this published comparison did much to encourage the improvement of existing instruments and the design of new state-of-the-art instruments (largely modeled after D1A at the ILL, which was clearly a superior machine in the comparisons).

Subsequent instrument comparisons have largely consisted of comparisons of individual new diffractometers to D1A. These comparisons have usually focused on overall count rate (time required to obtain a "full"

pattern), resolution, peak/background ratio, and the results of a Rietveld refinement for a standard sample (Al_2O_3).[2] In some review articles and talks, other criteria have been applied. These have ranged from the overall experimental productivity of an instrument (as measured by the number of publications) to the average of all standard deviations for refinements from a given instrument. Clearly, these latter criteria are not very meaningful.

In a recent workshop held at Shelter Island, New York, an attempt was made to quantitatively compare existing powder diffractometers in order to validate the methods of comparison and then to extend these methods to the evaluation of new instrument designs.[3] Unfortunately, this workshop did not result in suitable criteria being developed. Comparison of time-of-flight designs to constant-wavelength designs proved to be more difficult than anticipated. The problems result from the different resolution functions of the two instruments types and the effects of neutron flux versus wavelength for the time-of-flight case. As a compromise, the instrument comparisons in the final report were based on resolution at the point of highest resolution and an estimate of overall count rate as being equal to the product of the useful flux on the sample (Φ_s), the sample volume (V), and the total detector solid angle (Ω_d). When the product $\Phi_s V \Omega_d$ was calculated for the existing instruments D1A (at the ILL), D1B (at the ILL), GPPD (at IPNS), and 2XD (at MURR), the comparison was meaningful for fixed wavelength instruments of the same resolution. However, the performance of the pulsed source instrument appeared to be overestimated. The cause of this discrepancy was not fully understood. It presumably results from the fact that in the TOF case some of the total (time-averaged) flux on the sample is usually wasted, and the resolution is not matched to the required resolution (and, therefore, the integrated intensities of Bragg peaks are unnecessarily reduced) over a significant portion of the data range. Nevertheless, the resolution, count rate, and peak/background ratio are important quantities for the comparison of instruments.

Resolution is obviously an important quantity as it relates to the ability to gain additional information by separating overlapped Bragg peaks. Conversely, if the resolution elements become smaller than the spacing between Bragg peaks, nothing is gained. Hewat showed that the

resolution of a fixed-wavelength diffractometer can be nicely matched to the resolution required to resolve peaks in a cubic structure over a wide range of scattering angles.[4] In this case $\Delta d/d$ varies as d^2. For systems of lower symmetry, defining the required resolution is not as straightforward. On a plot of required $\Delta d/d$ versus d, points are typically spread over a wide range. For most cases it is clear that even the best instruments will not achieve sufficient resolution to resolve all of the peaks. Moreover, the sample-contributed broadening will probably place the actual limit on resolution. If this limit is due to particle-size broadening, the best possible resolution will be defined by $\Delta d/d = Kd/D$ where D is the particle size and K~1 (depending on particle shape).

Plots of the resolution curves for various instruments have usually been given as a function of the operating units for the particular instrument, i.e., θ for constant-wavelength instruments and d for time-of-flight instruments. Unfortunately, such plots are misleading since they obscure the fact that the density of Bragg peaks is not a constant across the plot. In the case where constant-wavelength and time-of-flight instruments are being compared, a more meaningful axis should be employed. Perhaps $\delta d/d$ versus $1/d^2$ is a logical choice.

Comparing count rates for constant-wavelength and time-of-flight instruments will undoubtedly continue to lead to inconsistencies whenever the resolution functions of the two instruments are dramatically different from one another and, in the TOF case, different from the required resolution. As mutltiple-angle TOF instrument designs are developed and guide tubes, bandpass choppers, etc., are employed so that essentially all of the time-averaged flux on the sample is being used, the product $\Phi_s V\Omega_d$ should be a suitable criterion. An alternative would be to determine the time required to collect a complete data set to a sufficient level of statistics to ensure a given level of precision in a Rietveld refinement. Unfortunately, such a criterion is not easily applied.

The measurement and comparison of peak/background ratios is of particular importance to ensure that instruments are performing as well as is possible. The original IUCr comparison study revealed large differences in peak/background ratios and motivated many laboratories to search for problems they had not previously realized were present. Similar experience has led to significant improvement of the instrument performance at IPNS.

Initial comparisons of the SEPD and BT1 and NBS showed that the SEPD exhibited backgrounds a factor of two higher than expected. The problems were traced to multiple scattering involving the sample, the walls of the sample chamber, and the inner surfaces of the instrument shielding. Additional boron carbide/epoxy shielding was added to the SEPD and GPPD and the backgrounds were lowered a factor of two, thus becoming competitive with the world's best instruments. For TOF instruments, particular attention must be paid to multiple scattering and delayed neutrons in order to achieve the lowest possible backgrounds.

Data from standard samples may offer the best method of comparing instruments. Specific data for standard Al_2O_3 samples were the basis of the successful IUCr comparison. These standard Al_2O_3 samples have continued to be used in many laboratories, with a Rietveld refinement being added to the list of results being reported. However, the Al_2O_3 sample may have outlived its usefulness as a suitable standard. Instrument performance has now outdistanced the complexity of the Al_2O_3 structure. It is probably time to identify a new standard sample for which the standard deviations of refined atom position parameters can be used as a meaningful comparison of instruments. In the case of proposed instrument designs, the refinement of simulated data for a standard structure may be a good way to evaluate the effects of resolution, count rate, incident spectrum versus wavelength (i.e., moderator design), etc., on overall instrument performance. After the new instrument is constructed, refinements of real data can be compared with refinements of simulated data to search for instrumental contributions to systematic errors.

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Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

THE SOLUTION OF UNKNOWN STRUCTURES FROM POWDER DIFFRACTION DATA

A. W. Hewat
Institut Max von Laue-Paul Langevin
BP 156X, 38042 Grenoble Cedex, FRANCE

ABSTRACT

Almost all of the work to date using high resolution neutron powder diffraction has consisted of the refinement of crystal structures first solved by X-ray single crystal measurements. In some cases it has been necessary to solve structures by trial and error from neutron powder data or to complete structures obtained only partially by X-ray crystallography. An example is the structure of hydrocarbons absorbed on zeolites: the basic zeolite structure was known and the absorbed molecules located by difference Fourier techniques. Fitch, Renouprez and Jobic [1] have thus obtained the structure of benzene in Y-zeolite from D1A measurements and with additional D11 small angle scattering experiments have demonstrated the aggregation of the benzene molecules in the zeolite channels.

With the new very high resolution diffractometers D2B and HRPD now becoming available, we expect to solve completely unknown structures by direct methods. This has already been demonstrated using the older diffractometer D1A for simple structures such as oxalates [2], s-triazine $C_3N_3H_3$ [3] and $Ca_5(SiO_4)_2(OD)_2$ [4]; the most recent example, using HRPD, is that of $FeAsO_4$ [5]. The steps in the solution are:

1) Fitting individual lines to obtain the first 20 d-spacings. Long wavelengths (3 Å or 6 Å) are used to spread out the large d-spacings and $\lambda/3$ is used to eliminate zero errors.
2) Indexing the diffraction pattern using the Visser [6] or Kohlbeck [7] programs. The volume of the formula unit and the figure of merit are used to select valid solutions, and reduced cells are calculated to check the relations between these solutions.
3) Refining the unit cell and extracting the structure factors using the Pawley program ALLHKL [8]. A few structure factors may be wrong due to strongly overlapping or degenerate reflections.

4) Construction of E-maps and searching for atom peaks or structure fragments: standard programs such as SHELX, MULTAN, MITHRIL are available. A relatively large number of structure factors are needed to produce unambiguous E-maps, so very high resolution diffractometers such as D2B or HRPD are needed for more complex structures.
5) Calculating difference Fouriers to complete the structure.
6) Profile refinement of the structure, possibly using constrained refinements of the Pawley [9] or Baerlocher [10] type.

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STRUCTURE REFINEMENT

Mike Eddy
Department of Chemistry, University of California at Santa Barbara
Santa Barbara, CA 93106

ABSTRACT

Throughout the last decade the curve fitting procedure originally devised by Rietveld [1] has received extensive modification. The improved resolution of the more recent instrumentation and the increasingly complex problems that are being investigated give rise to features which could not have been foreseen. The problems confronting any investigation which utilizes the profile refinement technique include:

- Peak Shapes [2,3,4]. This is particularly well understood for both time-of-flight and constant wavelength powder profiles collected on present instrumentation, such as SEPD/GPPD and D1A. Although the use of a simple Gaussian peak shape function is often no longer adequate in the constant wavelength case, modifications are possible which give additional information on strain and particle size. Non-systematic (hkl-dependent) reflection broadening may present a problem for the new generation of high resolution diffractometers.
- Background. Non-linear variations in the background resulting from diffuse scattering are to be seen in the profiles of some samples. This is particularly apparent in disordered systems at time-of-flight facilities, where the background resembles that of an amorphous material and must be refined using sophisticated polynomial expressions.
- Impurities. As the resolution of powder diffractometers has increased, contaminants that were previously hidden from the main phase by the much stronger reflections have been detected. This has necessitated the development of multi-phase refinement procedures. Because of the nature of the problems being planned for the high intensity instruments which are under construction at ILL and the Rutherford Appleton Laboratory, there will be an increasing demand for refinements of more than one phase.

- Sample size. Approximately a 10-gram sample is usually required for a normal experiment. This remains one of the major constraints on the type of sample which can be investigated by powder neutron diffraction. Even if sufficient compound is available, the procedures required to prepare the sample and to eliminate any hydrogen-containing species can sometimes be prohibitive. More intensity appears to be the only solution to this problem.
- Refinements which are underdetermined. In some cases the number of observations is insufficient to refine the structural parameters with adequate precision [5]. This is often further hindered by particle size effects which lower the number of independent observations still further. The simplest solution to this problem is to increase the resolution, thus providing more unique data. Another method has been used by Baerlocher [6] in his investigation of zeolite ZSM5. Additional observations are supplied in the form of expected bond lengths and angles (restraints), and these are used to stabilize the refinement, especially in the early stages.

The commissioning of the new generation of neutron powder diffractometers has opened up an exciting time in the field of profile analysis. The high resolution instruments, D20 and HRPD, extend the range of problems which can be investigated, in addition to opening up several new areas of research. Thus the major fields of interest which are envisaged are:

- Complex structural problems. The high resolution results in more unique observations, thus extending the number of parameters which can be refined without the need for distance constraints. In favorable cases, refinement of up to 300 parameters should be possible.
- Ab initio structure determination. The solution of structures from powder neutron diffraction data has already been demonstrated [7]. Because the neutron scattering lengths of many elements are so similar, structure solution by direct methods should provide the greatest chance of success. However, in special cases, Patterson constructions may provide useful information.

- Metallurgical applications. There is an increasing demand for studies of high spatial resolution to investigate bulk stress and strain in technologically important materials.

To complement these latter, high-resolution studies, the proposed instruments, D20 and HIPD at Rutherford, offer moderate resolution but high intensity. Thus complete diffraction patterns could be collected in a matter of seconds or less. This opens up opportunities in:

- Reaction kinetics. The ability to collect data in such short times allows the study of non-equilibrium chemical reactions. Those of particular interest involve solid surfaces (gas-solid, liquid-solid).
- Temperature induced transformations. This is possibly the simplest of the experiments to perform, primarily because so much time and effort has been put into perfecting reliable ancillary equipment. These transformations include phase transitions, crystallizations, and the observation of unstable species.
- Perturbations. The full potential of phasing an external pulse sequence (for example, from a laser or magnetic field) with data collection, has yet to be realised, but the increased intensity which will be available soon will test its feasibility.

Thus the future appears very promising, and the fruits of many years labor at the various neutron facilities, both pulsed and reactor-based, should be realized over the next two to three years.

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SPECIAL ENVIRONMENTS FOR POWDER DIFFRACTION

J. Faber, Jr.
Materials Science and Technology Division, Argonne National Laboratory
Argonne, IL 60439

ABSTRACT

The wide range of ancillary equipment developed for constant wavelength diffractometers[1] clearly reflects the need for experimentalists to control and adjust the environment of the sample under study. Special challenges and advantages exist for time-of-flight, variable wavelength diffractometers in that large solid angles of detectors at fixed 2θ values are emphasized. To gain back count rate for high resolution powder diffractometers, only moderate collimation between sample and detectors is considered. At pulsed neutron sources where epithermal neutron fluxes are an intrinsic characteristic of the source, particular care is required[2] to minimize multiple scattering and other parasitic scattering sources.

At the Intense Pulsed Neutron Source[3] (IPNS), most instruments have dedicated closed-cycle ($10 < T < 300$ K) refrigerators for cryogenic sample environments. One exchange gas cooled cryostat is operational that provides $T > 1.5$ K. For special experiments at ultra-low temperature, capability down to 50 mK with a dilution refrigerator is available. A 30 kbar pressure cell is operational, and plans to produce a more efficient (larger sample volume in the neutron beam) gas pressure cell with pressure $p < 4$ Kbar are underway. This particular gas cell design allows the sample under pressure to be easily mounted to cryogenic equipment so that an experiment can map the sample response in $T(< 350$ K)p coordinate space.

In the high temperature regime, the IPNS facility has a vanadium element vacuum furnace that provides for $300 < T < 1300$ K. The sample must be heated in the vacuum of the furnace environment. If other environments are required, a special vacuum-tight sample container must be used. A new research and development effort is underway at IPNS to provide for artificial environments at high temperature. With the artificial environment, restricted-angle high temperature furnace, we plan $300 < T$ 1700 K with in-

situ control of a gaseous sample environment. This effort marks a second-generation development in that samples can be inserted into the operating high temperature furnace. Figure 1 illustrates some of the unique capability of this furnace design. The Rietveld least-squares results are for $Co_{1-x}O$ at 1100° C. The restricted angle feature of this furnace is a direct consequence of collimation elements that eliminate Bragg interference scattering from the furnace components. In Fig. 1, only the Bragg scattering from $Co_{1-x}O$ is observed. The inset in the figure shows the results of in-situ experiments carried out at constant temperature, T = 1100° C. The composition of the sample, and hence the nonstoichiometric defect concentration, was determined by using $Ar-O_2$ or $CO-CO_2$ gas mixtures. These are flowed over the sample during the measurement. One important point is that high temperature alone is not sufficient to fix the equilibrium state of many interesting high temperature materials. If the partial pressure of O_2 in equilibrium with the sample is important, then the following coordinate space can be mapped: $1 > P(O_2) > 10^{-25}$ atm, $300 < T < 1700$ K.

The advent of higher-flux neutron sources and the newest developments in high resolution powder diffractometry lead us to consider opportunities to optimize ancillary equipment. The expectation is that ancillary equipment response time will become the rate-limiting step in experimental investigations. Hybrid designs that allow for both low and high temperature will certainly be important.

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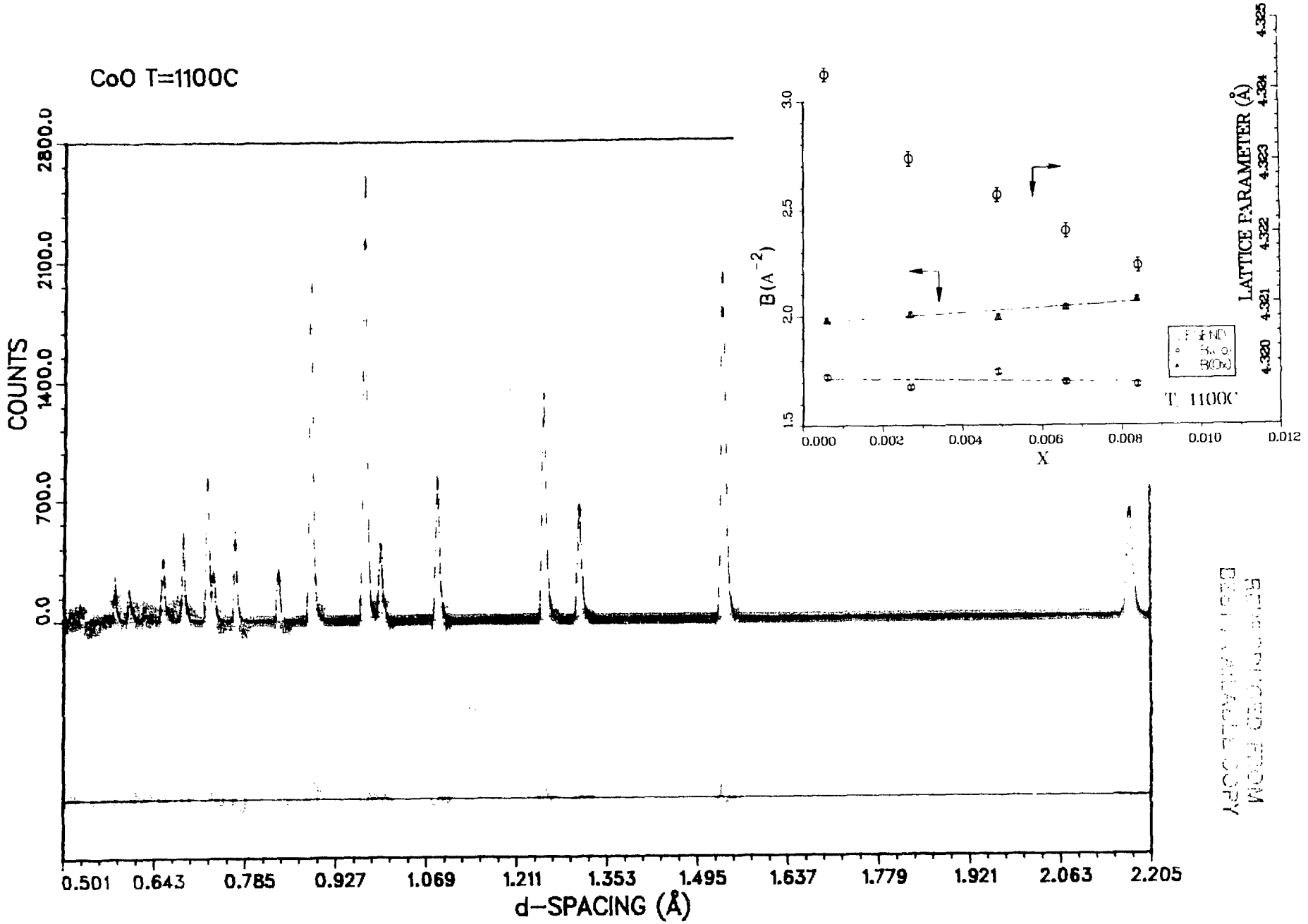
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1.211
1.353
1.495
1.637
1.779
1.921
2.063
2.205
d-SPACING (Å)
B(A^{-2})
3.0
2.5
2.0
1.5
0.000
0.002
0.004
0.006
0.008
0.010
0.012
X
LATTICE PARAMETER (Å)
4.325
4.324
4.323
4.322
4.321
4.320
T 1100C

Session 4: Future Prospects for Powder Diffraction at LANSCE. How Far can We Push the State of the Art at the Proposed Facility at LANL?

Chair: Joyce Goldstone, Los Alamos National Laboratory
Reporter Art Williams, Los Alamos National Laboratory

This session addressed the future of the neutron powder diffraction program at LANSCE. A brief overview of the future capabilities of the LANSCE facility was presented. The current powder diffractometer instrumentation and research program were outlined. Then the questions to be discussed were posed, and discussion on instrumentation desirable for the expanding research program followed.

Following is the current expected schedule for LANSCE for the next four years.

	1986	1987	1988	1989	
Current (μamp)	20	50		100	200 (?)
Percent availability	35	50	80	80[1]	
Repetition rate (Hz)	12	12		12	24[2]
Target	W	U	U	U-boosted (?)	
Moderators		H_2O/Liq H2		Liq/solid CH_4 (?)	
New Experimental Hall[3]		start	occupy		
Support building			start	occupy	
Instrument construction			----$4.5M------		

Notes: (1) A National users' program will be reinstated in 1989.
(2) To obtain 200 μamp, a repetition rate of 24 Hz will be used.
(3) Included in the construction funds for the new Experimental Hall and Support Building is $4.5M for the construction of instruments.

Currently two powder diffractometers exist at LANSCE, neither of which is well-engineered or properly optimized and supported. The current major

research programs being conducted on these instruments include the following five areas: actinides, magnetic materials, hydrides, adsorbates, and phase transitions. The science being pursued encompasses weapons work and other internal Laboratory interests, structure of liquids and amorphous solids, chemistry of solids, phase transitions, magnetism, and defect studies. Along with maintaining research in these areas, LANSCE is expected to become operational as a national users' facility sometime in 1989 with a time average flux an order of magnitude over the current value. Clearly the current status quo cannot hope to support such an ambitious future. The primary question addressed at this session concerned the future experimental powder diffraction capabilities at LANSCE: how many and what type of powder diffraction instruments will be required to satisfy the long term needs of both the Laboratory programmatic interests as well as the future users' community?

The general consensus was that the major use of neutron powder diffraction has been, and will continue to be, the refinement of known structures. Structure solution will continue to become increasingly important as well. With this in mind, as well as the very large flux which will be available with the PSR, the following general recommendations were agreed upon. It can be expected that most of the interest will continue to be in experimental conditions different from room temperature and pressure. For this reason special environment ancillary equipment must be considered from the start for every instrument, and such equipment should be interchangeable between instruments. Dedicated instrument capabilities for each instrument should include variable temperature equipment with a range of 1.5 K to 600 K. Refrigeration units should use cryogenic liquids, as the cooling capacity of the Displex units currently employed at LANSCE is far too low. Rapid sample changing capabilities with computer control will be required as well as rapid vacuum system cycling for the sample chamber to reduce turnaround time. Shared capabilities should include a dilution refrigerator, pressure cells, furnaces, and cryomagnets. A free radius of 60 cm was suggested for the sample chamber to ensure the accommodation of such ancillary equipment. Care should be taken to minimize magnetic (steel) components in the vicinity of the sample chamber in order that stray fields do not in the future become a problem for certain types of experiments. It was concluded that it is in the best interest of the facility and the users to construct several simple, specialized, well

optimized instruments rather than just a few sophisticated, versatile but poorly optimized instruments. The personnel support required for each instrument is two staff scientists and one technician, and an education program must be implemented for users so that they can run the instruments and analyze data themselves. To facilitate the participation of naive users, each instrument must be robust and well engineered with its own dedicated crane (≥ 1000 pound capacity).

There was a considerable discussion concerning the advisability of employing guide tubes on powder instruments. Since guides only give back a factor of two or three at 60 meters, they should not be considered for any instrument with a flight path shorter than this. On an instrument with a guide, it would be advantageous to build the guide with a higher vertical divergence than horizontal divergence either by using a nose or by using ^{58}Ni on the top and bottom and natural Ni on the sides. In any case a removable Soller collimator must be used between the end of the guide and the sample to reduce the divergence. Curved guides have the problem that high energy neutrons tend to be bunched up on one side of the guide. The most favored configuration for a guide was a straight guide with a chopper near the source. This avoids the problems with curved guides, is cheaper, does not sacrifice the short wavelength neutrons and chops off the power pulse. It was also pointed out that an instrument with a straight guide and chopper can support a 'piggy back' Bragg edge spectrometer, which may be of some advantage in the future.

Since structure determination is becoming more important in powder work and multiple angle Rietveld refinement codes reduce systematic errors, it is vital on all instruments to employ detectors over as wide a range as possible, from backscattering to as low as 30°. Also, since special environments will undoubtedly continue to play a leading role, all detectors in the 85° to 95° range should have as high a spatial resolution as possible. The question of the choice of detectors (gas tubes versus scintillators) was raised several times but not settled. The current experience at ISIS and IPNS has been that the Li glass scintillators have much higher backgrounds and are clearly very labor intensive to build. They may be preferred in the backscattering geometry, although at 90° position sensitive gas tubes would be just as effective. The question of an optimum moderator for powder diffraction work was also left unsettled, primarily because different experiments require different moderators.

Refinement of thermal parameters requires high flux at short wavelengths, which is sacrificed with a cold moderator. Cold moderators, on the other hand, provide slightly narrower peak shapes and more long wavelength neutrons which may be important for structure determination. An instrument with a chopper which is designed to accept only a narrow band of wavelengths and use a large angular range clearly requires a moderator which maximizes the flux in the band of wavelengths of interest.

It is a specific recommendation of this workshop that the future capabilities of LANSCE include at least three powder diffractometers which must be designed and constructed. It was estimated that each instrument will cost approximately $1M. The specifications for these three machines are listed below.

1) 10-meter Incident Flight Path

This instrument should be dedicated for experiments on the structure of liquids and amorphous solids. It will concentrate on the measurement of scattering at low angles, from approximately 1° to 90°. The moderator must be as cold as possible and poisoned with boron.

2) 30-meter Incident Flight Path

This is the 'workhorse' refinement diffractometer. It should have a resolution in backscattering of 1×10^{-3} and at 90° of 3×10^{-3}. It should incorporate detectors over a very large angular range from backscattering to about 30°. It should also have the capability to change the incident beam size easily - down to as small as 1 mm by 1 mm for metallurgical experiments.

3) 65-meter Incident Flight Path

This instrument should have a resolution which is about twice that of the 30-meter machine and close to the limit of sample peak broadening for even the best samples. It should use a chopper with a wavelength band of about 2.75 Å. The moderator used will depend on the waveband chosen. Full detector coverage should extend from 30° to backscattering and the capability of changing the beam size must also be included. The instrument should use scintillators in backscattering with a resolution of 5×10^{-4} and 90°-detectors providing a resolution of 1×10^{-3}. It may use a guide tube, in which case a Soller collimator must be provided.

The implementation and staffing of these three well-engineered, well-designed instruments along with the implementation of a users' education program and adequate in-house computing facilities are necessary to meet the future Laboratory and international user community requirements for neutron powder diffraction at LANSCE.

MULTIPLE-ANGLE TIME-OF-FLIGHT DESIGN CONCEPTS. ARE WE OVERLOOKING AN ORDER OF MAGNITUDE IN INSTRUMENT PERFORMANCE FOR GENERAL STRUCTURAL STUDIES?

James D. Jorgensen
Materials Science and Technology Division, Argonne National Laboratory
Argonne, IL 60439

ABSTRACT

Typical time-of-flight powder diffractometer designs emphasize the high resolution that can be obtained in back-scattering and exhibit flat resolution curves over a rather large range of d spacings by utilizing a large wavelength band. Such an instrument design sacrifices cons'derable count rate by measuring large d spacing reflections with too much resolution and too little flux. The high resolution at large d spacings is unnecessary for most problems (particularly for structural refinement) and the problems of frame overlap can be easily solved with bandpass choppers. If it is assumed that particle-size broadening places the ultimate limit on the resolution that can be used in a powder diffractometer, the optimum resolution function is one for which $\Delta d/d$ is proportional to d. Such an overall resolution function can be achieved by the use of detector banks at multiple scattering angles in a time-of-flight instrument. The count rate can be raised considerably by then using a much narrower band of wavelengths selected by su'table bandpass choppers in such a way that data from different scattering angles overlap. The wavelength band is selected from the high-flux portion of the incident spectrum, and high repetition rates can be utilized because frame overlap is eliminated by the choppers. Increased count rates thus result from a higher useful neutron flux on the sample and a larger detector area. Preliminary design calculations for such instruments indicate that an order of magnitude improvement in overall performance can probably be achieved for cases where a total diffraction pattern is desired (as in the case of Rietveld refinement).

A specific instrument design has been evaluated to illustrate these concepts. The instrument design parameters are:

Incident flight path	50 m
scattered flight path	2 m
wavelength band	0.8 - 2.8 Å
repetition rate	30 Hz
sample	1 x 1 x 4 cm
detector area	0.4 sterradians

The instrument resolution ($\Delta d/d$) varies from 0.00085 at $2\theta = 160^{\circ}$ to 0.0136 at $2\theta = 30^{\circ}$. The count rate can be estimated by calculating the product of the flux on the sample (ϕ_s), the sample volume (V), and the total detector solid angle (Ω_d). For a 10^{16} peak flux pulsed source, similar to ISIS or LANSCE, and a poisoned liquid methane moderator, $\phi_s = 1.5 \times 10^6$ n - cm^{-2} -s^{-1}. Thus, $\phi_s V \Omega_d = 2.4 \times 10^6$. This is approximately equal to the performance calculated for a back-scattering 65 m TOF powder diffractometer in the Shelter Island report,[1] even though the Shelter Island report assumes a 10^{17} source flux (an order of magnitude higher). Thus, the expected gain in performance is realized.

Additional advantages for the multiple-angle design include a lower delayed neutron background, resulting from the use of the bandpass choppers, and a reduction of systematic errors in Rietveld refinement because correlations to wavelength-dependent systematic errors in the data are reduced. Additionally, the proposed instrument design could be further improved by the use of a partial guide tube, a guide tube with ^{58}Ni on the top and bottom surfaces, or a guide tube with Soller slits in the incident beam. This would provide a more optimal match of incident and scattered angular divergence and simulate a large vertical divergence (which does not significantly degrade the resolution). The moderator temperature for a multiple-angle instrument should be chosen to give the maximum flux in the wavelength band that is used, consistent with the flight path length and the source repetition rate. The best choice may not always be a cold moderator. In order to match the desired resolution function, the scattered flight paths may be of different lengths at different scattering angles. Conversely, Soller collimators in the scattered flight paths may be found to be advantageous.

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Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

THE DETERMINATION OF THE COMPLETE NEUTRON SCATTERING LAW $S(k,\omega)$ FROM TOTAL SCATTERING EXPERIMENTS USING COMPUTER TOMOGRAPHY

M. W. Johnson
Neutron Division, Rutherford Appleton Laboratory
Chilton, Didcot OX11 OQX, UNITED KINGDOM

ABSTRACT

This paper describes how the considerable body of knowledge on image reconstruction from path integrals (computed tomography) may be applied to total, time-of-flight, neutron scattering experiments (i.e., those involving no experimental energy analysis) to obtain the neutron scattering law $S(k,\omega)$. We examine the feasibility in terms of possible instrument geometries and reconstruction algorithms. It is possible that such reconstruction techniques may have wide application in the fields of neutron powder diffraction, amorphous scattering, liquids scattering and quasielastic incoherent scattering.

In a time-of-flight neutron scattering experiment in which no energy analysis is performed, the recorded intensity in a particular detector and time channel is related to a curved path integral over the k,ω plane. Adjacent time channels from the same detector provide an integral over a neighboring, parallel, curved path. Typical paths for a detector at scattering angles (2θ) of 5°, 10°, 20° and 30° are shown.

If the path integral can be written down in terms of a scattering law which is path-independent, the problem may be mapped to the image reconstruction problem solved in real-space tomography.

In Section 2 we establish an algorithm for the solution of a tomographic problem with curved path integrals.

In Section 3 we show how a total-scattering time-of-flight experiment may be expressed in a form suitable for reconstruction.

Section 4 presents some preliminary results which show how quite remarkable resolution would appear to be possible using the technique.

Section 5 indicates some of the problems which remain to be solved and gives some preliminary definitions of the instrument design required to maximize the potential of this technique.

Published as RAL-86-041

A VERY HIGH COUNTRATE POWDER AND DIFFUSE SCATTERING INSTRUMENT FOR ISIS (HIPD/PADI)

R. Cywinski*, W. I. F. David and M. W. Johnson
Neutron Division, Rutherford Appleton Laboratory
Chilton, Didcot OX11 OQX, UNITED KINGDOM

ABSTRACT

This note presents a preliminary design study of a total scattering diffractometer for ISIS. The proposed instrument is intended for medium resolution powder diffraction and low resolution diffuse scattering studies. A schematic layout of the instrument is given and its performance evaluated. In particular it is noted that the instrument has potentially (at full ISIS intensity) the highest countrate of any existing or currently proposed powder diffractometer.

Pulsed neutron sources are ideally suited to diffuse scattering studies of short range structural and magnetic defects in solids as they allow simultaneous collection of data over a broad Q-range. However, there are at present no instruments in the ISIS suite which are optimized for such studies. The cross sections associated with defect scattering are generally small, typically 10-100 mb-st^{-1}.at.$^{-1}$. The major requirements of any diffuse scattering instrument are therefore a high incident neutron flux and a large detector area, such that experimental counting times are kept manageably short. Q-resolution, on the other hand, is relatively unimportant: diffuse cross sections vary slowly with scattering vector and the resolution can be relaxed to 5 or even 10%. Fortunately a trade of resolution for intensity can be achieved on a pulsed source simply by reducing the length of the incident flight path.

As diffuse scattering is generally measured over the Q.range $0.1\ \text{Å}^{-1} \leq Q \leq 5\ \text{Å}^{-1}$ the main detector array on a pulsed source diffuse scattering instrument will be in the forward direction. However, it must also be remembered that even on a short instrument the intrinsic Q-resolution over a backscattering detector array can be as high as 0.5%. Such resolution, which is comparable to that of the D1B powder diffractometer at ILL, is perfectly adequate for many powder diffraction studies. Clearly a large area backscattering array should be incorporated in the

design of an ISIS diffuse scattering instrument to allow simultaneous measurement of medium resolution powder diffraction and low resolution defect scattering. Such an instrument would be a unique and powerful tool in the increasingly important field of kinetic powder diffraction studies.

*J. J. Thomson Physical Laboratory, Reading University, Whiteknights, Reading, RG6 2AF, UNITED KINGDOM

Internal RAL Report Numbers NDR/P8/84, NDR/P9/85

X-RAY POWDER DIFFRACTION AT SYNCHROTRON LIGHT SOURCES

J. Faber, Jr.
Materials Science and Technology Division, Argonne National Laboratory
Argonne, IL 60439

ABSTRACT

The historical and technical development of the Rietveld method for the refinement of structural detail closely follows the evolution of high-resolution powder diffraction techniques using neutrons as the source probe. Both initial and subsequent developments of this analytical technique can be directly correlated with a number of important attributes of neutron scattering experiments. In particular, the observation that the Bragg peaks associated with a neutron powder diffraction experiment are closely Gaussian provided a straightforward analytical basis for describing the Bragg peak shapes. No simple analogue exists to describe the recent development of corresponding experiments with X-rays as the source probe.[1] (The preliminary experience gained on ultra-high resolution neutron powder diffraction machines suggests similar difficulties will arise with neutron experiments.) A number of important contrasts between the two techniques will be discussed.

There are a number of significant recent developments associated with high intensity X-ray sources, namely the advent of synchrotron light, that lead us to re-examine the potential for X-ray powder diffraction studies. Enormous fluxes, perhaps 2-3 orders of magnitude more intense with existing synchrotrons, allow for very high resolution powder diffractometers.

In this paper, we will discuss recent developments associated with only two photon beam lines at the National Synchrotron Light Source (NSLS): X13A and X18A. The X13A beam is white, i.e., polychromatic. The selection of a monochromatic beam is done in the experimental hutch. This beam line configuration provides for the possibility of either constant wavelength or energy-dispersive experiments.[2] To illustrate the capabilities for high-resolution powder diffraction, we show the results of X-ray Rietveld profile refinements on several zeolite materials.[3] The potential for high-resolution X-ray diffraction experiments to refine the structural detail and provide unique results is clearly demonstrated. The X18A beam line

employs a double-crystal incident beam monochromator assembly that allows for precise selection of incident beam wavelength or energy from the synchrotron continuum. Great flexibility in wavelength or energy selection is possible. Two monochromator crystals allow the photon beam incident on the sample to be fixed in space for any selected energy. Instrument alignment is thus facilitated. Preliminary high resolution data on several samples will be discussed.

The prospects for even high brightness sources with the 6 GeV synchrotron national facility[4] in the U.S. provide even more potential for high resolution X-ray powder diffraction. The use of tunable source characteristics to perform differential measurements is one example of how scattering contrast can be effectively exploited.

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Work supported by the U.S. Department of Energy, BES-Materials Sciences, under contract W-31-109-Eng-38.

NEW DEVELOPMENTS IN STRUCTURE REFINEMENT FROM POWDER DATA

R. B. Von Dreele
Department of Chemistry, Arizona State University
Tempe, AZ 85287

ABSTRACT

With the advent of new super-high-resolution neutron powder diffractometers, new software must be developed to take advantage of their capabilities.

For structure analysis, these machines are capable of examining problems with > 400 atomic parameters; however, current techniques of structure determination from powder data are very rudimentary and are generally adapted from single crystal techniques. An alternate approach may be to apply our considerable knowledge of structures to predict the unknown structure; this may require the coupling of artificial intelligence with energy minimization techniques. Techniques for reducing the parameterization of large structural problems are also needed; rigid body descriptions reduce the number of parameters but enforce presumptions about the structure. Soft constraints do not reduce the parameterization but can improve the control of a least squares refinement. Some combination may be needed.

The extremely high resolution provided by these new instruments can give detailed powder texture information. Strain, particle size, mosaic block size, and various defect structures all affect the powder diffraction profiles. Mathematical models consistent with instrument resolution are needed to describe these effects as they occur in samples for structure analysis. More elaborate techniques are needed for samples whose texture is of primary scientific interest. Obviously, sample selection is important for both structure and texture analyses.

AMORPHOUS/LIQUIDS DIFFRACTION. CAN A GENERAL PURPOSE POWDER DIFFRACTOMETER SATISFY THE NEEDS OF THE GLASS DIFFRACTION COMMUNITY OR IS A DEDICATED INSTRUMENT REQUIRED?

Art Williams
Los Alamos National Laboratory
Los Alamos, NM 87545

ABSTRACT

In February 1986 a small workshop was held at the Argonne National Laboratory to define the characteristics for a state-of-the-art time-of-flight neutron diffractometer for glass and liquid structure factor measurements. A 'reference design' was worked out at this workshop with a liquid methane moderator and an incident flight path length of 10 to 11.5 meters. The most important requirement that was identified was the absolute necessity of using detectors at small scattering angles in order to reduce or eliminate inelasticity corrections to the data. The instrument therefore relies primarily on scattering angles below 45 degrees.

At the 1984 Shelter Island Workshop on Scientific Opportunities with Advanced Facilities for Neutron Scattering, the performance parameters for a variety of advanced high-intensity powder diffractometers for future high-flux sources were investigated. Resolutions of 0.005 $\Delta d/d$ or better were considered useful for crystallographic studies, with an associated scattering angular range from backscattering to 90°. Examination of currently available detectors inserted into the Argonne 'reference design' for a liquid/glass diffractometer covering the range of scattering angles from 90° to 160° demonstrates that resolutions down to 0.0027 $\Delta d/d$ can be achieved on such an instrument. Further, the cold moderator and small scattering angles available with the instrument would allow access to Q values down to 0.01 or 0.02 $Å^{-1}$. This overlaps the typical range of small-angle diffractometers and will in fact make it possible to obtain information about long range density fluctuations on a scale of a few hundred Å.

The major disadvantage of a generalized machine is the sacrifice of simplicity of design and optimization for specific tasks. Two less sophisticated, fully-optimized instruments provide a higher throughput of

experiments and a less demanding division of labor and are easier to use, support, and maintain than a single very expensive generalized machine.

WORKSHOP ON ADVANCED NEUTRON POWDER DIFFRACTION

Session 6: What is still needed?
(Data Analysis)

Chair: Bill David
Reporter: Mike Johnson

1. Hardware

Each of the four sites represented used VAX computers (under VMS) for their principal data analysis. In addition, all sites had access to VT100 terminals and Tektronix 4010 emulation.

At present only two sites (IPNS, ISIS) are on BITNET, and the ILL will be included in the near future. LANSCE will probably remain outside the network.

2. Design Simulation Software

The following is a list of the instrument design and simulation software used at the sites shown. All programs are written in FORTRAN unless specified otherwise.

Site	Program Name	Function
IPNS	TOFDIF	Geometrical resolution calculation using a constrained Monte Carlo technique
IPNS	TOFSIMU	Time-of-flight powder pattern (including background) simulation
AERE	SIP	Instrument performance prediction. Calculate intensities and resolution for a large number of instrument types and neutron sources (in Proceedings of the Workshop on Neutron Scattering Data Analysis, Adam Hilger, UK, 1986)
AERE	SIMON	Geometrical resolution calculation using a constrained Monte Carlo technique (AERE R-9170, 1978)

RAL	MCGUIDE MCLIB	Constrained Monte Carol simulation of a neutron guide. Factors include multi-component guides, surface irregularity and abutment errors (RL-80-65, RL-78-90)
RAL	MCROTOR	Constrained Monte Carlo simulation of neutron Fermi chopper
RAL	SIMULATE	Time-of-flight and CW, neutron and X-ray powder pattern simulation

3. General Data Analysis

Site	Program Name	Function
IPNS	TOFMANY	Auto powder pattern peak search and least squares fitting using user-supplied peak shape
ILL	PTEK (Pascal)	Gaussian peak fitting program using maximum likelihood
ILL (Distributor)	TRACER	Finds reduced unit cell
Edinburgh (G. S. Pawley)	ALLHKL	Refines I_{hkl} and lattice parameters from a full powder pattern
RAL	GENIE	Data Display and manipulation package
RAL (Distributor)	AUTO.PEAK	Automatic peak-finding program
RAL (Distributor)	DECFUN	Deconvolutes Gaussian line shapes from neutron peak profiles
RAL	BACKER	Automative background fitting using orthoganal polynomials

4. Indexing

Site	Program Name	Function
ILL/RAL (Distributors)	VISSER	Auto Indexing
"	KOHLBECK	" "
"	TREOR	" "
"	LOUER	" "

"	QDAT	User interface for auto indexing
RAL	INDEX	User friendly version of QDAT

5. Graphics

Site	Program Name	Function
ORNL	ORTEP	
Chemical Design Co. Oxford, UK	CHEMX	Molecular graphics and energy minimisation package
R. Risher	STRPLT	Polyhedral plotting
ILL	SCHACKAL	Molecular display using dotted balls
ILL (Distributor)	CENG.ORTEP	User friendly ORTEP

6. Rietveld

Program	Feature Codes	Particle Size	Strain	Temp. Factor(#)	Constraints/ Restraints
ROTELLA	RTMB	GI	GA	≤ 4	
GSAS	XNTMDB	GI	GI	TLS	SC
HEWAT	RN	GI	GI	≤ 2	
YOUNG/WILES	XNMB	VI	VI	≤ 2	
CCSL	XNT	VI	VI	≤ 2	S
BAERLOCHER	XNB	GI	GI	≤ 2	R
PRINCE/FINGER	RNB	PI		≤ 4 TLS	C
COX	RXN	VI	VI	≤ 2	
PAWLS	NB	GI	GI	TLS	C
TAYLOR	N	GI	GI	TLS	C
COCKROFT	RNM	GI	GI	SH	

R=Rietveld deriv.	B=Background Refined	#=Tensor Rank
T=Time-of-flight neutron	G=Gaussian	TLS=Rigid Body Refinement
N=Const. wavelength neutron	V=Voigt	SH=Spherical Harmonics
X=X-ray	P=Pearson VII	S=Symmetry Constraints
M=Multi Phase	I=Isotropic	R=Restraint
D=Multi Data	A=Anistropic	C=Constraint