IUCr COMMISSION NEWS

Contributions intended for this section should be submitted to The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

COMMISSION ON POWDER DIFFRACTION

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Newsletter No. 4 (Extracts)

Powder diffraction at ISIS

ISIS is currently the most powerful pulsed spallation neutron source in the world, operating with an average current of 100 μA. Neutrons are produced every 20 ms by a high-intensity 750 MeV proton beam in sharp bursts that are undermoderated to produce a polychromatic pulse. The neutron pulse width and time of flight are both proportional to wavelength and thus the resulting ratio, the resolution, is essentially independent of wavelength and improves linearly with the length of flight path. Different neutron wavelengths may be discriminated by measuring the time of flight from moderator to sample to detector, and thus a complete diffraction pattern may be collected at a single Bragg angle. Additionally, the high epithermal flux below wavelengths of 1 Å permits d spacings as low as 0.2 Å to be observed.

The High Resolution Powder Diffractometer (HRPD) at ISIS is situated at the end of a 100 m neutron guide. The highest resolution ($\Delta d/d \simeq 4 \times 10^{-4}$) is obtained in backscattering ($170 < 2\theta < 178°$) where geometrical contributions are negligible. This high resolution is essentially independent of d spacing and thus HRPD is well suited for the study of phase transitions and subtle symmetry changes; peak splittings are not confined to one small 'high-resolution' section of the pattern but occur with roughly equal magnitude across the diffraction pattern. High resolution has proved invaluable for the profile refinement using data from crystals of complex molecules with large unit cells and *ab initio* structure determination. In the latter case an advantage of time-of-flight powder diffraction experiments is the ease of lattice-parameter determination from first principles when the highest-d-spacing information is available. Indeed, individual d spacings up to 6 Å may be measured with an accuracy of ~1 in 10^5. The narrow instrumental peak shape, although complicated, is well known, thus permitting the observation and study of line broadening effects. Recent successes in this field include the modelling of chemical concentration gradients in samples, and the study of effects due to anisotropic strain broadening and antiphase domains.

Medium-resolution high-intensity neutron diffraction is also available at ISIS on the POLARIS diffractometer. POLARIS is complementary to HRPD providing a resolution of $\Delta d/d \simeq 5 \times 10^{-3}$ but with increased flux because of its 10 m primary flight path.

Recent experiments on POLARIS include kinetic studies involving rapid experimental collection time of ~5 min and the study of powders at high pressures up to 50 kbar. With suitable collimation the fixed 90° detector geometry permitted by the time-of-flight method allows full diffraction patterns to be collected at elevated pressures without corruption of data by diffraction peaks from the pressure cell itself.

A suite of data analysis programs, developed and supported at ISIS, is available for use by the user community.

Informal enquiries should be made to the authors at the Neutron Science Division, Rutherford Appleton Laboratory. Beam time is allocated twice yearly following a peer review selection procedure. The closing dates for proposals are 16 April and 16 October each year. Application details can be obtained at the following address:

University Liaison Secretariat, R3
The ISIS Facility
Rutherford Appleton Laboratory
Chilton, Didcot
Oxfordshire OX11 0QX, England

Telephone: 0235-44592. Fax: 0235-445720.
Telex: 83159 RUTHLB G.

W. I. F. David, R. M. Ibberson

Comments on search/match procedures

In September 1989, the International Centre for Diffraction Data (ICDD) submitted a questionnaire to its members to survey the interests and concerns of industrial diffractionists. One recurrent concern is the efficient and reliable identification of multiphase powder patterns in regard to cost-effectiveness and turnaround time. Search procedures fall into two categories; namely, manual searching in search manuals and com-

puter searching on large mainframe computers or on PC's. Although computer searching has been practised since 1965, manual searching is still actively continued as evidenced by the undiminished demand for updated Hanawalt search manuals. However, with the addition of 2000 new powder patterns to the Powder Diffraction File (PDF), the future search manuals will become excessively bulky and costly. Search routines will have to be devised and tested that are more efficient and compact. Substantial condensation of the 1987 alphabetical index could be achieved by eliminating multiple listings of fluorides (3277), hydroxides (2069), chlorides (1907) and other common ions or radicals inasmuch as the particular fluorides, hydroxides *etc.* can be located more readily under the element name of the fluoride, hydroxide *etc.* For example, erbium fluoride would be located only under erbium.

Substantive improvements in computer-search routines would be much appreciated by powder diffractionists. General acceptance of computer search/match methods has been slow for several reasons: lack of uniqueness in the identification of an unknown mixture of phases (too many alternative matching candidates); lack of fast *reliable* automated digitization of precision powder diffraction data (obtained with Bragg–Brentano parafocusing diffractometers), and questionable cost benefits over manual search procedures. It is generally conceded that utilization of elemental data greatly reduces the number of pseudo-matches. Selective restrictions of the PDF database would be conducive to speeding up the various search/match routines. There are about a dozen computer programs that have been tested and are being used. However, all their algorithms have some limitations. It would be a challenge to devise an efficient cost-effective program which would embody the combined merits of the separate algorithms. A critical review of the appended pertinent references should serve to stimulate renewed efforts in meeting the needs of the worldwide diffraction community engaged in powder diffractometry. It is also proposed by CPD to sponsor a workshop on phase identification to address the above problems.

Selected references in chronological order

HANAWALT, J. D., RINN, H. W. & FREVEL, L. K. (1938). Chemical analysis by X-ray diffraction – classification and use of diffraction patterns. *Ind. Eng. Chem. Anal. Ed.* **10**, 457–512.

FREVEL, L. K. (1944). Chemical analysis by powder diffraction. *Ind. Eng. Chem. Anal. Ed.* **16**, 209–218.

Index (Inorganic to the Powder Diffraction File) (1963). ASTM Special Technical Publication 48-M2. American Society for Testing and Materials, Philadelphia, PA, USA.

SMITH, D. K. (1963). A Fortran program for calculating powder patterns from atom coordinates. Am. Crystallogr. Assoc. Annu. Meet., 28–30 March. Paper E11.

FREVEL, L. K. (1965). Computational aids for identifying crystalline phases by powder diffraction. *Anal. Chem.* **37**, 471–482.

NICHOLS, M. C. (1966). A Fortran II program for the identification of X-ray powder diffraction patterns. Report UCRL-70078. Lawrence Livermore Laboratory, CA, USA.

JOHNSON, G. G. JR & VAND, V. (1967). A computerized powder diffraction identification system. *Ind. Eng. Chem.* **59**, 19–26.

FREVEL, L. K., ADAMS, C. E. & RUHBERG, L. (1976). A fast search-match program for powder diffraction analysis. *J. Appl. Cryst.* **9**, 199–204.

YOUNG, R. A., MACKIE, P. E. & VON DREELE, R. B. (1977). Application of the pattern-fitting structure-refinement method to X-ray powder diffractometer patterns. *J. Appl. Cryst.* **10**, 262–269.

MARQUARDT, R. G., KATSNELSON, I., MILNE, G. W. A., HELLER, S. R., JOHNSON, G. G. JR & JENKINS. R. (1979). Search–match system for X-ray powder data. *J. Appl. Cryst.* **12**, 629–634.

EDMONDS, J. W. (1980). Generalization of the *ZRD-SEARCH-MATCH* program for powder diffraction. *J. Appl. Cryst.* **13**, 191–192.

FREVEL, L. K. (1982). Structure-sensitive search–match procedure for powder diffraction. *Anal. Chem.* **54**, 691–697.

HUANG, T. G., PARRISH, W. & POST, B. (1983). Computer search/match of standards containing a small number of reflections. *Adv. X-ray Anal.* **26**, 93–98.

CHERUKURI, S. C. & SYNDER, R. L. (1983). Comparison of the Hanawalt and Johnson–Vand computer search/match strategies. *Adv. X-ray Anal.* **26**, 99–104.

GOEHNER, R. P. & GARBAUSKES, M. F. (1983). Computer-aided qualitative X-ray powder diffraction phase analysis. *Adv. X-ray Anal.* **26**, 81–86.

LIN, T. H., ZHANG, S. Z., CHEN, L. J. & CAI, X. X. (1983). An improved program for searching and matching X-ray powder diffraction patterns. *J. Appl. Cryst.* **16**, 150–154.

CARR, M. J., CHAMBERS, W. F. & MELGARD, D. (1986). A search/match procedure for electron diffraction data based on pattern matching in binary bit maps. *Powder Diffr.* **1**, 226–234.

SKROBIAN, M. & HAVLIK, T. (1986). Searching matching of X-ray powder diffraction patterns using a programmable calculator. *Powder Diffr.* **1**, 235–239.

MARQUART, R. G. (1986). *μPDSM*: mainframe search/match on IBM PC. *Powder Diffr.* **1**, 34–39.

JENKINS, R. & HOLOMANY, M. (1987). *PC-PDF*: a search/display system utilizing the CD-ROM and the complete Powder Diffraction File. *Powder Diffr.* **2**, 215–219.

L. K. Frevel

Program Information Exchange Bank

D. K. Smith has been appointed consultant to the CPD. His primary role as a consultant will be that of the development and operation of a Program Information Exchange Bank, where 'program' means computer programs for powder diffraction analysis and collection. A first writeup of the Program Data Bank has appeared as a chapter in the book *Modern Powder Diffraction*, which

is available from the Mineralogical Society of America (US $ 20).

At the planning stage is a compendium of program descriptions that can be maintained at some central location where users can dial in for current information on any programs or category of programs. It is envisioned that a central computer facility could put the list where it could be reached *via* dial-in and be queried for the updated information desired.

The Program Information Exchange Bank project will be further discussed at the Powder Diffraction Symposium in Toulouse, 1990.

Anyone who has developed or modified a program suitable for the program bank is urgently requested to communicate this to Professor D. K. Smith, 239 Beike Building, Department of Geosciences, The Pennsylvania State University, University Park, PA 16802, USA.

Rietveld refinement round robin: update

Round-robin packages have been circulated to participants in 28 X-ray and neutron powder diffraction laboratories around the world. These packages contain:

(i) a detailed set of instructions,

(ii) forms for documenting the refinement and data-collection procedures and associated Rietveld refinement results,

(iii) two powder samples (one simple, and one complex) for in-house data collection and crystal structure analysis, and

(iv) a magnetic tape containing two 'standard' X-ray and neutron powder diffraction data sets for in-house analysis (also to be used for the return of data sets collected on the above samples).

The crystal structure/profile refinement results and diffraction data returned by participants over the next few months will be surveyed by the CPD and a preliminary report will be presented at the Symposium on Powder Diffraction, a satellite meeting of the XV Congress of the IUCr in Toulouse, France, 16–19 July 1990.

If any reader wishes to participate in the survey and has not yet registered their interest, please write to Dr R. J. Hill, CSIRO Division of Mineral Products, PO Box 124, Port Melbourne, Victoria 3207, Australia.

Call for contributions to the Commission and its Newsletter

Members of the powder diffraction community are invited to contact any member of the Commission on Powder Diffraction with matters for possible consideration by the Commission and/or inclusion in subsequent (biannual) Newsletters. A matter for which input from the diffraction community is certainly needed relates to the selection (if deemed desirable) of a logo for the Commission.

The names and addresses of Commission members are given in Newsletter No. 2, published in *Acta Cryst.* (1989). A**45**, *FC*19–*FC*23.

P.-E. Werner
Editor, Newsletter No. 4