COMISSION ON POWDER DIFFRACTION

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- **Accuracy in Powder Diffraction III**
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- **International Workshop on the Rietveld Method (RW2000-PL),**
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CPD Chairman’s Message

The last EPDIC conference in Barcelona (May, 2000) was a real event for the Powder Diffraction (PD) community. In addition to a qualified and comprehensive scientific program and commercial exposition, several new initiatives were presented, among which the birth of a new society on X-ray applications (IXAS, International X-ray Analysis Society), presented by the President *Bob Snyder*. We all wish a fruitful collaboration between the IUCr-CPD and IXAS.

Powder diffractionists may now look forward at the forthcoming Accuracy in Powder Diffraction III (Gaithersburg, May 2001), and at the Size-Strain III conference (Trento, December 2001) (see the “What’s on” page for details). Next EPDIC8 has also been announced and it will take place in Sweden, during the late spring of 2002, before the IUCr general assembly of August 2002 in Israel. The list is completed by the Denver conference that will be held every August as usual, and by several schools and workshops concerning or including powder diffraction. A relatively new field, which is gaining an increasing interest, is that of pharmaceutical applications of PD; ICDD is very active in this area, and will organise a workshop in Europe following the successful PPXRD of last September (see Newsletter No 22).

It is worth underlying that IUCr can support congresses/workshops/schools, so we encourage colleagues who are willing to organise PD-related events to submit a request for financial support to IUCr. Forms to be used to apply for support can be requested to the IUCr Calendar Committee, 2 Abbey Square, Chester CH1 2HU, England, or they can be downloaded from the CPD web-site.

In this issue of the CPD Newsletter we welcome several new commercial sponsors who contributed to the editorial and publishing activity and to maintain the CPD webpage by placing their advertisements on the present Newsletter. Before the main topic of the issue, which is “*Synchrotron radiation, non-ambient XRD, parallel beam optics*”, we introduce the letters to the CPD Chairman. The new space can be used for ongoing discussions on new developments in PD, but also for presenting different or new things, like “ *Teaching and Learning Powder Diffraction across the Internet* ”. Readers are invited to contribute. Newsletter No 23 also reports on recent updates on the CPD projects, which presently include two Round Robin (RR)activities: next issue will focus on one of the two projects (the size-strain RR), whereas the other one on quantitative phase analysis is close to a very successful end.

Finally, we wish to draw the reader’s attention on the Computer Corner, an useful presentation of new software on PD, edited by *Lachlan Cranswick*. Suggestions and contributions to the next issue will be very welcome. Readers are also invited to send reports on schools and congresses.

Paolo Scardi

CPD projects

Size/Strain Round Robin

During the last CPD meeting of Barcelona (May 2000), Davor Balzar communicated that a large batch of an intended size-broadening standard specimen has been successfully prepared by Daniel Louër and Nathalie Audebrand at the University of Rennes. Daniel Louër described the synthesis of the sample, from a hydrated ceria precursor (190 Å particle size), heated to 700°C, to yield CeO_2 with substantial line broadening. Details on the preparation are to appear soon in a paper by Daniel Louër and co-workers in Chem. Mater.

Davor Balzar has prepared an “instrumental broadening” sample by annealing at elevated temperature commercial-grade CeO_2 powder. Both samples were sent to participating laboratories for collection of the representative diffraction patterns. The intent was to include a wide variety of experimental conditions (sealed and synchrotron X-ray, CW and TOF neutron sources). These diffraction patterns will be sent to the round-robin participants, who will then apply different methods of line-broadening analysis to the same sets of data. The representative diffraction patterns are being collected at the following facilities:

Laboratory X-ray sources:
  Common instrumental set-up: University of Le Mans (*Armel Le Bail*),
  Incident-beam monochromator: University of Birmingham (*J. Ian Langford*).

Synchrotron x-ray sources:
  2nd-generation synchrotron, flat-plate geometry: NSLS, Brookhaven National Laboratory (*Peter W. Stephens*),
  3rd-generation synchrotron, capillary geometry: APS, Argonne National Laboratory (*Richard Harlow*) and ESRF (*Olivier Masson*).

Neutron sources:

Constant wavelength: ILL, Grenoble (*Alan Hewat*) and NIST, Gaithersburg (*Brian Toby*),
Spallation: ISIS (*Mark Daymond*).

The CeO_2 sample prepared at University of Rennes is an intended size standard. Davor Balzar will continue the search for a strain-only standard. Readers are invited to send suggestions directly to Davor Balzar (balzar@boulder.nist.gov).

Quantitative Phase Analysis Round Robin

Last issue contained an extended report by Ian Madsen on the Quantitative Phases Analysis RR. Now a paper on the RR results has been prepared by Ian Madsen and co-workers, and we look forward at a very rapid editorial processing and publication on the *Journal of Applied Crystallography*. The CPD wishes to include a reprint of this paper in one of the next Newsletters.

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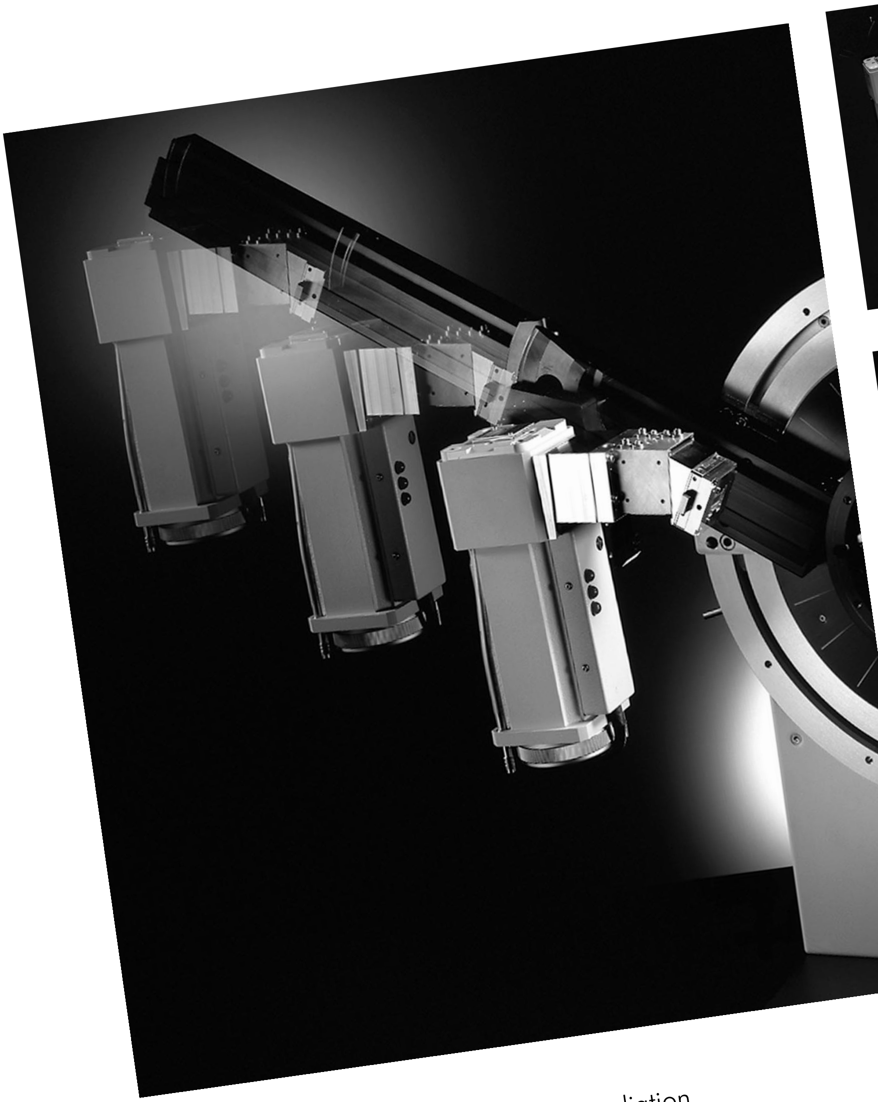

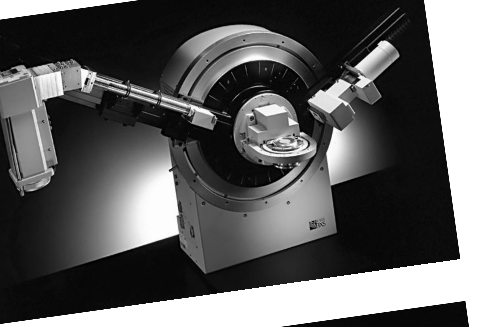

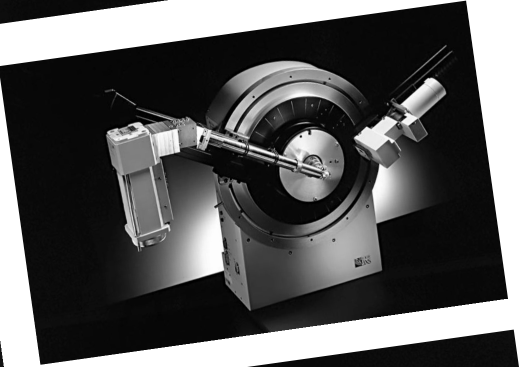

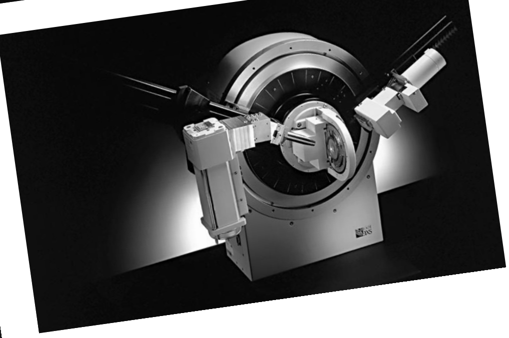

Improved Size/Strain Accuracy/Detection Limits by Advanced Fundamental Parameters Method - A Contribution to Line Profile Analysis and Rietveld Method: Crossing Paths?

(M. Leoni and J.I. Langford, CPD Newsletters **20** (1998) p. 30)

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INTRODUCTION

In the summer 1998 issue of the CPD newsletters, we talked about BGMN: a Rietveld program based on an unique raytracing fundamental parameters approach. Here we report about further development of this program by the so-called “tube tails” correction. Usage of such tube tails correction enables one to make a much more accurate profile estimation. Thereby, the accuracy/detection limits of size/strain measurements may be improved significantly.

BGMN uses a convolution of a Lorentzian

$$I\left(\frac{1}{d}\right) = \frac{\pi b_{1k}}{b_{1k}^2 + \left(\Delta\frac{1}{d}\right)^2}$$

and a squared Lorentzian

$$I\left(\frac{1}{d}\right) = \frac{2\pi b_{2k}^3}{\left(b_{2k}^2 + \left(\Delta\frac{1}{d}\right)^2\right)^2}$$

for modelling the diffractive part of the profile function. b_{1k} is set by the phase specific parameter $B1$, describing size value. b_{2k} is set by the formula

$$b_{2k}^2 = k_1 b_{1k}^2 + k_2\left(\frac{1}{d_k}\right)^2$$

whereas $0 \leq k_1 \leq 1$ describes the shape of the size distribution and $\sqrt{k_2}$ is the r.m.s strain value.

We introduced the simulation of the tube tails into our raytracing algorithm. Corresponding to a measurement as given in figure 1, a certain part of the random ray paths originates outside the proper rectangular line focus. Doing so, we get a geometric part **G** which is corrected for tube tails.

Computation of the crystallite size starts with the formula given in [2]. From the formula given there, we evaluate the mean crystallite size (size value)

$$\overline{D} = \frac{4}{3\pi b_1}\frac{1+2\sqrt{k_1}}{(1+\sqrt{k_1})^2}$$

by assuming spherical crystallite shapes. In addition, we determine the relative width of the crystallite size distribution:

$$\frac{\Delta D}{\overline{D}} = \frac{\sqrt{13+52\sqrt{k_1}+7k_1}}{4\sqrt{2}(1+2\sqrt{k_1})}$$

Since the time of the first usage of the fundamental parameter profile model, our calculations are disturbed by so-called “tube tails”. A relevant part (5%...30%) of the X-rays is produced not from a proper rectangular line focus shape but from supplementary tails on both sides (Fig. 1). This effect depends on type, manufacturer, voltage/current and life stage of the tube. We measured the SRM 660 (LaB6) with three different tubes (two Cu-Kα and one Co-Kα radiation) using three different slit set-ups on two diffractometers. For demonstration of remaining errors, we give results using two different Cu-Kα spectra as cited from [1] and [4], respectively. Table 1 shows the results. This table illustrates the success of the tube tails correction. Without the correction, all size values are obviously too small and depend on the tube type. The microstrain broadening was calculated to be zero. After tube tails correction, the values agree within the errors of 3σ using the same spectra. In our opinion, tube tails are the strongest fault of classical fundamental parameter profile description.

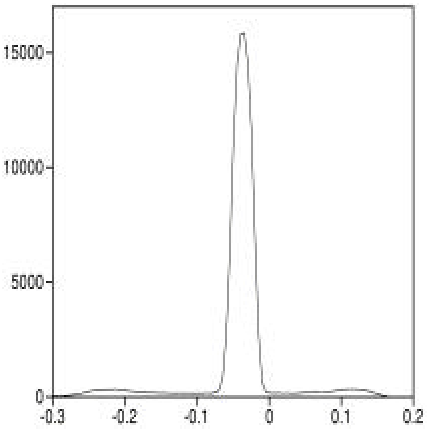

Fig. 1. *Strong tube tails as measured for an older AEG fine focus tube. A lead foil containing a 40 µm hole placed on sample position was used for reproduction of tube focus onto receiving slit*

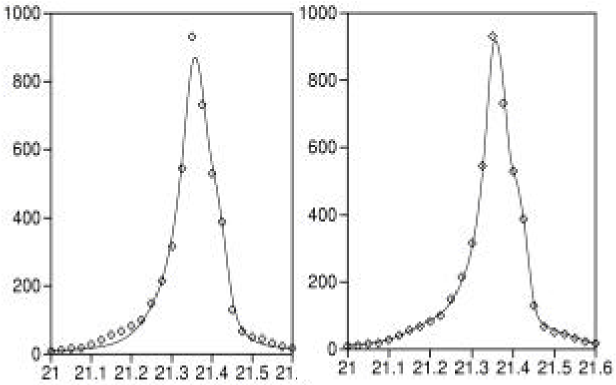

Fig. 2. *Rietveld difference plots for the (100) line of the SRM 660 standard. Left: without tube tails correction (R_{wp}=16.02%), Right: with tube tails correction (R_{wp}=12.55%). R_{exp} was 10.51%..*

Table 1. Comparison of size/microstrain values of SRM 660 as gained using three different tube types, two different Cu-K_a spectra data sets and peak modelling without and with tube tails correction

Λ	Cu K_α [1]			Cu K_α [4]			Co K_α [4]
Diffractometer	XRD3000TT						URD-6
Tube Type	1	2		1	2		3
Divergence slit	Fixed		ADS	Fixed		ADS	Fixed
	without tube tails correction						
size/nm	324(4)	496(6)	510(8)	308(4)	468(6)	474(5)	610(10)
r.m.s.$\times 10^6$	0	0	0	0	0	0	0
	with tube tails correction						
size/nm	1109(51)	995(38)	1056(37)	884(31)	793(23)	824(21)	944(34)
r.m.s. $\times 10^6$	156(7)	152(7)	157(5)	115(8)	105(8)	113(6)	96(10)
[3]	Size: 1300(700) nm						

Obviously, the inaccuracies of different Cu-K_α spectra overrule the standard uncertainties of the fundamental parameter approach. Otherwise, the measurements show the real structure caused broadening of the line profile standard. The total error of the approach, including Cu-K_α inaccuracy, is much less compared to the line standard real structure broadening.

Tube tails correction faciliates the usage of fundamental parameter profile description in size/microstrain analysis. We cite from [3]: "It is possible to recognize when low levels of specimen broadening are present in the data". The BGMN peak shape model again diminished the minimum detectable values of size and microstrain broadening and their errors compared to [3].

Now the limits should be:

- above 1µm for size
- below 10^{-4} for microstrain.

Therefore, we recommend to test the Rietveld program BGMN [5] for size/microstrain analysis.

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Teaching and Learning Powder Diffraction across the Internet

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There is no doubt that the advent of the Internet has rapidly changed many peoples' lives: business transactions are now regularly carried out across the Internet in a way not envisaged even a decade ago. Research, training, and education methods have also been strongly affected by the growth of the World Wide Web. The School of Crystallography at Birkbeck College, University of London, has been at the forefront of these developments since 1993, with three Advanced Certificate Courses: the Principles of Protein Structure on the Internet (PPS), Protein Crystallography on the Web (PX), and now Powder Diffraction on the Web (PD). This article briefly discusses the development of the latest of these courses, namely, Powder Diffraction on the Web, which is running for the first time in 1999/2000.

There are obvious advantages in learning powder diffraction across the Internet. Students are no longer required to attend a local institution; study time is chosen at the convenience of the student, and not tied to the scheduling of traditional face-to-face lectures; and fees are low by western standards. Additionally, Internet teaching can provide research students with a training that may not be available at their place of study or work. One disadvantage, common to all distance learning courses, is that time management and maintaining motivation can be a big problem for the student.

Like our other courses, Powder Diffraction runs on a part-time basis and is delivered annually. It consists of 3 units: Instrumentation & Fundamental Crystallography for Powder Diffraction, Analysis of Powder Diffraction Data, and Project Work. The first unit provides the relevant crystallographic theory taught from the perspective of the experimentalist using powder diffraction, while the second is concerned with various types of data analysis from qualitative and quantitative analysis through to structure solution and Rietveld refinement. Finally, the third unit provides students with an opportunity to consolidate their learning and to put achievements into practice by analysing some powder diffraction data provided by us.

The course material is accessed using standard Web-browser technology. We avoid the use of some of the most up-to-date technology (such as Java) so that all students can study the material, and not just those with the latest hardware and software. However, we have exploited CGI programming to interface simple analysis programs with the web browser. Currently, we insist that students have access to a windows-based PC, in which the symbol font is automatically configured for use with the Web browser: in practice, workstations can be used as long as the symbol font is enabled under X-windows. The course is strongly tree-structured to aid navigation through the material. It is important that students don't get "lost in hyperspace", and links to the outside world are clearly indicated with warning icons.

Student support is provided via private email, an email discussion list, assignment feedback, and a course notice board. In practice, as with our other Web-based Advanced Certificate courses, we find that students often prefer to communicate on a one-to-one basis with the tutors rather that using discussion lists. The downside of this is that the workload on tutors may become excessive.

The Large Debye-Scherrer Camera Installed at SPring-8 BL02B2 for Accurate Structure Studies

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This camera is designed for charge density studies by powder specimens in the area of materials science. This instrument makes it possible to collect high-angular and high-energy resolution powder data, which must contribute to increase the accuracy of structure analysis of crystalline material using powder data[1-5]. This Debye-Scherrer Camera with radius 286.5mm is available in a wide range of temperatures (15-1000K). The displex cryostat, which can cool the specimen down to 15K, is installed within the *w*-stage of this camera (Fig.1). A high temperature gas flow system can be also installed for high-temperature experiments (Fig.2). As a detector, it has an Imaging Plate (IP) on the *2q* arm. The pixel size of the IP can be varied from 50×50µm to 100×100µm. It is also possible to record several powder patterns (max. 10) on the same IP using a long vertical slit attached before IP. The high-energy beam with high flux allows us to collect much more Bragg reflections (high-resolution in real space imaging) with good counting statistics. The diffraction experiments are performed by transmission geometry. By using high-energy X-ray photons of SPring-8, the effects of absorption become insignificant even for heavy materials involving, *e.g.*, rare-earth metals. These will make it possible to measure high quality powder data of crystalline materials even at low temperature.

It should be noted that there are many levels of structural studies, for example, to measure just lattice constants, to determine space group by observing super-lattice reflections, to refine atomic distances and to obtain accurate electron densities at various temperatures. Recently, the performance of the camera is tested with standard materials, such as CeO_2, LaB_6, etc. (Fig.3). By doing structural analyses at various levels for these standard materials, extremely high performance of the camera has been proved, particularly for accurate charge density studies when the data are analysed bythe combination of Rietveld refinements and the Maximum Entropy Method, MEM/Rietveld Analysis [1-5].

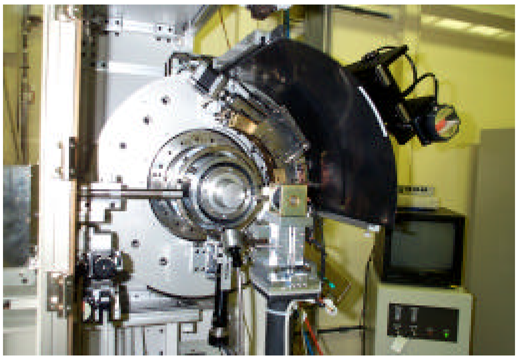

Fig.1. The Large Debye-Scherrer Camera with the displex cryostat at BL02B2 SPring-8

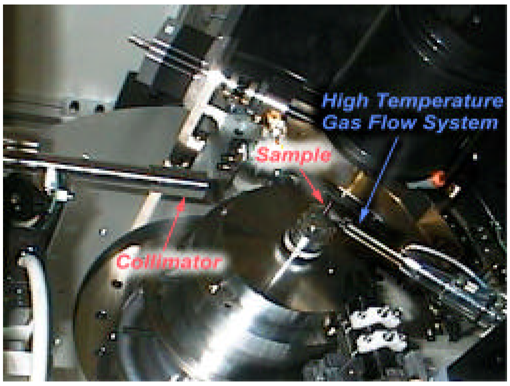

Fig.2. The High Temperature Gas Flow System for high temperature powder experiment

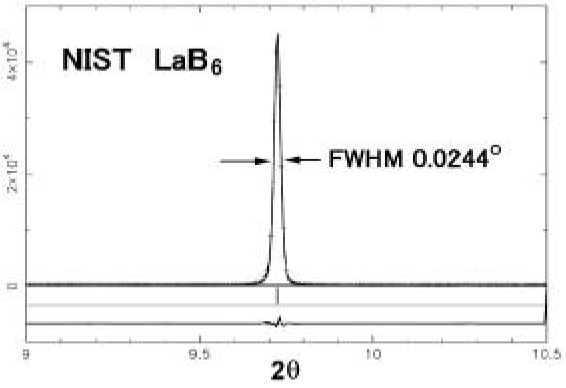

Fig.3. The powder profile of NIST LaB_6. λ=0.5Å

Such a high performance of the Large Debye-Scherrer Camera at BL02B2 is achieved by taking the advantage of intense, highly parallel and high-energy X-ray beams of SPring-8. This camera can play an important role to reveal the mechanism or origin of the novel function of materials, such as orbital order, mechanism of structural phase transitions and structural differences of super- and non-super conductors, if they exist. For a detailed description of the diffractometer visit the BL02B2 website: (**http://www.spring8.or.jp/ENGLISH/facility/bl/PublicBeamline/BL02B2/index.html)**.

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Blowing Cold – what can liquid nitrogen do for you?

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The diffraction instrument of Station 2.3 at the laboratory was initially constructed for ambient high-resolution powder studies [1,2] based on parallel beam optics. In recent years, the hardware and software have been adapted and upgraded for versatility to cater for several diffraction geometries, including Debye-Scherrer and reflectivity [3]. In addition, low- and high-temperature devices have been successfully commissioned to enhance the capacity of the instrument [4]. More recently, an Oxford cryostream [5] has been sought for low-temperature work on capillary samples. The cryogenic system is capable of cooling from 375 to 80 K with a stability of ±0.1 K. It was, however, designed for use on small crystals rather that powder specimens. With the availability of high flux and well collimated beam from the synchrotron, a small incident beam on to a thin powder sample (0.5 mm or less) is usually practiced with capillary mode on the station. The cryogenic device can therefore be used for low temperature studies. To improve thermal stability, a double- skinned can was constructed, and fitted over the nozzle and the sample during data collection.

The commissioning of the apparatus was carried out on the cubic structure of ammonia chloride (NH_4Cl) powder. The material exhibits a first order transition at approximately 242 K, from the β (space group *Pm3m*) to δ (*P43m*) phase. The structural behaviour is well known, mainly from the work reported in references [6,7]. Diffraction data were collected from T=230 to 250 K, through the transition temperature (λ=1.1 Å). Fig. 1 shows two peaks about the (3 1 0) position at T=235.0 (open squares), 237.5 (solid circles) and 239.0 K (crosses). The peak positions and intensities are clearly temperature dependent. Fig. 2 is the integrated intensity as a function of temperature for the low and high angle peak. Both sets of data show a first order transition behaviour. The transition temperature is about T=239.5 K which is marginally lower than those reported previously. It is very likely that the discrepancy is due to the sample used in our case as the physical properties do vary slightly from one sample to another. The results have shown that the device is a viable apparatus for low temperature work, and it is now supported equipment on the instrument accessible to our users.

The cryostream can similarly be used on the other powder instrument, Station 9.1, for example, the low temperature study of cryosolvents [8]. These liquid mixtures are important materials in the study of proteins at low temperature.

Potential candidate mixtures incorporating alcohols, diols, and of course water, have been investigated on

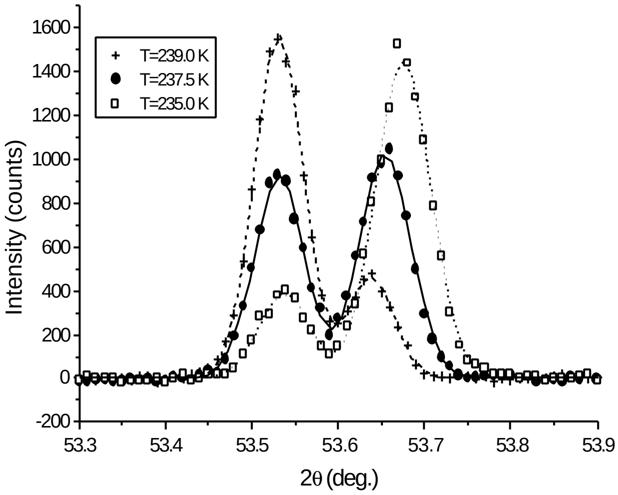

Fig. 1. Temperature dependence of the (3 1 0) plane.

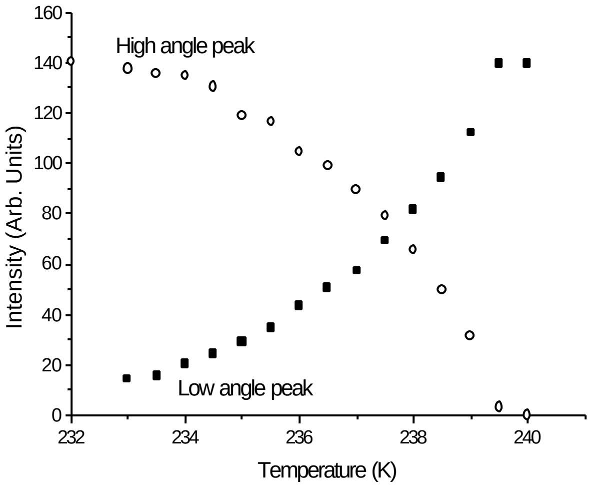

Fig. 2. Integrated intensity as function of temperature.

this station using the cryostream and the curved image-plate (CIP) technique [9].conventional incremental point scanning methodologies, important in observing any High quality data at temperatures down to 113 K were collected. The CIP technique enables full image data collection, in a fraction of the time required for crystallisation and texture that may arise during the cooling process. The suitable solvent mixtures will aid in the study of proteins since reactions are slowed, facilitating the study of mechanisms, enzyme structure, function and dynamics. It is thus critical that these studies be undertaken in a fluid medium that will resist phase separation and crystallisation [8]. A mixture of 70% methanol: 10% ethandiol: 20% water is sufficiently fluid down to at least 148 K for functional studies and is a suitable solvent for such studies down to at least 113 K.

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Powder diffraction of inorganic and inorganic-organic hybrid microporous materials

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Microporous solids are important catalytic materials in many commercial processes, as well as having applications in ion exchange and gas adsorption technologies. The main advantage over other catalysts is their ability to discriminate between chemical species on the basis of shape and size, and there are a number of examples where this selectivity has been used in zeolite catalysis [1]. Their utility in industry is therefore intimately connected with their crystalline architecture, and knowledge of the structure is vital in rationalising behaviour and identifying possible new uses.

Unfortunately, it is quite common in zeolite preparations for single crystals produced to be too small for conventional laboratory single crystal X-ray diffraction to be successful. For some time now, powder diffraction has been the only method open to investigators who need to undertake a full crystallographic study of a material when large single crystals are not available. *Ab initio* methods of structure solution from powder diffraction data have improved markedly over recent years, and have been successfully used in a number of cases to solve quite complex new materials.

Microporous materials are often made using organic ‘templates’, which are encapsulated inside the inorganic frameworks. To produce useful microporous materials these templates have to be removed, usually by quite aggressive thermal treatment. Even when single crystals of the original templated material are available, this calcination treatment can sometimes lead to degradation of the single crystal quality. This means that powder diffraction is then the only way to study the materials in their microporous state. Many of the most interesting properties of microporous materials occur after the materials have been calcined, and so powder diffraction is sometimes the only way to crystallographically probe these materials.

The better known properties of microporous materials, such as catalysis, have been studied using *in situ* powder diffraction techniques for a number of years. This *in situ* work has also been extended to study the synthesis of microporous materials.

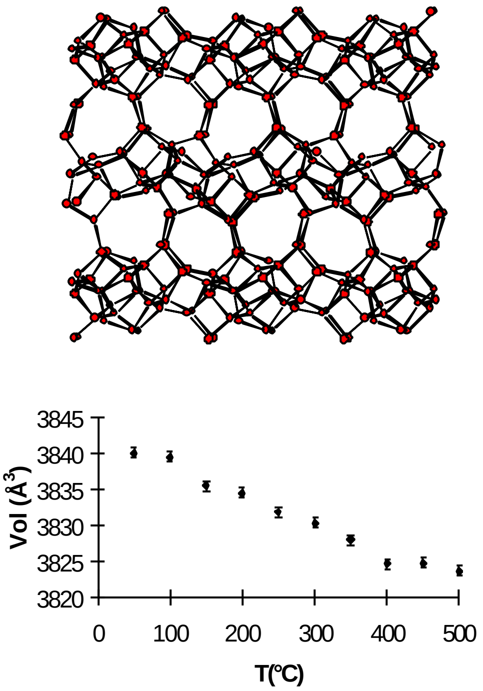

Fig. 1. The structure of calcined zeolite SSZ-23 as obtained for Rietveld refinement against synchrotron X-ray powder diffraction (only Si atoms are shown) and the variation of unit cell volume of SSZ-23 with temperature, as measured by laboratory powder X-ray diffraction.

More unusual properties such as negative thermal expansion are now being studied more and more. This property seems much more widespread than was previously thought and variable temperature powder diffraction is playing an important role in identifying materials in which this phenomenon occurs, as well elucidating the mechanism on an atomic scale. An example of a microporous material that contracts on heating is SSZ-23, a complex zeolite containing seven and nine-membered ring channels. The calcined structure of this solid was first characterized using synchrotron powder X-ray diffraction [2] and the negative thermal expansion properties followed using laboratory X-ray diffraction. [3]

As well as purely inorganic materials, such as the zeolites, there are an increasing number of research groups interested in inorganic-organic hybrid materials, where rather than removing the organic groups from the structure they remain an integral part of the framework. Their great advantage is the possibility of tailoring the organic functionality to give chemoselectivity that is not available with purely inorganic porous materials. These types of materials include methylphosphonates, where methyl groups line the pores of the material and macrocycle-containing materials where a metal complex is covalently bonded to a zeolite-like framework. Powder diffraction has played an important part in characterizing these materials, including variable temperature work to identify an unusual solid state phase transformation in the methylposphonates [4] and the interesting substitution patterns in the macrocycle containing materials [5] (Figure 2).Despite advances in other diffraction facilities, such as the recent microcrystal X-ray diffraction stations at the Daresbury and Grenoble synchrotron sources, powder diffraction remains a pivotal tool in a materials chemist's armoury. Development of *in situ* diffraction techniques for the study of synthesis or catalysis, and variable temperature studies of negative thermal expansion and similar properties has increased our insight into these interesting materials. Another way to improve our capability is to combine powder diffraction methods with other structural methods, such as solid state NMR. Once this becomes routinely feasible, then the amount of structural information we will be able to obtain from diffraction studies will be further enhanced.

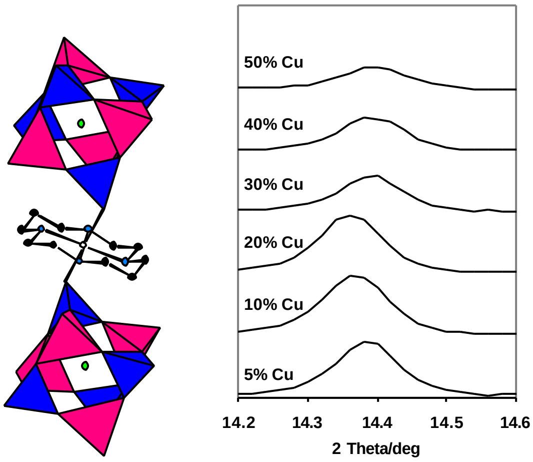

Fig. 2. A portion of the structure of Ga-Cyclam-GaPO (left) showing how a gallium macrocycle complex links two double four ring units in the structure, and the effect on the (211) peak of substituting copper for the gallium in the macrocycle complex. Up to a Ga:Cu ratio of 4:1 (20% copper) the unit cell increases in size. Above 20% copper substitution phase segregation occurs and no substitution into the complex is observed.

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Parallel-Beam Powder Diffractometer Using Laboratory X-Ray Sources

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The Bragg-Brentano para-focusing method has been used extensively in powder diffractometry using Laboratory X-ray sources. This method is, however, sensitive to the sample displacement error and the flatness of the sample. As a result, systematic errors are commonly occurred. On the other hand, accurate data free from these systematic errors can be obtained by using a parallel-beam method, and more precise measurement for profile analysis such as structure analysis will be possible. The conventional incident optical system for parallel beam method generally consists of a narrow incident slit, a parallel slit, and/or a single crystal monochromator. Since these optical systems realise highly collimated incident beam by selecting very small part of the divergent X-ray beam that is generated by a laboratory X-ray source, the resolution and intensity of these conventional optics are not always enough.

In order to overcome these problems and obtain high-intensity, a new high resolution and high accuracy parallel beam powder diffractometry has been

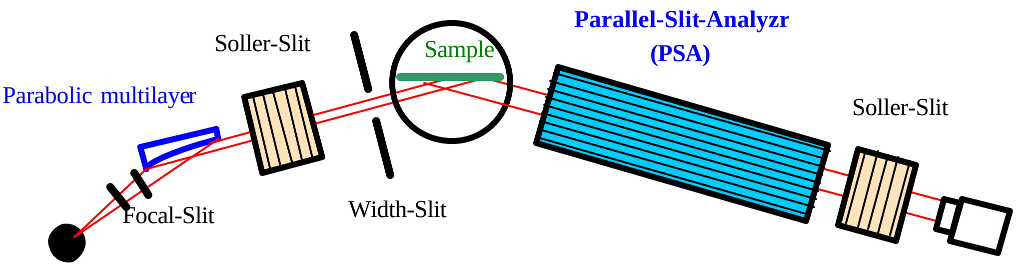

Fig.1 shows a schematic diagram of high-resolution parallel beam optical system.

developed for laboratory X-ray sources. Fig.1 shows a schematic diagram of high-resolution parallel-beam optical system [1]. Its characteristic is in the use of a graded d-spacing parabolic multilayer and a parallel slit analyser (PSA). The grated d-spacing parabolic multilayer is used in the incident beam side. The sintered and hot-pressed tungsten (W) PSA is used for the purpose of lowering tails in diffraction profiles from powder.

In the present work, four different materials were used for the foils: W, cold-worked stainless steel (SUS), beryllium bronze ($Cu_{98}Be_2$) and chemically surface-processed beryllium bronze (CuOx). Fig.2 shows a comparison of direct-beam profiles, which were scanned by using the W, SUS and $Cu_{98}Be_2$ PSAs. Some of the refined parameters of the individual profile fittings are presented in Table1. Refined parameters were flat background (b_0), integrated intensity (I), peak-top (T), the minimum full width at half-maximum(Γ), asymmetry for profile width(A) and η parameters on the low-and high-angle sides of peak (η_L and η_H, respectively). The average values, defined by $\eta_{av}=(\eta_L+\eta_H)/2$. The W PSA gave the narrowest Γ and a nearly Gaussian profile shape.

In this time, an example of measurement, which the high-resolution parallel beam optics is suitable for, will be shown. In case of lattice constant refinement using the Bragg-Brentano method, the observed diffraction angles, are commonly calibrated using an internal standard reference material. In a high-temperature experiment, it can be difficult to select a proper internal standard which will not react and/or overlap with the sample/sample holder. On the other hand, with a parallel-beam method, most systematic errors are essentially eliminated.

The error caused by vertical divergence can be calibrated using an external standard. As an example, the results of temperature dependence of lattice parameters for Al_2O_3 are shown in Fig.3 [2].

PSA	Y_{max}(counts)	Y_{min}(counts)	I	Γ(°)	η
W	65003	9	3838	0,0505	0,17
SUS	65003	13	5284	0,0607	0,70
$Cu_{98}Be_2$	65003	78	5652	0,0608	0,95
CuO_x	65003	1	4066	0,0563	0,21

Y_{max} and Y_{min} are observed maximum and minimum intensities, respectively.

Table 1. Refined parameters in the profile fitting for direct-beam profiles normalised to the peak height of $Cu_{98}Be_2$ PSA.

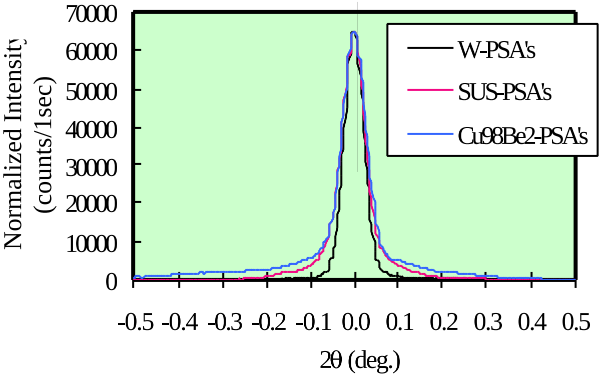

Fig.2. Direct-beam profiles scanned using W, SUS and $Cu_{98}Be_2$ PSA's, normalized to the peak height of $Cu_{98}Be_2$ PSA

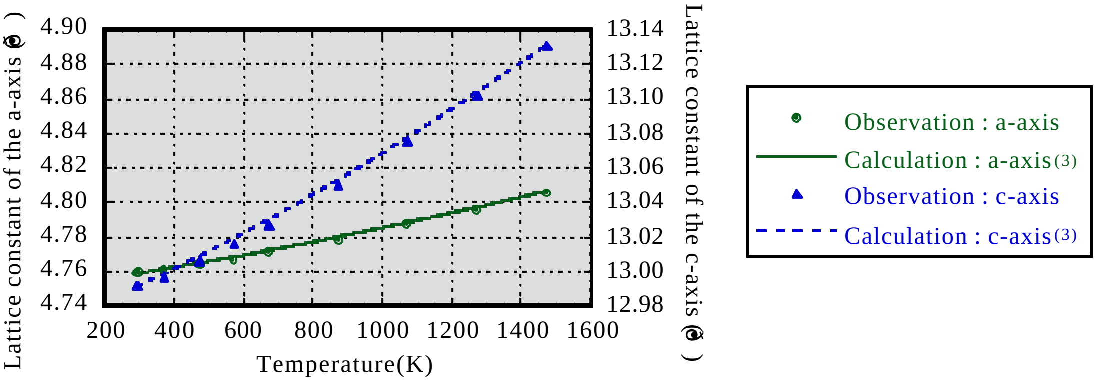

Fig.3 Dependence of Al_2O_3 lattice constants on temperature

The lattice parameters were the average values calculated from 7 reflections. The solid and the dotted lines show temperature dependence of lattice parameters of the a and c axes calculated using reported thermal expansion coefficients [3], respectively. The observed and the calculated lattice parameters have very good agreement, to better than 0.04%. The Debye characteristic temperature derived from the decrease in the integrated intensities caused by thermal vibration was also obtained.

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Measurement of Phase Transformation Rates During the Reduction of Iron Oxides Using High-Temperature X-Ray Diffraction

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INTRODUCTION

Recent advances in X-ray diffraction (XRD) technology have made it possible to conduct powder XRD measurements on samples at high temperatures during reaction. State-of-the-art detectors are now capable of rapidly acquiring diffraction patterns across a wide angular range (typically $120^{\circ}2\theta$) enabling phase transformation rates to be measured directly during sample reaction.

Traditionally, the kinetics of iron ore reduction reactions have been measured thermo-gravimetrically, and the relative phase abundance determined by examination of quenched samples. Recent developments in high-temperature X-ray diffraction (HT-XRD) technology, together with high-speed computational analysis of the diffraction patterns by the Rietveld method, now make it possible to measure the relative phase abundance at the temperature of the reaction, and hence determine the reaction rate parameters directly from the rates of change of the amounts of the various phases present. This paper describes a technique whereby the reduction of hematite by hydrogen was observed and quantified by HT-XRD *in situ*.. The technique involves the use of a curved, position-sensitive detector (PSD) that is able to acquire an X-ray diffraction pattern over a wide angular range simultaneously. This has significant advantages over conventional Bragg-Brentano detector geometries where the diffraction pattern is acquired sequentially over the angular range. The conventional geometry had virtually precluded its use in studying all but the slowest reactions, as typical diffraction pattern acquisition times are usually in the order of 20 – 40 minutes. The use of a PSD has meant that a diffraction pattern that would previously have taken 40 minutes, can now be collected over 10 - 20 seconds, depending on the resolution required. Experiments were carried out between 500 - 700°C, using a 5 per cent H_2 in N_2 gas mixture. The XRD data were quantitatively analysed by the Rietveld method to yield the abundance of hematite, magnetite, wustite and metallic iron, as functions of time during the reduction process. A first-order reactions-in-series model was proposed, and the rate constants were determined from the XRD data.

EXPERIMENTAL

Gas system

The reagent gas used in the experiments was 5 per cent hydrogen in nitrogen (BOC high-purity grade). The gas flow rate selected was 3 L/min. The choice of 5 per cent H_2 in N_2 was enough to allow the almost complete reduction of hematite to iron, yet attenuate the reaction rate enough to allow the acquisition of an X-ray diffraction pattern at regular intervals.

High-temperature system

An Anton-Paar HTK high-temperature system was used, employing a platinum resistance strip capable of achieving 1200°C in air. The strip contained a small sample well and the temperature at the centre of the well was measured by a Pt/Pt-10% Rh thermocouple connected to the underside of the heating strip. The apparatus was water-cooled and had sealed mylar windows for X-ray transmission. The temperatures used were 500, 600 and 700°C.

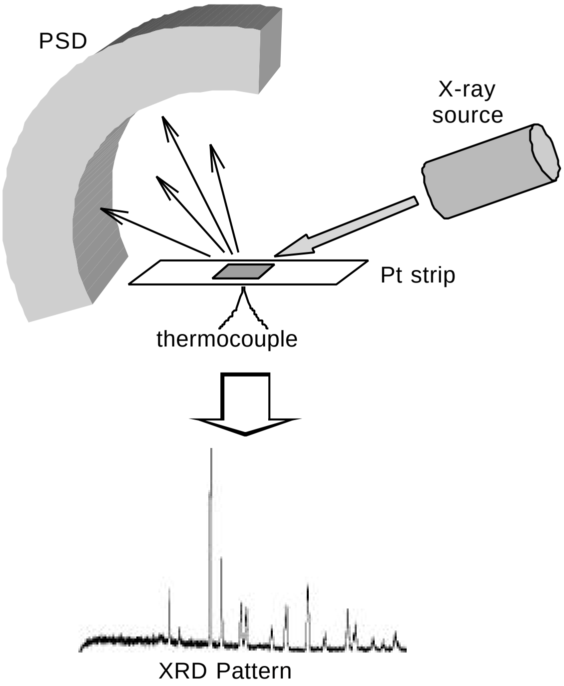

Fig. 1. Schematic representation of the HT-XRD system.

X-ray system

An Inel X-ray diffractometer employing a CPS-120 curved, position-sensitive detector was used. The angular range of the detector was between 5 – 125°2θ. The X-ray source was a cobalt long fine focus X-ray diffraction tube operating at 35 kV and 35 mA. A graphite, incident beam monochromator was used to eliminate undesirable wavelengths while the beam was defined using a vertical slit of 0.2 mm and a horizontal slit of 8 mm. Figure 1 is a schematic representation of the experimental apparatus.

Real-time XRD pattern acquisition

The high-temperature system was enabled so that the target temperature was reached at a heating rate of 100°C/min, using a 2 L/min flow of air over the sample. At the target temperature, a 15-sec data set was acquired to provide the pre-reaction phase abundance (essentially 100 per cent hematite). The high-temperature system was then evacuated for approximately 30 seconds, then the 5 per cent H_2/N_2 mixture admitted at a flow rate of 3 L/min. The time of hydrogen admittance was deemed to be t = 0. A period of 30 seconds was allowed for the reaction to begin before the next scan was undertaken.

A consideration of factors including (i) the observed X-ray intensity, (ii) acquisition speed and (iii) software processing speed, led to a data collection regime of a 15 seconds acquisition every 60 seconds being devised (ie. acquire a spectrum for 15 seconds followed by a 45-seconds gap before acquiring the next 15-seconds scan).

The Inel PSD was calibrated by using powdered Y_2O_3 as a peak position standard.

Quantitative phase abundance determination

Quantitative phase abundances were determined for hematite, magnetite wustite and iron using the Rietveld analysis package developed by Coelho, Madsen and Cheary (1997). The Rietveld scale factors were converted to phase abundances using the algorithm of Hill and Howard (1987).

Reaction rate model

A simple first-order reactions-in-series model was proposed to describe the reduction of hematite by hydrogen:

$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O$………($k_1$)

$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O$…………($k_2$)

$FeO + H_2 \rightarrow Fe + H_2O$……………...($k_3$)

The rate constants k_1, k_2 and k_3 were calculated simultaneously using the *Microsoft® Excel 97®* spreadsheet program based on the analytical solution presented. The model was constructed so that the theoretical abundance of hematite, magnetite and wustite were calculated at each time point coinciding with the XRD data. To simplify the calculation the abundance of iron was determined by difference. Therefore, at each time point there was a measured abundance and a calculated abundance for the three phases based on arbitrary values for k_1, k_2 and k_3. The calculated abundance was subtracted from the measured abundance (for each phase) and the resulting value squared. The ***Solver*** function within *Excel 97®* was then used to minimise the sum of the squares for each phase by manipulating the rate constants k_1, k_2 and k_3. In essence, the calculation involved manipulating the three rate constants in such a way that the difference between the calculated abundance and the measured abundance for hematite, magnetite and wustite was minimised. In this way, it was possible to calculate the three rate constants simultaneously. If the experimental data obeyed the proposed first-order reactions-in-series model, then the theoretical abundance should closely approximate the actual abundance.

RESULTS

Estimation of apparent rate constants

Having decided on the sample mass (20 mg) and the 5 per cent H_2/N_2 flow rate (3 L/min), a set of triplicate reduction experiments were conducted at each of the three temperatures. Typical phase abundance results for the 500, 600 and 700°C runs are shown in Figs 2 – 4 respectively, along with the results of the first-order reactions-in-series model that was used to "fit" the data and yield the apparent reaction rate constants k_1, k_2 and k_3. Measured phase abundance values are shown as solid data markers joined by a dotted line, whereas the calculated abundance values are shown as a solid line.

It can be seen from Figs 2 - 4 that it is difficult to accurately determine the rate constant k_1 (hematite → magnetite) when there is only opportunity to acquire 2 - 4 data points before all the hematite is transformed to magnetite. To compound the problem, there was a small time delay between the initiation of hydrogen gas flow and the reaction beginning. This time delay was allowed for in the model by approximating a logarithmic regression to the first few data points of hematite and determining the starting point of the reaction using the intercept in the least squares fit. Considering the hematite to magnetite step, a plot of the rate constant against 1/T was used to calculate an activation energy of 49.4 kJ mol^{-1}. This compares favourably with a value between 37 and 67 kJ mol^{-1} generally found by most authors (Turkdogan and Vinters, 1971; Klissurski *et al*, 1986; Viswanath, Viswanathan and Sastri, 1977), although values as high as 167 kJ mol^{-1} have been reported (Gallegos, 1988).

It can be seen from Fig. 2 that there were, unexpectedly, trace amounts of wustite present during the 500°C run. Due to this, the determined value of k_3 at this temperature, although quite reproducible, is virtually meaningless in this context due to the small amounts of wustite present (1-3 wt per cent). It is interesting, however, that trace wustite diffraction peaks were observed at such a low temperature, in contradiction to the widely held view that below about 570°C magnetite is reduced directly to iron. Of course, the observation of a metastable wustite below 570°C may only be possible via an *in situ* technique such as HT-XRD.

CONCLUSIONS

The HT-XRD configuration described in this paper allowed the acquisition of complete X-ray diffraction patterns from a sample within 15 seconds, at temperatures between 500-700°C under a 5 per cent hydrogen in nitrogen reagent gas. This enabled direct measurement of the transient phase abundance during the reduction of hematite by a hydrogen-containing gas. The method has the potential to reveal much more information about the kinetics of phase transformations in solid-solid and solid-gas reactions than the conventional gravimetric techniques. Combined with dynamic temperature and atmosphere control, it is possible to use the facility to follow the time-temperature-gas composition trajectories of these reactions, and reveal non-isothermal effects. It is also possible to “drive around” a phase diagram by Another advantage of an XRD-based technique is the ability to discern subtle changes in the thermal coefficient of expansion (reflected in changes to the unit cell parameters) and crystallite size and strain (reflected in changes in the observed peak width and shape).

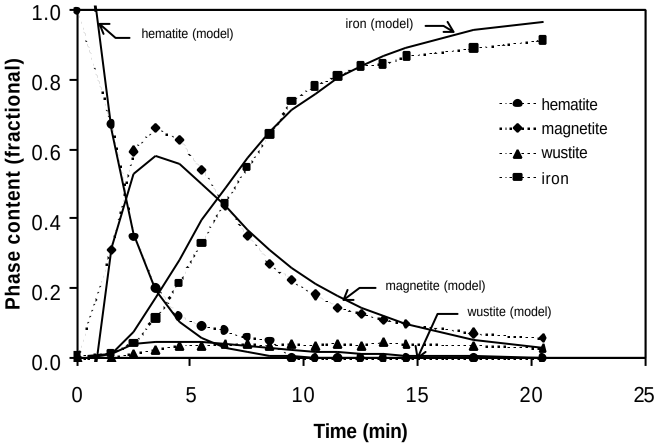

Fig. 2 Typical phase abundance relationships for the direct reduction of hematite at 500°C.

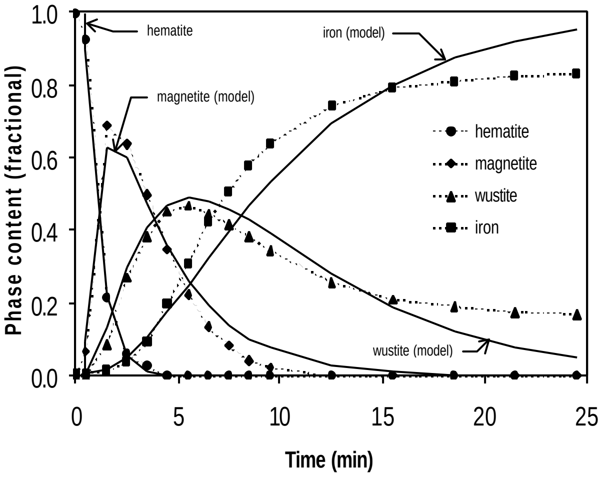

Fig. 3 Typical phase abundance relationships for the direct reduction of hematite at 600°C.

varying the temperature, gas composition or gas pressure in the reaction chamber. Whole regions of a phase diagram may even be investigated from a single sample manipulated in this way.

A shortcoming of the current configuration is the relatively long acquisition time (15-seconds) and the dwell time between measurements (45 seconds). It is anticipated that this problem will be addressed in the near future with an upgrade of the X-ray optics and the acquisition control software. This is expected to provide data collection times of approximately 2 to 3-seconds and dwell times in the order of 2 to 5 seconds, potentially allowing somewhere between 7 to 30 scans per minute, compared to a single 15-second acquisition under the current configuration. This capability will dramatically increase the resolution when studying very fast reactions..

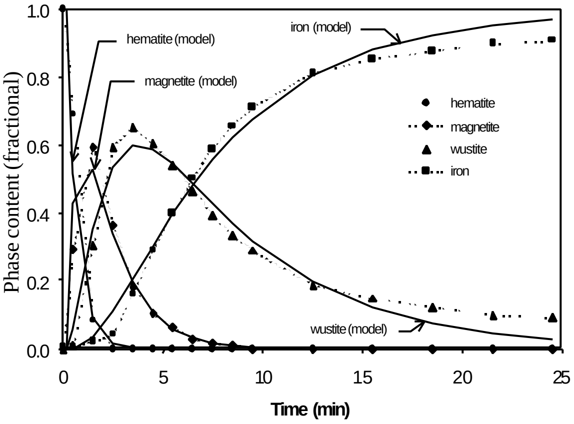

Fig. 4 Typical phase abundance relationships for the direct reduction of hematite at 700°C.

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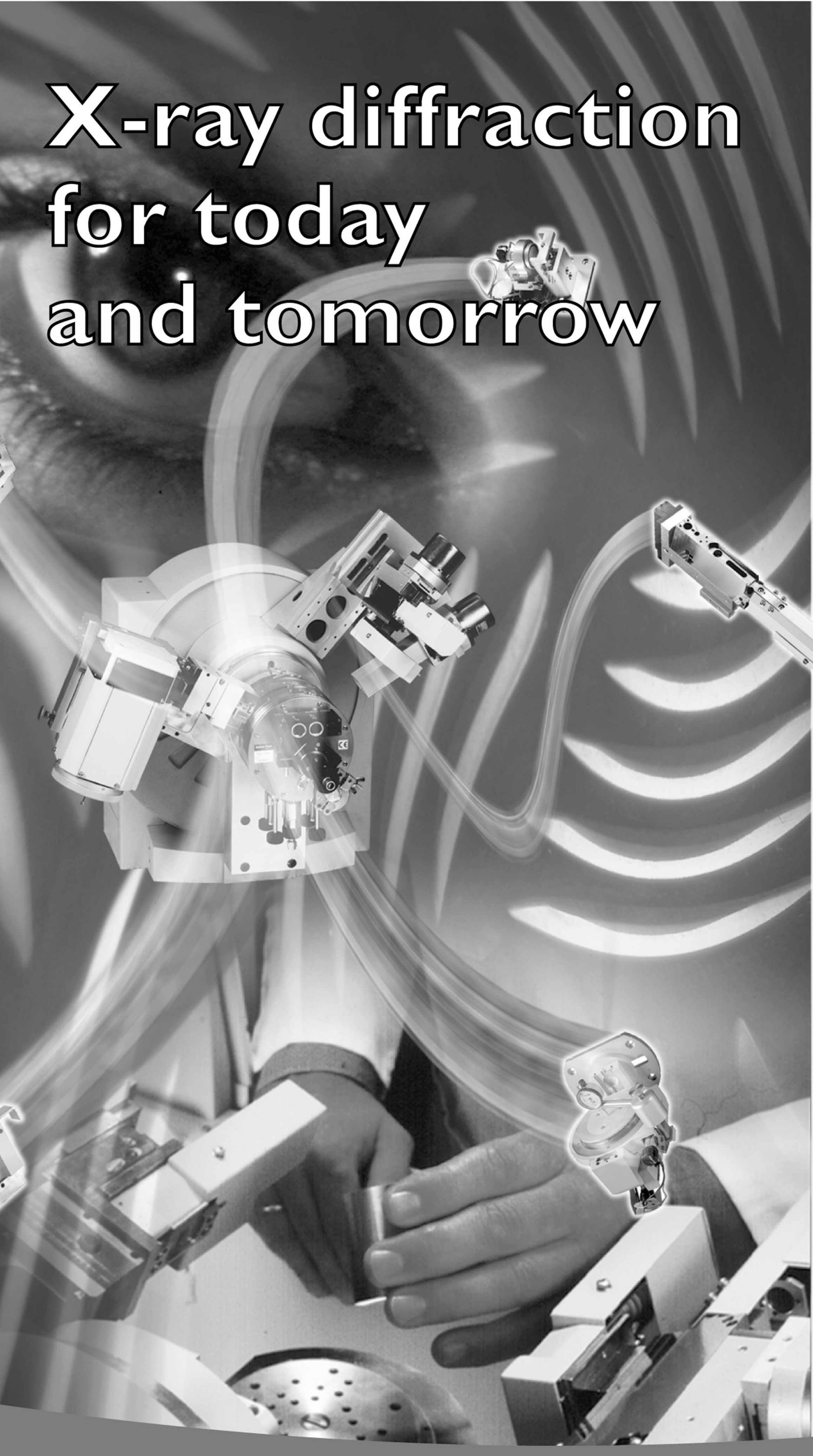
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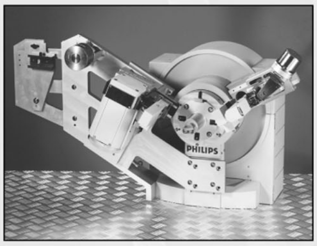

MEETING AND SCHOOL REPORTS

X-ray Powder Diffraction Schools in Venezuela

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Two X-ray Powder Diffraction Schools have been recently conducted at the *Laboratorio Nacional de Difracción de Rayos-X* (LNDR-X), *Universidad de Los Andes* (ULA) in Mérida, Venezuela, under the auspices of the National Laboratory Program of CONICIT, the Venezuelan Science and Technology Office.

The first School (Characterization of Polycrystalline Materials using X-ray Diffraction Techniques) was held from January 24-28, 2000. This School was primarily focused on the analytical aspects of X-ray Powder Diffraction. However, it also included general lectures on the fundamentals of structural analysis and microstructure characterization of materials using powder diffraction data.The invited lecturers for this School were Dr. Ron Jenkins of ICDD, Prof. Robert L. Snyder of Ohio State University (USA), Prof. José Antonio Henao of Universidad Industrial de Santander (Colombia). Drs. Reinaldo Atencio and Rodolfo Vargas (IVIC), José Rafael Marcano and Rafael Guevara (UNEXPO). The members of the Crystallography Group of ULA (Profs. Miguel Delgado, Asiloé Mora, Graciela Díaz de Delgado, Belkis Ramírez, and Gerzon Delgado) also participated as Instructors. The course began with lectures on the fundamentals of symmetry and diffraction, sample preparation, data acquisition, qualitative and quantitative analysis. General reviews of the structure determination and refinement processes were presented by Profs. M. Delgado and A. Mora. Prof. Snyder gave a very comprehensive lecture on microstructure analysis and how it can be

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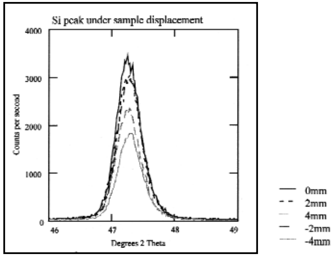
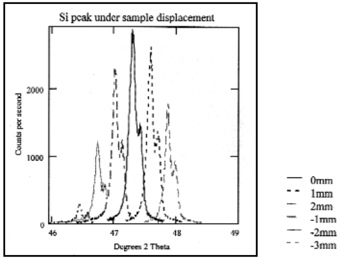
Parallel Beam Geometry



Bragg-Brentano Geometry



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carried out nowadays using diffraction data. The lectures were conducted in the mornings and the practical sessions in the afternoons. During the practical sessions, several PC programs dealing with the different aspects of powder X-ray diffraction: use of the ICDD database, indexing, etc., were used and/or demonstrated.

The number of participants was limited to 50 in order to ensure access to the computing facilities of the LNDR-X and adequate supervision by the instructors during the practical sessions.

The second school (Structure Determination and Refinement using X-Ray Powder Diffraction Data) took place from May 2-5, 2000. The invited lectures were Dr. Andy Fitch from ESRF, Grenoble (France) and Prof. José Antonio Henao of Universidad Industrial de Santander (Colombia). Also participated as Instructors, Drs. Reinaldo Atencio and Rodolfo Vargas (IVIC), Prof. Rafael Guevara (UNEXPO), and the members of the Crystallography Group of ULA. The emphasis of this school was on the fundamentals of structure determination and refinement using powder diffraction data with the classical approach (Patterson and Direct Methods). Also, a number of interesting examples of structures determined using Monte Carlo, simulated annealing, systematic grid search and genetic algorithms were discussed in some detail in the practical sessions. The demonstrations of the use of WinMProf carried out by Dr. Fitch were particulary well received by the participants of this School. A few students presented some of the results obtained in the thesis projects they are advancing as part of their graduate programs.

The majority of the attendees of both Schools were graduate students and young scientists from Venezuela and Colombia. Requests from other Latin American countries were received but, unfortunately, could not be accommodated because of the limited funds available. For future schools, applications for financial support will be presented before International Organizations such as the International Union of Crystallography

WWW SITES OF GENERAL INTEREST TO POWDER DIFFRACTIONISTS

The Commission on Powder Diffraction (CPD): http://www.iucr.org/iucr-top/comm/cpd/
The International Union of Crystallography (IUCr): http://www.iucr.org
The International Centre for Diffraction Data (ICDD): http://www.icdd.com
The International X-ray Analysis Society (IXAS): http://www.ixas.org
General crystallography: http://www.unige.ch/crystal/w3vlc/crystal.index.html

Submitting a proposal for neutron diffraction or Synchrotron Radiation X-ray Diffraction is possible at many Large Scale Facility (LSF) in the world. It represents an important and frequently unique opportunity for powder diffraction experiments. A useful guide and information can be accessed through the following web-sites, maintained by *R. Dinnebier*:

http://www.pulverdiffraktometrie.de or http://www.powderdiffraction.com

This list is far from being complete and needs input from users and readers of the Newsletter. Please, send comments directly to *R. Dinnebier* (robert.dinnebier@uni-bayreuth.de)

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If you would like to advertise in this two yearly newsletter, please contact
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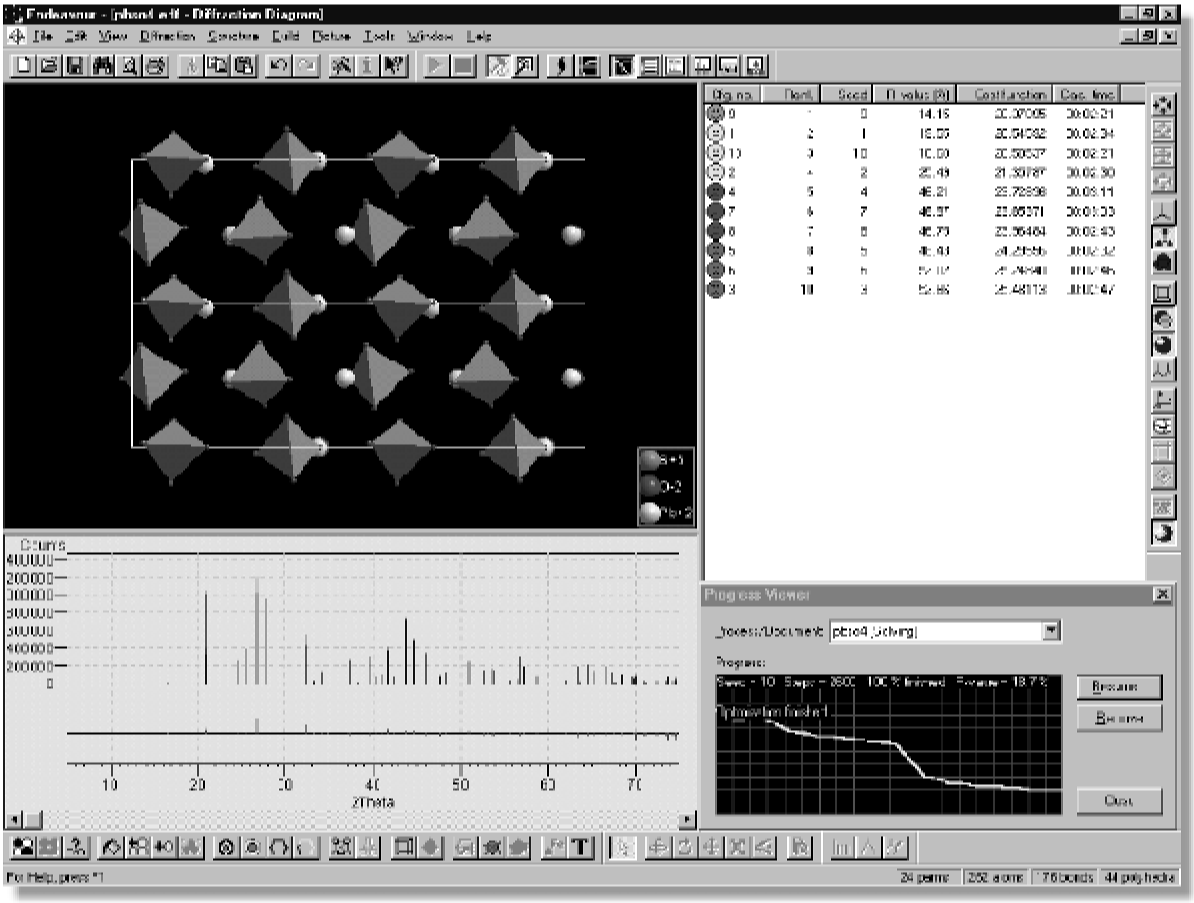
How to receive the IUCr CPD Newsletter

If you wish to be added to the mailing list for the Newsletter of the IUCr Commission on Powder Diffraction or have changed address, please contact the Chairman or simply send an e-mail to : CPD@ing.unitn.it


Endeavour - [pbso4.etf - Diffraction Diagram]
Progress Viewer
2Theta
Counts

News from the International Centre for Diffraction Data (ICDD)

12 Campus Boulevard
Newtown Square, PA 19073-3273
U.S.A.

Phone: +610.325.9814
Fax: +610.325.9823
E-mail: INFO@ICDD.COM

http://www.icdd.com

New Board of Directors Announced

The ICDD is pleased to announce its new slate of officers and directors who will serve the Centre for the term 2000–2002:

Chairman - Camden R. Hubbard
Vice Chairman - Brian H. O'Connor
Treasurer - Julian Messick
Executive Director - Ron Jenkins
Chairman, Technical Committee - James A. Kaduk

Directors-at-Large, Board of Directors:
Jeffrey N. Dann
Raymond P. Goehner
Jeffrey E. Post
Charles T. Prewitt
David F. Rendle

Past Chairman - Robert L. Snyder

The new ICDD Board of Directors

ICDD Hosts Annual X-ray Clinics

The ICDD recently hosted its annual X-ray Clinics at their headquarters office. Two week-long sessions in X-ray fluorescence and two week-long sessions in X-ray diffraction were presented this spring to both new and experienced users working in academic, industrial, and government environments. The clinics offered students the opportunity to learn the principles and practices of these disciplines from some of the pioneers and leaders in the XRD and XRF fields.

A Few Clinic Instructors

XRF Clinic

Fundamentals of XRF was held 1–5 May, where 24 students participated. *Advanced Methods in XRF* was held 8–12 May; 18 students participated in this session. The faculty included John Anzelmo and Larry Arias of Bruker AXS; Gene Bertin, Emeritus, RCA Laboratories; Dick Bostwick, SPEX CertiPrep; John Criss, Criss Software; John Croke, formerly of Philips Analytical, Inc; Terry Derstine, PA Department of Environmental Protection; Ron Jenkins, ICDD; Gerry Lachance, formerly of the Geological Survey of Canada; and Mary Ann Zaitz, IBM Microelectronics. During both XRF sessions, Bruker AXS and Philips Analytical, Inc. offered an evening demonstration of their software applications.

XRD Clinic

Fundamentals of XRD, held 5–9 June 2000, fared as the largest-attended session in the ten-year history of the ICDD clinics with 44 participants. During the week of 12–16 June 2000, *Advanced Methods in XRD* hosted 15 participants. The faculty included Mike Bennett, ICDD; Tom Blanton, Eastman Kodak Company; Harlan Clark, ICDD; Terry Derstine, PA Department of Environmental Protection; John Faber, ICDD; Catharine Foris, DuPont Central Research and Development; Greg Hamill, formerly of Rigaku/USA; Ron

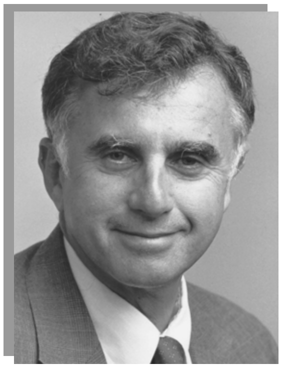
Jenkins, ICDD; Jerry Johnson, formerly of The Pennsylvania State University; Frank McClune, ICDD; Sue Quick, The Pennsylvania State University; and Earle Ryba, The Pennsylvania State University. Both Philips Analytical, Inc. and the ICDD offered demonstrations of their software applications during an evening session of the advanced week.

Donation to the ICDD

The ICDD was the proud recipient of a generous donation recently made by Howard McMurdie. Howard has been actively involved with the ICDD for over five decades, serving the majority of that time as an Editor of Ceramics and Inorganics for the Powder Diffraction File®. The bulk of the donation was used to establish a Video Conferencing Center, which was named in honor of Howard McMurdie, at the ICDD Headquarters. The remainder has been slated to initiate a biennial award in Howard's name. The first award will be presented at the 2000 Denver X-ray Conference. Recently celebrating his 96th birthday, Howard continues to serve the diffraction community through his work as an ICDD editor.

The Jerome B. Cohen Student Award for Best Paper at the Denver X-ray Conference

The Denver X-ray Conference Organizing Committee recently announced the Jerome B. Cohen Student Award, new for 2000. This award is instituted in the memory of Professor Jerome B. Cohen, who was one of the leaders in the field of X-ray analysis, and in the training of students in this art. The award is intended to recognize the outstanding achievements of student research in this field. Students, graduate or undergraduate, who are working in any field of X-ray (or neutron) analysis, can submit their work. The research must be original, of high quality, and must be primarily the work of the student. The paper must be presented at the upcoming Denver X-ray Conference as an oral or poster presentation.



Students interested in participating in this year's competition must submit their papers, in final publication form, along with the required certification form (available on the DXC web site: WWW.DXCICDD.COM) to MAGUIRE@ICDD.COM by 15 July 2000. The winner will be selected by a committee of researchers in the field, announced at the Plenary Session of the conference, and listed in the proceedings. The award for the year 2000 will be in the amount of $1,000.

Workshop at EPDIC-7

A one-day workshop was sponsored at the recent EPDIC-7. On Saturday, 20 May 2000, Dr. John Faber, ICDD's Principal Scientist and Dr. Camden Hubbard, ICDD's Chairman, presented "Application of Crystallographic Databases to Materials" and "Effective Use of Retrieval Software for the PDF: Alphabetical, Hanawalt and Fink Searches" to over 40 attendees. The ICDD participated as an exhibitor at the conference as well.

ICDD Demo Pack

The ICDD is pleased to announce the availability of its complimentary ICDD Demo Pack. Designed as a venue to introduce users to the various ICDD products, the Demo Pack contains samples of the following:

- ☐ Sets 31 and 78 of the Powder Diffraction File® in flat-file and relational database formats
- ☐ Special versions of PCSIWIN® and PCPDFWIN® which have been adapted to work on Sets 31 and 78
- ☐ Excerpts of Volume 42 of *Advances in X-ray Analysis*™, proceedings of the 1998 Denver X-ray Conference

For your convenience, the ICDD products catalog is also included. Contact the ICDD for your free copy of the Demo Pack today!

Crystallography Scholarships Available for 2001

Applications for the 2001 Ludo Frevel Crystallography Scholarship Awards are now being accepted, with 31 October 2000 as the deadline. The name of the awards was recently changed to honor the founder of the fund, Dr. Ludo Frevel. This program was established to encourage promising graduate students to pursue crystallographically-oriented research. Since the program's inception in the early 90s, the ICDD has awarded 33 scholarships with the most recent awards in the amount of $2,250 each. Complete details about the awards and the application process can be found on the ICDD web page.

Terry Maguire, Manager of Conference Services

COMPUTER CORNER

Updates on Freely Available Crystallography and Powder Diffraction Software

Lachlan M. D. Cranswick
Collaborative Computational Project No 14 (CCP14) for Single Crystal and Powder Diffraction
Daresbury Laboratory, Warrington, Cheshire, WA4 4AD U.K
E-mail: L.Cranswick@dl.ac.uk
WWW: http://www.ccp14.ac.uk

Software presented in this section is a selection and a minor subset of freely available programs that can be evaluated at anytime by downloading off the internet using the given internet address and CCP14 software mirrors. Readers are invited to submit short reviews to the CPD Chairman or directly to the Computer Corner Editor, Dr. L. Cranswick.

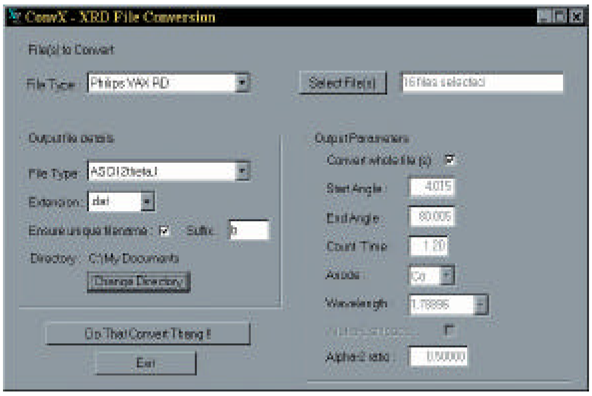
ConvX – Data File Conversion Software for Windows95

Mark Bowden
Ceramics Team, Industrial Research Limited,
P.O.Box 31-310, Lower Hutt, NEW ZEALAND
E-Mail: m.bowden@irl.cri.nz - WWW:
http://www.ceramics.irl.cri.nz/

Some readers may be familiar with the DOS programme CONVERT, which reads and writes powder diffraction files in a variety of formats. The author has finally got around to upgrading this programme to a Windows95 version and has added a few new useful features.

If you want to interchange data between powder formats, then ConvX could just be the baby for you. It will read and write files in the following formats:

- Philips binary files (VAX RD, PC RD and PC SD) (http://www.analytical.philips.com/)
- Siemens/Bruker DiffracPlus RAW (http://www.bruker-axs.com/)
- ASCII columns of 2-theta, I
- GSAS
- DBW-type Rietveld programmes (e.g. LHPM1, Rietica) (http://www.us.iucr.org/iucr-top/comm/cpd/Newsletters/no20summer1998/art15/art15.htm)
- Sietronics CPI (also used in Diffraction Technology programmes) (http://www.sietronics.com.au/) (http://www.ozemail.com.au/~difftech/products/siroqnt.htm)
- ScanPI (a film scanner we have in our lab)



File Type: Philips VAX RD
16 files selected
File Type: ASCII2theta,I
Extension: dat
Ensure unique filename: ☑ Suffix: b
Directory: C:\My Documents
Convert whole file (s): ☑
Start Angle: 4.015
End Angle: 80.005
Count Time: 1.20
Anode: Co
Wavelength: 1.78896
☐
Alpha-2 ratio: 0.50000

Fig. 1: The ConvX interface.

In addition to the expected GUI interface, the new version also sports the facility to convert many files at once and can trim the data to a restricted 2-theta range. A further option checks to see if the output file already exists, adding a few characters of your choice to the filename to avoid overwriting. And more than just the intensity data are converted – where the file formats allow, other information such as wavelengths, time and date, and count time are automatically preserved in the output file. Well mostly, and I'll get around to writing the rest of the code before too long.

So if this sound like it could help you out, grab a copy from the Industrial Research Ceramics Website (http://www.ceramics.irl.cri.nz/Convert.htm). Oh, and I'll get around to updating that sometime, too. So remember, if you need to turn powder data from one format into another, don't just convert it – ConvX it!

If you have any comments, or would like some bugs fixed, try e-mailing the author: m.bowden@irl.cri.nz.

Happy ConvX'ing.

DEBVIN: A Computer Program For Powder-Profile Refinement Using Generalized Coordinates And Geometrical Restraints.

Sergio Brückner
Univ. of Udine, Italy.
E-mail: sergio.bruckner@dstc.uniud.it

DEBVIN is a program aimed to carry out Rietveld refinements with X-ray or neutron powder diffraction data. The program is a development of PREFIN, a program originally written by Immirzi (1), whose main feature was that of combining the Rietveld approach with the use of generalized coordinates (g.c.).

Improvements present in DEBVIN are the result of experience accumulated in a number of years of applications particularly in the field of polymer crystallography (see,e.g., 2 and 3). The main improvements relative to PREFIN are:

1) Possible switching between PEARSON VII and PSEUDO-VOIGT peak shape.

2) Refinement of different crystallite dimensions along three directions parallel to the unit cell axes.
3) Generation of the structural model through proper instructions to be given in the input file.

Point (3) is of particular importance since the structural model must be constructed with the aid of suitable g.c. and this job was accomplished , in PREFIN, by writing, for each problem, an “ad hoc” subroutine (SUBROUTINE LAGRG) that translated g.c. into crystallographic fractional coordinates. This job required to the user noticeable experience in computational programming and it was always necessary to re-compile the program for every new structural problem.

DEBVIN allows for a few tens instructions that are sufficient, in our experience, to build up a wide variety of structural models and one can also indicate which structural parameter is to be refined and which is not. This procedure requires no experience in computational programming and does not require any new compilation of the program, that can, therefore, be distributed in an executable version. Point (2) is also of importance in polymer crystallography, since polymer crystallites (lamellae) are often characterized by strong differences of dimensions along different directions. This anisotropy is reflected in different FWHM’s for different hkl triples. The theoretical background for this kind of refinement is present in a paper by Perego, Cesari & Allegra (4).

DEBVIN Rietveld can be downloaded off the internet via ftp://ftp.cc.uniud.it/DEBVIN/ and is mirrored at the CCP14 (http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/debvin/DEBVIN/).

REFERENCES

1) Immirzi, A. (1980). *Acta Cryst.* B36, 2378-2385.
2) Brückner, S. (1988). *Chim. Ind.* 70, 48-53.
3) Brückner, S., De Rosa, C., Corradini, P., Porzio, W., Musco, A. (1996). *Macromolecules* 29, 1535-1539.
4) Perego, G., Cesari, M. & Allegra, G. (1984). *J. Appl. Cryst.* 17, 403-410.

CCP14 Based Tutorial On Solving Organics From Powder Diffraction Data

A new web tutorial on solving organic structures from powder diffraction data (based around the classic cimetidine structure) is available via http://www.ccp14.ac.uk/solution/powder_structure_solution_pathways/. This tutorial runs through data conversion, peak profiling, powder indexing and spacegroup assignment, Cambridge database cell and structure searching, structure solution, Rietveld refinement options, hydrogen placement options, powder pattern calculation, and photorealistic rendering and graphical output. The main emphasis is on available software to assist the diffractionist in performing structure solution from powder diffraction data.

The “new” Chekcell for Windows graphical powder indexing and spacegroup assignment helper tool. Part of the LMGP suite for Windows by Jean Laugier and Bernard Bochu.

A new freely available program that takes much of the drudgework out of powder indexing and spacegroup assignment is the Chekcell for Windows (part of the LMGP suite by Jean Laugier and Bernard Bochu). This not only allows the very easy graphical evaluation of trial cells but also will suggest the best spacegroups consistent with the observed lines. Chekcell is closely integrated with Robin Shirley’s CRYSFIRE powder indexing suite (which itself links to Ito, Treor, Dicvol, Taup, Lzon, Kohl, Losh and Fjzn). Chekcell will import the Crysfire *.SUM summary file allowing the user to browse through the list of trial cells, graphically seeing the calculated lines overlaid with the raw data, and profiled peak positions. Chekcell has “Best Group” and “Best Solution” to automatically go through the trial cells and spacegroups to see graphically which looks the best. This can save much time; though as with all programs, it has to be used intelligently, especially if impurity peaks are present. The graphical nature of Chekcell makes it far easier to evaluate solutions for marginal data of poor resolution and with possible impurity peaks. Chekcell can be run concurrently with CRYSFIRE; where updating of the *.SUM summary file can be performed at the click of a button. At the time of writing, the latest version of Chekcell is 15th April 2000, though a new version that can handle non-standard settings (including the six possible orthorhombic settings) should be available at the time this newsletter is available.

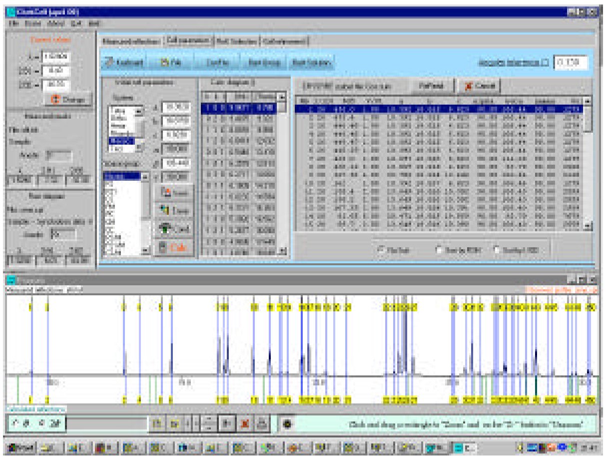


***Fig 1**: LMGP suite Chekcell interface. Raw data, observed and calculated peaks based on one of the Crysfire trial cell list. Ability to change space group is mid left, with buttons for automatic spacegroup assignment and best solution on the top. The list of trial cells generated via Robin Shirley’s CRYSFIRE powder indexing suite in on the top right window.*

The ability to "optimise" the tolerance for matching observed and calculated HKLs will also allow for more accurate automatic spacegroup and cell assignments. Any indexing program that outputs a file in the CRYSFIRE *.SUM summary file format can make easy use of Chekcell. Chekcell tutorials and download information is available at http://www.ccp14.ac.uk/tutorial/lmgp/. Robin Shirley's CRYSFIRE powder indexing suite can be via the tutorial page at:
http://www.ccp14.ac.uk/tutorial/crys/.
The above mentioned tutorial pages point to CCP14 based download sites in UK, Australia and Canada.

Platon/"System S" for user-friendly searching the Cambridge Organic and Organometallic Structure Database

New functionality in Ton Spek's Platon (http://www.cryst.chem.uu.nl/platon/) includes the ability to act as a user friendly interface to the Cambridge Database Quest program for Cell and Structure searching. Further enhancements have also been added to the Addsym algorithm (an implementation of Yvon Le Page's Missym) to improve finding missing symmetry in solved crystal structures. This includes "the detection of approximate higher symmetry due to either missing atoms or a few atoms that do not comply with the higher symmetry (either real or refinement artifact)". Routine application of Platon's Addsym should be considered mandatory for anyone solving and refining structures from powder and/or single crystal data (Inorganic and Organic). Examples of structures in the Cambridge database that Addsym has found to be wanting is viewable on the web at http://www.cryst.chem.uu.nl/platon/pl000401.html

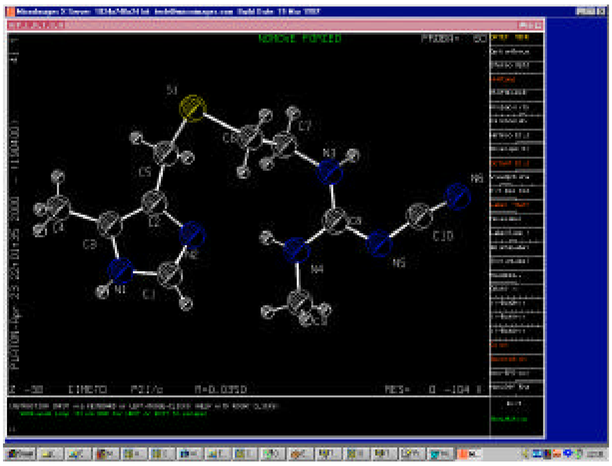


Fig 2: Results from a CSD search via Platon. Scrolling through structures related to Cimetidine.

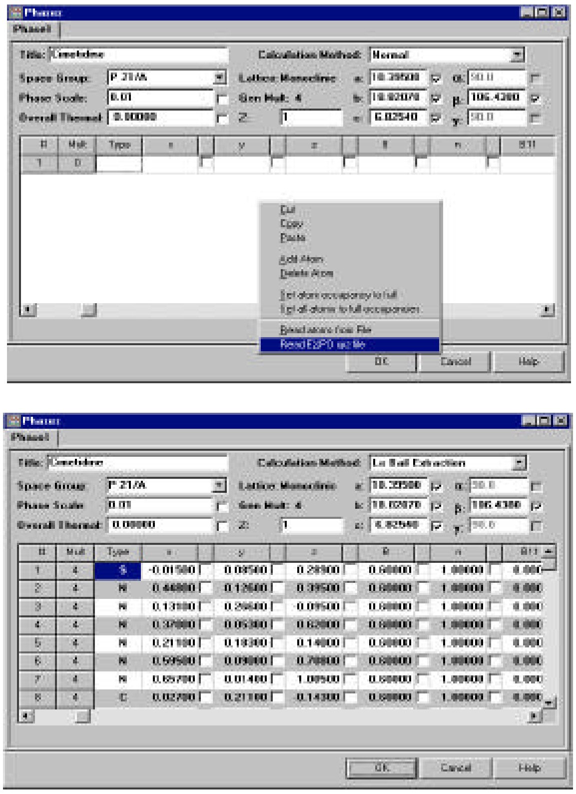
Rietica-LHPM Rietveld software, interface to Sirware EXPO and Internet updating at the press of a button.

Rietica-LHPM GUI Rietveld for Windows by Brett Hunter now allows updates over the Internet (or from update files on a local disk) at the click of a button from within Rietica. Via the main menu, selecting Help, Update Rietica will prompt for a mirror site on the Internet from which it can check for updates. If it finds any updates, it will then download and install them.

Site: ANSTO FTP Site
Status: Closed Internet connection
This is the current version of Rietica.

Fig 3: Internet Update window from Rietica-LHPM Rietveld.

As is the trend of powder diffraction programs to become friendly to other relevant software (Fullprof/Winplotr being a prime example), Rietica-LHPM will now export Le Bail fit results to the EXPO structure solution software by creating both an HKL file and EXP starting file. After EXPO obtains a structure solution, Rietica can then import the resulting XYZ coordinates file; avoiding errors that can typically occur using manual methods. Rietica can also import GSAS, DBWS and Fullprof structure files. The Sirware EXPO direct methods structure solution from powder diffraction data software (sequel to Sirpow and Extra) is freely available for academic use. Information on obtaining the package can be viewed on the Sirware webpage at http://www.ba.cnr.it/IRMEC/SirWare_main.html.



Title: Cimetidine
Calculation Method: Normal
Space Group: P 21/A
Lattice: Monoclinic
Phase Scale: 0.01
Gen Mult: 4
Overall Thermal: 0.00000
Z: 1
a: 10.39500 ☑ α: 90.0 ☐
b: 10.02070 ☑ β: 106.4380 ☑
c: 6.82540 ☑ γ: 90.0 ☐

Title: Cimetidine
Calculation Method: Le Bail Extraction
Space Group: P 21/A
Lattice: Monoclinic
Phase Scale: 0.01
Gen Mult: 4
Overall Thermal: 0.00000
Z: 1
a: 10.39500 ☑ α: 90.0 ☐
b: 10.02070 ☑ β: 106.4380 ☑
c: 6.82540 ☑ γ: 90.0 ☐

#	Mult	Type	x	y	z	B	n	B11
1	4	S	-0.01500	0.09500	0.29900	0.60000	1.00000	0.000
2	4	N	0.44000	0.12600	0.39500	0.60000	1.00000	0.000
3	4	N	0.13100	0.29600	-0.09500	0.60000	1.00000	0.000
4	4	N	0.37000	0.05300	0.62000	0.60000	1.00000	0.000
5	4	N	0.21100	0.19300	0.14000	0.60000	1.00000	0.000
6	4	N	0.59500	0.09000	0.70000	0.60000	1.00000	0.000
7	4	N	0.65700	0.01400	1.00500	0.60000	1.00000	0.000
8	4	C	0.02700	0.21100	-0.14300	0.60000	1.00000	0.000

Fig 4a,b: Importing a structure from the Sirware EXPO into Rietica-LHPM

New GSAS for Linux and updated EXPEDIT Graphical User Interface for UNIX and Windows

There is a new Linux version of GSAS by Bob von Dreele and Alan Larson was released on the 21st of April 2000 (as well as the usual DOS version). This is available from the GSAS ftp site and CCP14 regional mirrors in the UK, Canada and Australia.

USA home site: ftp://ftp.lanl.gov/public/gsas/
UK: http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/gsas/public/gsas/
CA: http://ccp14.sims.nrc.ca/ccp/ccp14/ftp-mirror/gsas/public/gsas/ms-dos/
AU:ftp://ftp.minerals.csiro.au/pub/xtallography/ccp14/ccp/ccp14/ftp-mirror/gsas/public/gsas/

Users should also routinely check for updated version of the EXPEDT software for UNIX and Windows by Brian Toby. This enables a point and click GUI interface into GSAS; as well as retaining the ability to interact with the standard GSAS menu system.

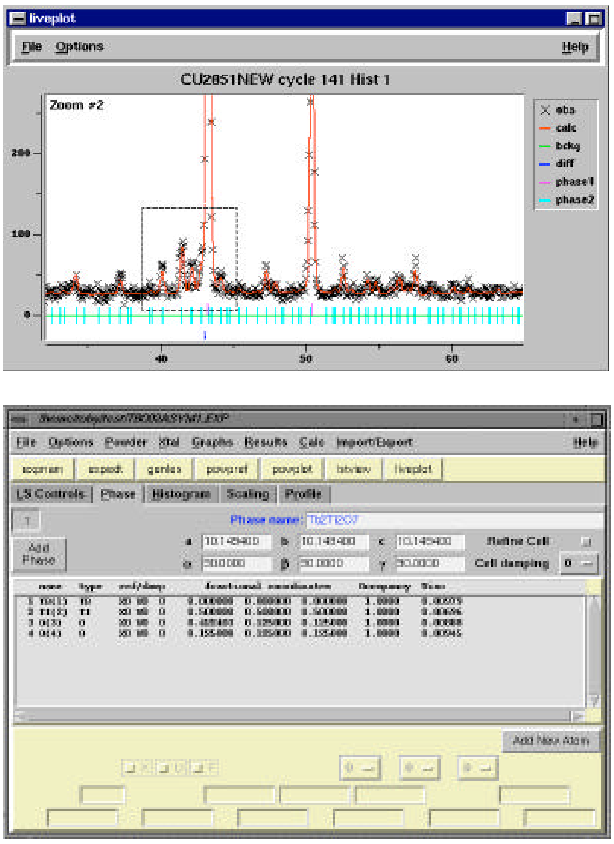


Fig 5a,b: Examples of some of the GUI based graphics with EXPEDT

EXPEDT can be downloaded via Brian Toby's webpage at http://www.ncnr.nist.gov/programs/crystallography/software/expgui/expgui_intro.html and CCP14 mirrors.

Tutorials for creating secure dual boot PCs with both Windows and Linux (or FreeBSD UNIX) for crystallographic applications are available via the CCP14 website at:

http://www.ccp14.ac.uk/solution/linux/#install

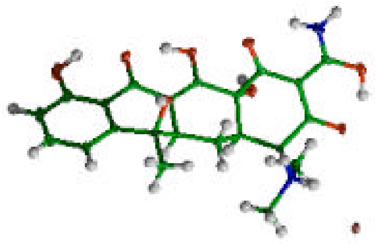


Fig 6: Screen dump of a rotating web animation of an organic structure generated in ORTEX

Graphical Void finding and GIF animations of structures in ORTEX Single Crystal Suite by Patrick McArdle

The latest ORTEX single crystal suite (using a structure file in Shelx format) allows the finding of voids in a structure in via a GUI point and click interface. As well as this, the photorealistic rendering option now allows the generation of animated structures in the Web friendly GIF animation format. As will be an oft repeated statement in this article, single crystal software can also be very usefully applied to powder diffraction problems. ORTEX can be downloaded off the web via: http://www.nuigalway.ie/cryst/software.htm (and CCP14 mirrors)

Latest GUI ORTEP III for Windows by Louis Farrugia

If you are a user of ORTEP III, you should look for the latest version 1.0.3 of ORTEP, released on the 31st of January 2000: (http://www.ornl.gov/ortep/ortep.html). One implementation that is very user-friendly is the version ported to Windows with an added Graphical User Interface by Louis Farrugia of Glasgow University. This also reads in a variety of structure formats including some Rietveld formats, (GSAS, Fullprof and LHPM-Rietica)

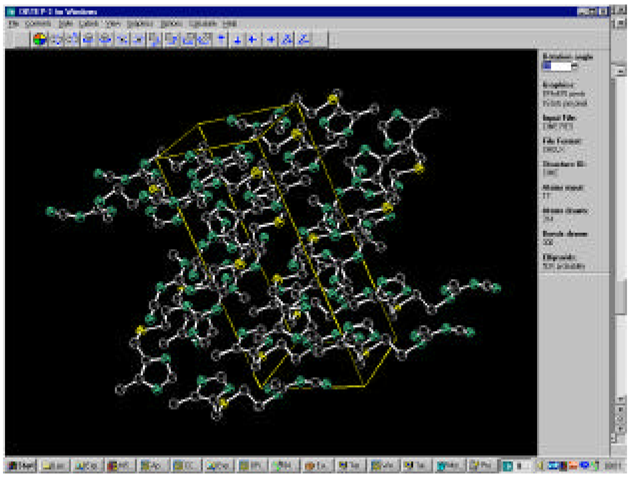


Fig 7: Cell packing of an organic solved from powder diffraction data using GUI WinORTEP.

SXGRAPH GUI Shelx Interface by Louis Farrugia

By the time this goes to press, the latest version of WinGX Single Crystal Suite by Louis Farrugia of Glasgow University should be released. Some of the enhancements include Lazy Pulvarix for calculating powder patterns as well as SXGRAPH, a Graphical User Interface over Shelxl. This includes the ability to graphically define the hydrogen placement commands as well as fragment manipulation for passing onto fragment based structure solution programs such as Dirdif, Patsee and ESPOIR. This and many other crystallographic tools available in WinGX make it very useful for powder diffraction applications. It can be obtained off the web at http://www.chem.gla.ac.uk/~louis/software/ and CCP14 mirrors.

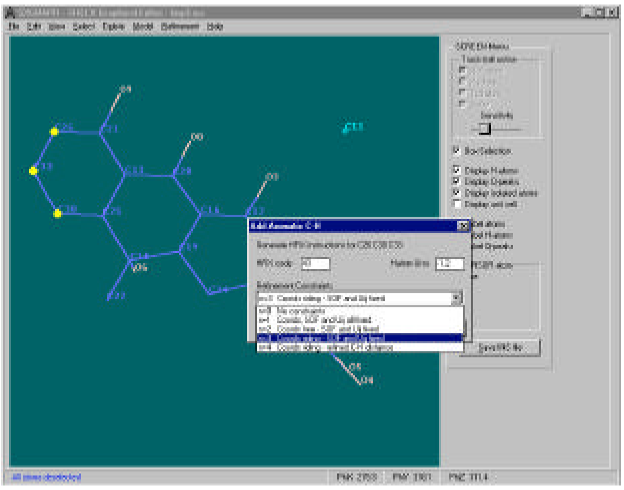


Fig 8: Graphically selecting and generating Shelxl hydrogen placement commands via the SXGRAPH Graphical User Interface.

ESPOIR 3 Monte Carlo Structure Solution software for Powder Diffraction data by Armel Le Bail

The latest version 3 of the freely available ESPOIR Monte Carlo structure solution software for powder diffraction can be downloaded via http://sdpd.univ-lemans.fr/sdpd/espoir/. Windows binaries (and Linux binaries ported by Lubomir Smrcok) are available as well as the Fortran source code. As this is released under the GPL (GNU Public License), it can be freely modified and redistributed, as long as the modified source code is also included. The latest version can handle multiple rigid bodies and fragments. The PRESPOIR program now inserts comments in the ESPOIR control file to make it easier to read and modify by hand. ESPOIR can also solve on a reconstituted powder pattern; thus handling structures with severe reflection overlap. Advice on using ESPOIR for different types of structures (organics and inorganics) is available from the ESPOIR site.

No GNUs is bad News

One possible trend that existing and new program authors may like to take into account; is crystallographic software now being released (or re-released) under the GNU Public License (GPL). This license allows anyone to freely copy, modify the source code and further distribute the software on the proviso that derivative software is also under the GPL. This can mean software under the GNU license can exist and propogate without the uncertainty of other types of software licensing systems. It can also assist in developing a community effort around the source code. It is on this basis that community efforts such as the high quality, freely available Linux Operating System and Apache web server have been developed.

Crystallographic programs presently under the GNU Public License include:

ESPOIR structure solution from powder diffraction (written in Fortran)
http://sdpd.univ-lemans.fr/sdpd/espoir/

MAUD for Java; Materials Analysis Rietveld including Stress and Texture
http://www.ing.unitn.it/~luttero/

Xtal Single Crystal Suite (Rational Macro - RatMac/Fortran)
http://xtal.crystal.uwa.edu.au/

ZEFSA zeolite structure solution from powder diffraction (written in C)
http://www.mwdeem.chemeng.ucla.edu/zefsaII/

Being under the GNU Public License does not preclude Industrial and Commercial sponsorship of software to the benefit of those actively developing the source code. The recent version 3 of the GPL’d ESPOIR software was financially sponsored by Dupont. While only a personal opinion of the author, the GNU license can save much on the complexity of these sponsored arrangements: the commercial sponsor get what they want, users and code developers minimize the risk of the software getting “jailed” and the software developers are unconstrained in pathways for further development of the source code (the GNU license guarantees this). Please feel free to inform the author of other programs available under the GPL License; and of different interpretations of the GNU license if you disagree with the above. The above is obviously generalizing to fit within article size constraints.

Internet Available Rietveld Software Updates:

It is always best to check (each morning ?) if there might be minor to major updates to your favorite Internet available crystallographic software. Updates as of time of writing (most likely out of date by the time you read this) to some of the available Rietveld refinement programs include:

BGMN (16th April 2000)
http://www.bgmn.de/

Debvin (10th March 2000)
ftp://ftp.cc.uniud.it/DEBVIN/

GSAS (21st April 2000)
ftp://ftp.lanl.gov/public/gsas/

LHPM-Rietica (30th March 2000)
ftp://ftp.ansto.gov.au/pub/physics/neutron/rietveld/Rietica_LHPM95/
MAUD for Java (15th February 2000)
http://www.ing.unitn.it/~luttero/
Powder Cell for Windows (now does user friendly Le Bail fitting) (29th April 2000)
http://www.bam.de/a_v/v_1/powder/e_cell.html
Winplotr/Fullprof (20th April 2000)
http://www-llb.cea.fr/winplotr/winplotr.htm
XND (30th March 2000)
ftp://old-labs.polycnrs-gre.fr/pub/xnd/
ftp://labs.polycnrs-gre.fr/pub/xnd/

All the above Rietveld programs are also available via the CCP14 based mirrors in UK, Australia and Canada.

Non-Crystallographic Utilities of Interest – Junkbuster for the World Wide Web:

A freely available piece of GPL'd software for UNIX ,Windows and other operating system that may or may not be useful is JunkBuster. This is a web proxy program that filters common annoying web advertising and also intercepts web "Cookies" that could be sending information on your browsing habits to commercial companies. Another side effect is that it can speed up your connections to websites what have a plethora of banner and other sorts of advertising. The original version can be obtained from http://www.junkbusters.com; and an improved version from http://www.waldherr.org/junkbuster/.

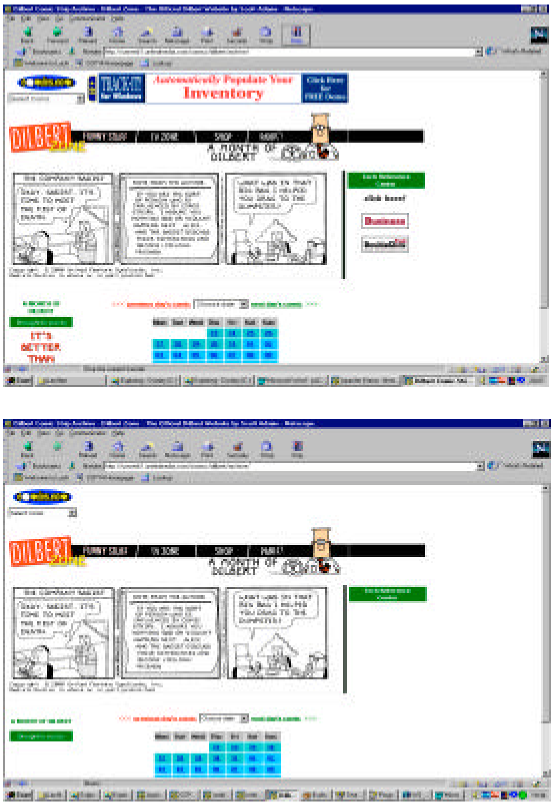


Fig 9a,b: Browsing the web a) without junkbuster and b) with junkbuster.

Crystallographic Nexus Software CD-ROMs

Academics and students in crystallography working in laboratories in the developing world which are isolated from the Internet are invited to register for Crystallographic Nexus Software CD-ROMs. The CD-ROM is free of charge.

Crystallographic Nexus CD-ROMs (1) are being organised and produced in batch amounts for distribution to laboratories, academics and students isolated or poorly linked to the Internet in the developing world. The ability to produce these CD-ROMs is primarily due to the permission of software and web site custodians; with sponsorship and guidance from the International Council for Science (ICSU) (2), International Union of Crystallography (3) and CCP14 Project for Single Crystal and Powder Diffraction (4).

The Crystallographic Nexus CD-ROM is a virtual Internet (or virtual web browser cache) on CD-ROM containing Web and FTP sites housing a variety of crystallographic software packages and crystallographic resources. These include a wide genetic diversity of single crystal software; powder diffraction programs; educational resources and miscellaneous crystallographic information. Using the CD-ROM, a modern crystallographic data analysis facility for single crystal and powder diffraction can be implemented using this cache of freely available software.

The intention is to mail regular updates of the CD-ROM. Due to limitations in present software tools used to create the template CD-ROM image, initial CDs will be optimised for MS-DOS and MS-Windows operating systems; but will contain Mac and Linux binaries that can be copied from the CD on these operating systems. While not a substitute for a fast connection to the real Internet, this SMIP method (Snail Mail Internet Protocol) can hopefully assist those who at present do not have the Internet at their fingertips. Academics and students from the developing world are warmly encouraged to register for these virtual Internet CD-ROMs. The NeXus project is organized by the IUCr Committee on Electronic Publishing, Dissemination and Storage of Information (CEP) which will be responible for selecting recipients from the requests received. A list of Developing Countries as defined by the OECD is available on the World Wide Web (5).

Requests for NeXus CD-ROMs should be addressed to Lachlan M. D. Cranswick (CCP14 Secretary)

1. Xtal Nexus CD-ROM homepage at Univ. of Geneva: http://www.unige.ch/crystal/stxnews/nexus/index.htm
2. ICSU (International Council for Science): http://www.icsu.org
3. IUCr (International Union of Crystallography): http://www.iucr.org
4. EPSRC funded CCP14 Project (Collaborative Computational Project No 14 for Single Crystal and Powder Diffraction): http://www.ccp14.ac.uk
5. OECD List of Developing Countries in Alphabetical Order: http://www.oecd.org/dac/htm/ldc-alfa.htm

WHAT'S ON

Conferences

31 July to 4 August 2000
Denver, Colorado, U.S.A.
The 49th Annual Denver X-ray Conference:
X-ray Analysis in the 21st Century

The Denver X-ray Conference has evolved into an international forum for discussions of state-of-the-art techniques and indications for future developments in X-ray analysis. The format consists of two days of tutorial workshops and poster sessions, followed by two and a half days of technical sessions. In addition to providing sponsorship, the ICDD publishes the conference proceedings in CD-ROM format through the series *Advances in X-ray Analysis.*

For further information contact:
Conference Coordinator
International Centre for Diffraction Data
12 Campus Boulevard
Newtown Square, PA 19073-3273
Tel: +(610) 325-9814
Fax: +(610) 325-9823
E-mail: dxc@icdd.com
Web-site: www.dxcicdd.com

May 2001
Gaithersburg, MD, U.S.A.
Accuracy in Powder Diffraction III

This is the third APD conference after the previous editions of 1981 and 1991. It is intended to cover all important aspects of X-ray powder diffraction techniques, in order to present the state of the art in this field.

For further information contact:
James P. Cline
Ceramics Division
National Institute of Standards and Technology
100 Bureau Dr. stop 8523
Gaithersburg, MD 20899-8523 USA
Tel: 001 (301) 975 5793
Fax: 001(301) 975 5334
E-mail: Cline@Credit.NIST.gov
Web-site: www.nist.gov

2 – 6 December 2001
Trento, Italy
Size-Strain III - Analysis of Microstructure and Residual Stress by Diffraction methods

After the successful editions of Liptovski Mikulas (Slovak Rep.) in 1995 and Freiberg (Germany) in 1998, this conference will gather most of the specialists in Line Profile Analysis for the study of lattice defects and microstructure, as well as residual stresses by diffraction techniques.

For further information contact:
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Tel: +39 0461 882417 / 67
Fax: +39 0461 881977
E-mail: Paolo.Scardi@ing.unitn.it
Matteo.Leoni@ing.unitn.it
Web-site: bragg.ing.unitn.it/sizestrain

Workshops

4 – 8 October 2000
University of Bayreuth, Laboratory of Crystallography, Germany
VII. Workshop Powder Diffraction Structure Determination and Refinement from Powder Diffraction Data
For further information contact:
Robert E. Dinnebier & Sander van Smaalen
Laboratory of Crystallography,
University of Bayreuth,
D-95440 Bayreuth, Germany
Tel: (+49) 921 553880
Fax: (+49) 921 553770
E-mail: robert.dinnebier@uni-bayreuth.de
Web-site: www.uni-bayreuth.de/departments/crystal/workshop2000

7 – 9 September 2000
Katowice, Wisla, Poland
International Workshop on the Rietveld Method (RW2000-PL),
For further information contact:
SECRETARIAT XVIII CAC, Dr Danuta Stróz
University of Silesia
Institute of Physics and Chemistry of Metals
ul. Bankowa 12
40-007 Katowice, Poland
tel./fax +(4832) 59-69-29
e-mail:dana@us.edu.pl

ICDD clinics:

January 2001
Charles University, Praha, Czech Republic
X-ray Powder Diffraction Workshop

Topics include acquisition of good X-ray powder diffraction data and phase identification, set up and calibration of the diffractometer, specimen preparation, and semi-quantitative phase analysis.

30 April - 4 May 2001
ICDD, Newtown Square, Pennsylvania, U.S.A.
Fundamentals of X-ray Fluorescence Spectrometry
Covering basics of X-ray spectra, instrumentation design, methods of qualitative and quantitative analysis, specimen preparation and applications for both wavelength and energy dispersive spectrometry.

7 – 11 May 2001
ICDD, Newtown Square, Pennsylvania, U.S.A.
Advanced Methods in X-ray Fluorescence Spectrometry
Emphasizing quantitative methods, use of automated X-ray spectrometers, review of mathematical matrix correction procedures, and new developments in XRF.

4 – 8 June 2001
ICDD, Newtown Square, Pennsylvania, U.S.A.
Fundamentals of X-ray Powder Diffraction
Covering instrumentation, specimen preparation, data acquisition, and qualitative phase analysis.

11 – 15 June 2001
ICDD, Newtown Square, Pennsylvania, U.S.A.
Advanced Methods in X-ray Powder Diffraction
Emphasizing computer-based methods of data collection and interpretation, both for qualitative and quantitative phase analysis.

For further information on the ICDD clinics contact:

Education Coordinator
International Centre for Diffraction Data
12 Campus Boulevard
Newtown Square, PA 19073-3273

Tel: +(610) 325-9814
Fax: +(610) 325-9823

E-mail: clinics@icdd.com
Web-site: www.icdd.com/education/clinics/

Call for contribution to the next CPD Newsletter (No 24)

The next issue of the CPD Newsletter will be edited by *Davor Balzar*, to appear in December of 2001. Davor will greatly appreciate contributions from readers on matters of interest to the powder diffraction community, e.g. meeting reports, future meetings, developments in instruments, techniques and news of general interest. Please contact him for sending articles and suggestions. Software developments can be directly addressed to *Lachlan Cranswick* or to the Editor of Newsletter No 24 (addresses are given below)

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