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Rietveld Refinement from Powder Diffraction Data

(Robert Dinnebier, Editor)

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CPD Chairman's Message 26

The international activity concerning Powder Diffraction will be quite rich in 2002. The major events are the 8th European Powder Diffraction Conference (EPDIC 8) in Sweden (Uppsala, 20-23 May; http://www.mkem.uu.se/epdic8) and the XIX IUCr World Congress in Switzerland (Geneva, 6-14 August; http://www.kenes.com/iucr/). The programs of two conferences were designed following different philosophies: while the EPDIC mostly focuses on methodologies, through dedicated sessions, the IUCr conference includes several sessions (microsymposia) on different PD applications. Despite the vicinity of the two conferences, attending both is therefore an interesting perspective. Same consideration applies to the 51st annual Denver X-ray conference (Colorado Springs, 29.7-2.8.2002, http://www.dxcicdd.com), whose PD program is rich as usual.

In this frame considerable attention will be given to the Rietveld method and to the many emerging related applications. The present issue of the CPD Newsletter is mainly devoted to this broad topic and provides a sufficiently wide variety of new methods and applications, as well as revision of existing software and algorithms. Even if not exhaustive, this review of recent developments can be an useful update for experts and a valid starting point for novices; even more so since the scientific articles which compose the core of the present issue are completed by the detailed review on new software (Rietveld method and other PD software) by *Lachlan Cranswick*. The issue is enriched by the short introduction by *Hugo Rietveld* who recalls the early times when the method bearing his name was conceived.

Once more, thanks to guest editor *Robert Dinnebier* and to the many contributors, we can expect No 26 will be an useful reading for the nearly 2000 powder diffractionists currently receiving the paper copy, and for the many other who download the electronic-format newsletter from the CPD web site.

Paolo Scardi

CPD projects

Quantitative Phase Analysis Round Robin

The International Union of Crystallography (IUCr) Commission on Powder Diffraction (CPD) has sponsored a round robin on the determination of quantitative phase abundance from diffraction data. The first of two papers detailing the outcomes of this study has now been published (Madsen *et al*, 2001) and the results presented and discussed at APD III (Accuracy in Powder Diffraction III, 22-25 April 2001, National Institute of Standards and Technology (NIST), Gaithersburg, Maryland, USA). The aims of the round robin have been detailed in Madsen *et al* (2001) and summarized in Issue 22 of this newsletter. The first paper (Madsen *et al.*, 2001) covered the results of sample 1 (a simple three-phase mixture of corundum, fluorite and zincite). The remaining samples used in the round robin covered a wide range of analytical complexity, and presented a series of different problems to the analysts. The results pertaining to these samples are discussed in the second paper which is currently in press. The analytical problems included severe preferred orientation (sample 2), the analysis of amorphous content (sample 3), microabsorption (sample 4), complex synthetic bauxite and natural granodiorite mineral suites along with complex pharmaceutical mixtures with and without an amorphous component.

The outcomes of the second part of the round robin support the findings of the initial study. The presence of increased analytical problems within these samples has only served to exacerbate the difficulties experienced by many operators with the sample 1 suite. The major difficulties are caused by lack of operator expertise and become more apparent with these more complex samples. Some of these samples also introduced the requirement for skill and judgement in sample preparation techniques. The second part concluded that the greatest physical obstacle to accurate QPA for X-ray based methods is the presence of absorption contrast between phases (microabsorption) and may prove to be insurmountable in many circumstances.

Ian Madsen

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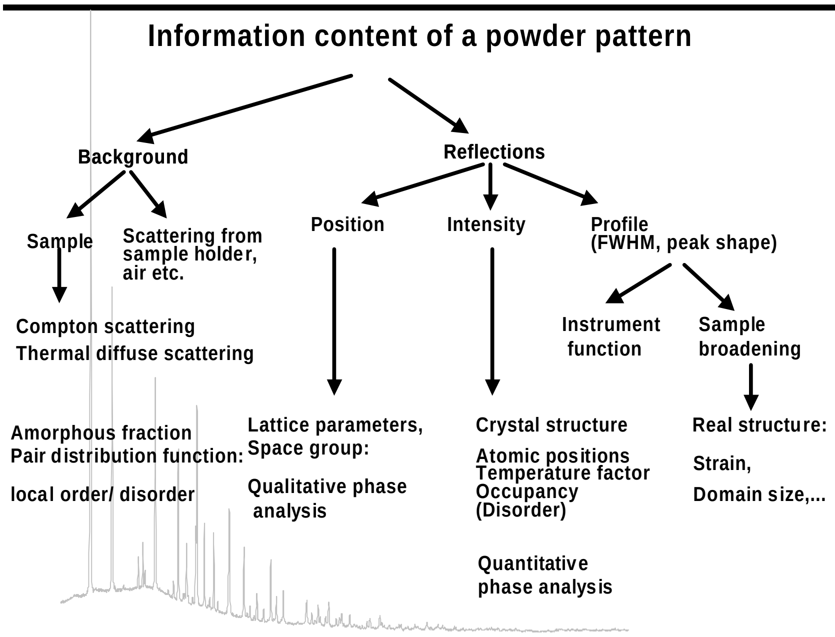
Madsen, I.C., Scarlett, N.V.Y., Cranswick, L.M.D. and Lwin, T. (2001) "Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: Sample 1A to 1H" J. Appl. Cryst. (2001), **34**, 409-426.

(The paper can be freely downloaded from the CPD web-site as an annex to the CPD Newsletter No 25. Courtesy of the IUCr editorial office.)

From the Editor of Newsletter 26

The basic idea behind the Rietveld method is to calculate the entire powder pattern using a variety of refinable parameters and to improve a selection of these parameters by minimizing the weighted sum of the squared differences between the observed and the calculated powder pattern using least squares methods. That way, the intrinsic problem of the powder diffraction method with systematic and accidental peak overlap is overcome in a clever way. It was the intention of Hugo Rietveld, who invented the method a few decades ago, to extract as much information as possible from a powder pattern. At the beginning this was mainly restricted to atomic positions from neutron diffraction patterns. On the other hand, there is much more information hidden in a powder pattern which may be subjected to Rietveld refinement as the scheme below may illustrate.



Therefore it was only a question of time before researchers started to extract this information using Rietveld's algorithm. Nowadays, applications of the Rietveld method range from the refinement of small protein structures to standardless quantitative phase analysis, the latter being of significant industrial importance. The availability of high resolution synchrotron and neutron radiation with little instrumental contribution to the line shape enables the analysis of microstructural properties. As an example, the special distribution of the lattice strain can be deduced from anisotropic peak broadening during a Rietveld refinement. A lot of information about defects and disorder is hidden in the background of a powder pattern and when the normalized powder diffraction data are Fourier transformed into real-space coordinates the atomic pair distribution function can be obtained which allows one to investigate the local structure in parallel to the average crystal structure.

Simultaneous Rietveld refinements of several datasets can e.g. be used for full texture analysis. In general, fast detectors like image plate readers in combination with powerful microcomputers reveal a new aspect of Rietveld-refinement: time dependence. By recording full powder patterns in short time intervals, the change of the crystal structure in dependence on pressure, temperature or during a chemical reaction is monitored and dynamical processes can be visualized. Not to forget that the Rieveld decomposition formula can be iterated in a way that at the point where calculated structure factors |F| are entered a set of identical |F| is given instead. The Rietveld refinement then calculates a set of "|Fobs|" from the decomposition formula, which are then used as new |Fcalc| and so on, which is generally known as the LeBail method. This trick allows one to separate the refinement of the profile from the refinement of the crystal structure and the extracted intensities can be used for crystal structure determination. There is still a lot more potential in the method and it is my pleasure to devote an issue of the CPD newsletter to some of the various aspects of modern Rietveld refinement.

Robert Dinnebier

Thirty five years ago

Thirty five years ago in the search for mechanically stable fuel elements for nuclear reactors, the structure of some uranates had to be determined. Because of the small crystal size only powder diffraction data were available. This restriction was an immense obstacle, because in those days only single crystal diffraction data could lead to a successful refinement. Powder diffraction was regarded to be obsolete for refining structures, because of the problem of overlap with low symmetry compounds and at high diffraction angles. Step scanning yielded a powder diagram that showed definite detail in the profile of these overlapping peaks. The information contained in this detail could however not be extracted by conventional means and one had to resort to taking the sum of these overlapping peaks as data for the least squares refinement. It was therefore clear that no full use was made of the information contained in the powder diagram.

My experience with computers, built up over years of doing single crystal diffraction work, gave me a head start in tackling this problem of extracting the maximum of information from a powder diagram. My efforts ultimately led to what is now known as the Rietveld Method. When the method was first reported in Moscow in 1966 at the IUCr Congress, there was hardly any response. A few years later, when I wrote a more comprehensive computer program, first in Algol 60 and later in Fortran IV, the demand for the program and its subsequent use increased, but only for neutron powder work. When the program was adapted to X-ray diffraction by others, in the mid seventies, did the popularity of the Rietveld Method grow. I already had foreseen that it could be used for X-ray data, but due to the lack of an actual problem, I did not pursue it any further.

I am totally amazed looking at the ever increasing use that is being made of the method. Yearly, hundreds of publications use or refer to the method. What began as a solution for a particular problem, turned out to be a tool of much broader value. Now it is not only applied to structure refinement, but also to such divers fields as quantitative phase analysis, measurement of strain and size and the analysis of time-resolved data. I am deeply gratified that I could have been instrumental in reviving the powder diffraction method. This in itself would have given me enough satisfaction. Receiving the Gregori Aminoff Prize in 1995 from The Royal Swedish Academy of Sciences for my work gave an added lustre.

Hugo Rietveld

WWW sites related to powder diffraction

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
CCP 14: http://www.ccp14.ac.uk/index.html

Submitting a proposal for neutron diffraction or Synchrotron Radiation X-ray Diffraction is possible at many Large Scale Facilities (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-site, maintained by R.Dinnebier*:*
http://www.pulverdiffraktometrie.de

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

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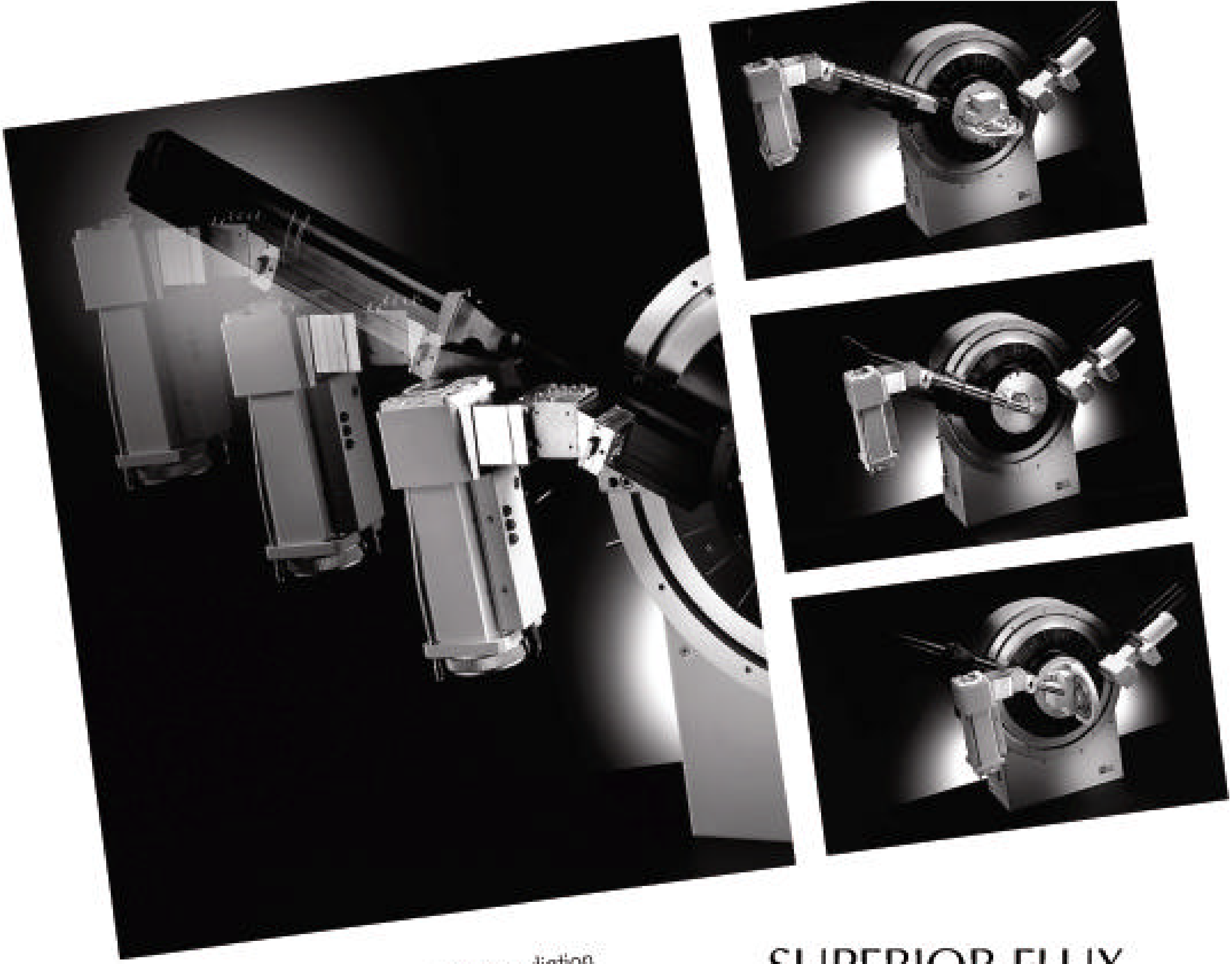

Beyond the abilities of Rietveld analysis: MEM-based pattern fitting with synchrotron X-ray powder diffraction data

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The maximum-entropy method (MEM) is a versatile approach to the estimation of a model from a limited amount of information by maximizing information entropy under constraints consistent with observed physical quantities. In recent years, Takata *et al.* [1] have applied it actively to the determination of electron densities, r, using synchrotron X-ray diffraction (XRD) data. MEM infers electron densities in such a way that they provide the maximum variance of structure factors, F_c(MEM), within errors in observed structure factors, F_o. Detailed structural information can effectively be extracted from the diffraction data and reflected on the resulting densities ($r > 0$) by MEM if the data have been appropriately measured. Because MEM can estimate non-zero structure factors of high-Q reflections excluded in the analysis of powder diffraction data, the termination effect is less marked in MEM analysis than in Fourier synthesis. Thanks to these excellent features, MEM gives less noisy density maps than Fourier synthesis [2].

Takata *et al.* [1] estimate observed integrated intensities on the basis of the result of Rietveld analysis when dealing with overlapping reflections. That is, the observed net intensity at each point is apportioned in the ratio of profiles calculated from final structure and profile parameters and summed up for each reflection [3]. This expedient technique is also utilized to evaluate R_B and R_F in Rietveld analysis, integrated intensities in the Le Bail method [4], and electron/nuclear densities in Fourier synthesis. However, 'observed' structure factors, F_o(Rietveld), estimated in this manner are doubly biased towards a structural model in the Rietveld analysis because both phases and calculated profiles used for the intensity partitioning are derived from the model [2]. This approximate nature of the procedure for extracting integrated intensities lowers the accuracy of electron/nuclear densities determined by combining Rietveld and MEM analyses, *i.e.*, the MEM/Rietveld method [1].

We have integrated a versatile pattern-fitting program RIETAN-2000 and a MEM program MEED into a system named REMEDY [5–7] to overcome the serious defect in the MEM/Rietveld method. With REMEDY, the bias imposed on electron/nuclear densities can efficiently be reduced by an original technology called **M**EM-based **P**attern **F**itting (MPF). This article describes the principle of the MPF method and its applications to XRD data of three samples to demonstrate its strength relative to the MEM/Rietveld method. In contrast to our previous work [5–10] using XRD with CuKα radiation and neutron diffraction, synchrotron XRD data were analyzed to test the performance of MPF in structure refinements with the high-resolution XRD data.

Figure 1 illustrates a flow chart of structure refinement by the MEM/Rietveld method (upper frame) and subsequent repetition of MPF (lower frame). F_o(Rietveld) data estimated at the end of Rietveld analysis [3] are analyzed by MEM to yield electron/nuclear densities, which may urge us to modify a structural model. Rietveld and MEM analyses are alternately carried out until a reasonable structural model is reached [1].

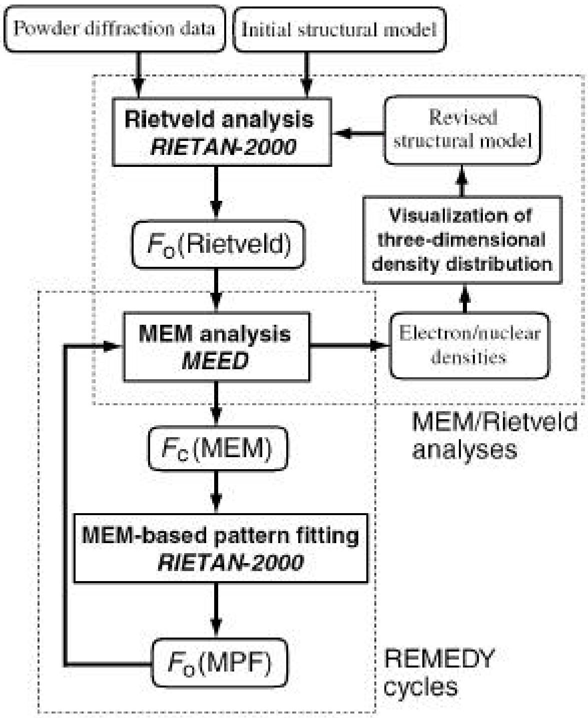

Fig 1 Structure refinement by Rietveld and MEM analyses followed by iterative pattern fitting based on MEM. A new program to visualize crystal structures and electron/nuclear densities is under development.

The undesirable bias imposed by the structural model enlarges with increasing degree of overlap of reflections and lowering resolution in a powder pattern. The MEM/Rietveld method, which certainly serves to modify imperfect structural models [1,8,9], is far from perfect for determining accurate electron/nuclear densities. Nevertheless, MEM allows us to extract structural details from the F_o(Rietveld) data because they contain contributions that have been neglected in the structural model. In addition, actually observed structure factors, F_o, can be determined for isolated reflections without any approximation.

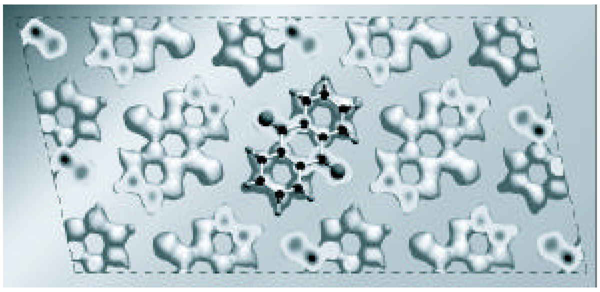

Fig 2 Electron-density image of anthraquinone viewed along $[0\bar{1}0]$ with an equi-density level of 0.7 e/Å^3 and cross sections at $y = 0$.

To minimize the bias to the structural model, MEM/Rietveld analyses are followed by iteration of MPF. MEED evaluates F_c(MEM) by the Fourier transform of electron/nuclear densities. Then, we fit the calculated pattern to the observed one by fixing structure factors at values of F_c(MEM) obtained by the previous MEM analysis and refining only parameters irrelevant to the structure. F_o(MPF) data estimated after the pattern fitting according to Rietveld's procedure [3] are analyzed again by MEM. MEM analysis and pattern fitting are alternately repeated until R factors in the pattern fitting no longer decrease. Such an iterative procedure is referred to as REMEDY cycles, as noted in Fig. 1. Repetition of MPF weakens the influence of the structural model on F_o(MPF). In other words, intensity repartitioning for overlapping reflections can become more accurate with increasing number of cycles owing to extraction of additional structural information from observed intensities of Bragg reflections.

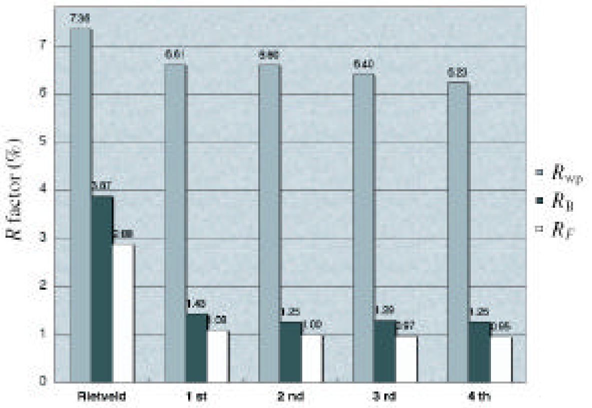

Fig 3 Changes in R factors for the final Rietveld analysis and subsequent two cycles of MPF for $Sr_{9.3}Ni_{1.2}(PO_4)_7$.

The above sophisticated methodology achieves a significant breakthrough in adequate representations of disordered atomic configurations, chemical bonds, nonlocalized electrons, and anharmonic thermal motion. Crystal structures are expressed not by structure parameters but by three-dimensional electron/nuclear densities in MPF. Therefore, the above purposes are attainable more satisfactorily by the MPF method than by the conventional Rietveld method. The establishment of this technique leads to the availability of an ultra-high-resolution 'X-ray/neutron microscope' that enables us to visualize powder diffraction data as three-dimensional density images. X-Ray and neutron diffraction can be utilized complementarily for (a) more adequate expression of chemical bonds and (b) analysis of anharmonic thermal vibration and disordered structures [10], respectively.

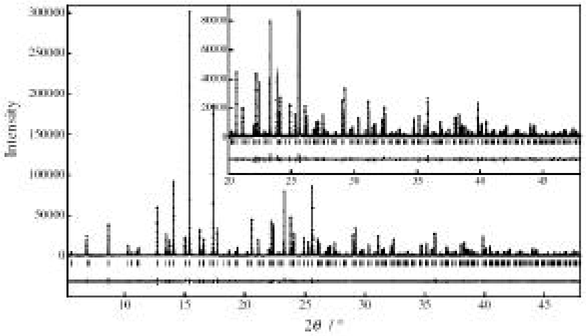

Fig 4 Observed, calculated, and difference patterns fo the last MPF for $Sr_{9.3}Ni_{1.2}(PO_4)_7$. The patterns between 20° and 48° are magnified in the inset.

The synchrotron XRD data of the three samples were measured on a powder diffractometer (beam line BL15XU at SPring-8) with the Debye-Scherrer geometry using capillary tubes rotated at a speed of 60 rpm. Incident beams from an undulator were monochromatized with inclined double-crystal monochromators of Si(111). An instrumental resolution at the top international level is attained in this diffractometer.

We expected that anisotropic thermal vibration, subtle orientational disorder, and σ and π bonds in aromatic compounds would not satisfactorily be depicted by conventional Rietveld analysis. Then, the MPF method was applied to the XRD data (l = 1.5496 Å) of anthraquinone ($C_{14}H_8O_2$, $P2_1/c$) [11] at room temperature. R_{wp}, R_B, and R_F were respectively 5.37%, 3.54%, and 7.13% in the final Rietveld refinement and 4.90%, 0.78%, and 1.33% after subsequent three REMEDY cycles. Figure 2 shows an electron-density image resulting from the final MEM analysis. C–C and C–O bonds are visible with a difference in expansion of the isosurface. H atoms bonded to C atoms in benzene rings look like mamillae.

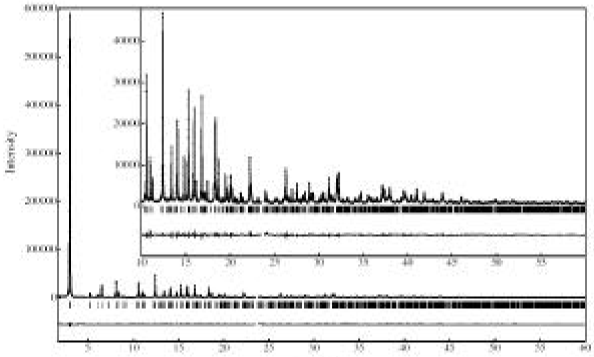

Fig 5 Observed, calculated, and difference patterns for LTL. The patterns between 10° and 60° are magnified in the inset.

XRD data of a whitlockite-like phosphate, $Sr_{9.3}Ni_{1.2}(PO_4)_7$ $(R\bar{3}m)$ [12], were taken at 100 K with a wavelength of 0.8000 Å and a Ge(111) analyzer. Most sharp profiles could be observed with FWHM ranging from 0.008° to 0.019°. In the structure of $Sr_{9.3}Ni_{1.2}(PO_4)_7$, parts of Sr^{2+} and PO_4^{3-} ions exhibit highly disordered arrangements, which cannot be well expressed by a split-atom model in its Rietveld analysis. R_{wp}, R_B, and R_F respectively decreased from 7.38%, 3.87%, and 2.88% in the final Rietveld refinement adopting a split-atom model to 6.23%, 1.25%, and 0.95% after four REMEDY cycles (Fig. 3). R_B and R_F dropped dramatically in the first cycle. A very excellent fit between observed and calculated patterns was attained in the final MPF (Fig. 4). These preliminary results reveals that the MPF method is effective even in the structure refinement using the XRD data measured with the very high resolution.

A dehydrated zeolite LTL ($K_9Al_9Si_{27}O_{72}$, $P6/mmm$) [13], is a microporous material with a disordered structure including large one-dimensional channels parallel to the c axis. Its XRD data (l = 1.2000 Å) were collected at room temperature with the Ge(111) analyzer. R_{wp}, R_B, and R_F were respectively 4.90%, 1.60%, and 1.59% in the final Rietveld refinement and 4.46%, 0.69%, and 0.84% after two cycles of MPF. Figure 5 shows the final profile fit to be excellent. An electron-density image (Fig. 6) clearly displays a framework consisting of highly covalent (Si,Al)–O bonds. We also found that electron-density distribution around K^+ ions incorporated in the framework is not spherical but anisotropic.

The number of REMEDY cycles required for convergence generally increases with lowering resolution in a diffraction pattern because observed intensities of Bragg reflections are repartitioned with F_c(MEM) calculated from F_o(Rietveld) or F_o(MPF). Even with high-resolution synchrotron XRD data, at least one cycle of MPF proved to be indispensable for the determination of more accurate electron densities. In MPF, parameters other than structure parameters are refined, and partition of observed intensities is successively improved because of the use of F_c(MEM). The MPF method is, hence, so much superior to the MEM/Rietveld method, in which the analytical method in the Fourier synthesis of F_o(Rietveld) data is merely replaced with MEM [1].

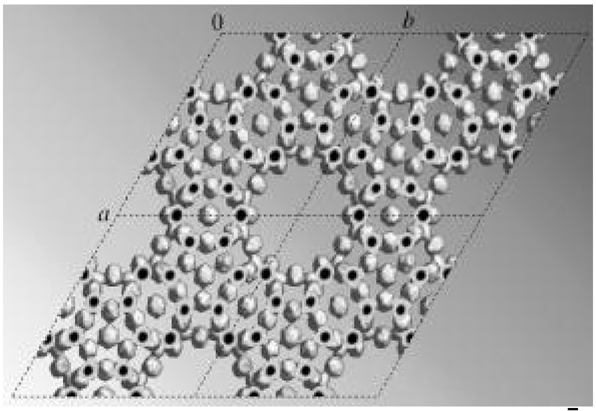

Fig 6 Electron-density image of LTL viewed along [00$\bar{1}$] with an equi-density level of 0.5 e/Å^3 and cross sections at z = 0.

From the significant results presented above for the three compounds, we conclude MPF to be a powerful method of structure refinement where imperfect structural representations in conventional Rietveld analysis are supplemented with model-free MEM.

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Anisotropic Peak Broadening in High Resolution Data on RbC$_{60}$.

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Anyone familiar with Rietveld refinements knows that the method depends on having an accurate model for the powder diffraction profile. We wish to present a brief story about data that created some disappointment when it looked like the sample contained serious impurities, but that was eventually resolved once we recognized that we needed a lineshape model that was as good as the data. Instruments with better resolution are becoming more widely used: synchrotron radiation sources, high resolution diffractometers at pulsed neutron facilities, and parallel-beam optics in the laboratories of individual researchers. Data with improved resolution and counting statistics generally reveal more information about the sample. This is not always welcome because it demands that the user think about (or at least model) aspects of the experiment that may seem secondary to finding out where the atoms are.

The one-dimensionally polymerized fullerenes AC$_{60}$ (A = K, Rb, Cs) are interesting and incompletely understood. All three are thermodynamically stable at room temperature and below, and have a structure consisting of chains of fullerenes linked by [2+2] cycloaddition, but there are significant differences both in their structures and in their physical properties. This observation cries out for clarification from structural studies. They were thought to be isostructural (orthorhombic) when first discovered, but the fact that RbC$_{60}$ is monoclinic was later discovered independently by Lanois *et al.* [1] and by us [2]. The real importance of our high resolution structure solution lies in the fact that it is the first analysis of a fulleride with lower than cubic symmetry in which the position of every atom is measured. Substantial deformations from icosahedral symmetry are observed throughout the buckyball. Indeed, there is an overlap of the distances seen in nominally single and double sp^2 bonds. The interested reader is referred to our full results in Reference 2; we only remark here that it requires a very high quality refinement to have confidence in such unexpected results.

When we first collected data in 1998 on approximately 1 gm of material at the High Resolution Powder Diffractometer of the ISIS pulsed neutron source, it was obvious that the orthorhombic cell would not work, and we quickly found that a monoclinic lattice distortion of only 0.3° was required to fit the data. We quickly found a good starting structure, but when we got home and worked to refine it, there were several strong, sharp peaks that appeared in the difference plot (Fig. 1a). Did our carefully prepared sample contain impurities? Scouring the databases, we found some Rb oxides, hydroxides, etc., with some d-spacings close to our peaks, but no positive

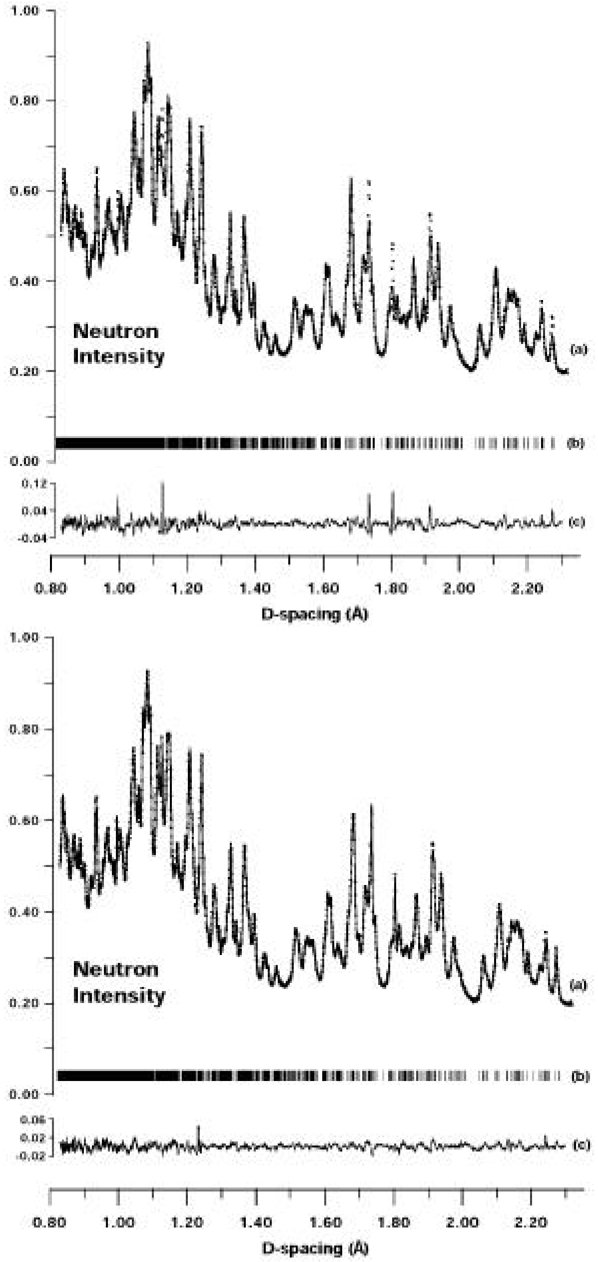

Fig 1 Rietveld refinements of data on RbC_{60} at 200K, taken at the time-of-flight neutron diffractometer HRPD at ISIS. (top panel): Fit using standard Rietveld lineshape method, with Gaussian and Lorentzian widths a smooth (parameterized) function of reflection spacing *d*. This fit has. (bottom panel): Fit with anisotropic broadening model from Ref. 3; $R_{wp} = 1.48\%$, $\chi^2 = 4.33$.

identification. It's painful to recall the efforts we made to find out what new phase was in our sample, and how many old samples we rechecked with x-rays and found to be significantly contaminated by the same phase. This had no peaks observable in the raw data, and only overlapped with measurable RbC_{60} data. The last straw was the discovery that the impurity phase disappeared when we heated a test sample to 200°C, where the fulleride transforms into a cubic rock-salt structure. Actually, we probably should have noticed earlier that all of the peaks in the difference curve actually coincided with allowed diffraction peaks from the polymeric fulleride structure, and indeed that they are reflections on or very close to the polymeric chain axis.

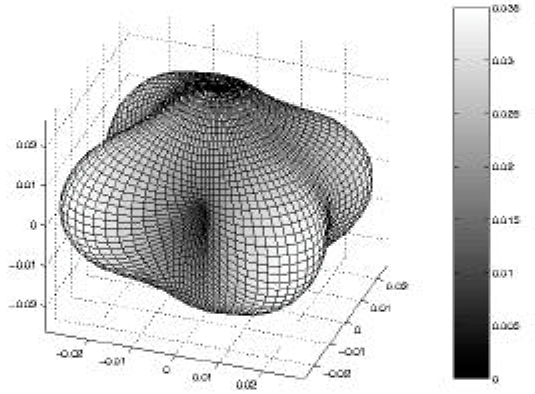

Fig 2 Distribution of strain broadening, $\delta d/d$, from the anisotropically broadened lineshape model in the Rietveld refinement of RbC_{60} discussed in the text.

So if these extra-sharp peaks are intrinsic to the structure, we need to ask two questions: Why? What can be done about it? Tackling the second one first, we should remember that the premise of Rietveld refinement is to parameterize the diffraction lineshape in some meaningful way, so that the data can help to do an optimal job of assigning the intensity at a given observed point in the spectrum to the appropriate Bragg reflections. If the peaks widths do not follow a smooth dependence on *d*-spacing, that can be modeled just like any other set of refineable parameters. There have been numerous observations of the problem, and attempts to deal with it. However, it is important that any such phenomenological account of lineshape broadening should respect the symmetry of the problem, *e.g.*, so that peaks with symmetry equivalent Miller indices should have the same width. Several authors, including one of us (PWS) had previously shown that certain kinds of anisotropic strain broadening can be described by a model incorporating quartic combinations of Miller indices [3]. This was originally justified as the most general joint distribution of lattice metric parameters, but has been more recently tied to distributions of elastic strains caused by defects, at least for cubic and hexagonal systems, and can be used to determine density and arrangement of dislocations [4].

A Rietveld refinement with the nine anisotropic broadening coefficients is shown in Fig. 1b. Clearly, the model has taken care of the family of extraordinarily sharp peaks that were so upsetting in Fig. 1a. It is interesting to look at the microstrain distribution that results from this refinement. That is illustrated in Fig. 2, which shows the width of the distribution in microstrain, $\delta d/d$, as a function of direction in reciprocal space. The cusp facing the viewer is in the direction of the monoclinic *b* axis, which is the chain axis. This agrees with intuition that the structure should be most rigid along the chains of covalently linked buckyballs, and would have more flexibility in other directions, where the bonding is van der Waals. We emphasize that the parameters all have a physical meaning (albeit somewhat obscure), compatible with the structural symmetry of the material. This is not the case with other approaches, which, *e.g.*, model microstrain as an ellipsoidal function of direction of the Bragg diffraction direction relative to the crystalline translation axes.

In this example, we have seen that a reassessment of the diffraction lineshape led to a qualitative change in the evaluation of the experiment: there is nothing wrong with the sample and the result is a valid solution of the structure. However there is also a less dramatic, but quantitatively important improvement in the quality of the refined parameters. The statistical esd's are smaller, generally by a factor of two, with the anisotropic lineshape model. One expects this because χ^2 is smaller by a factor of about four, due to the improved fit. But we also see that the refined bond lengths shift, typically by twice the esd from the Rietveld of the isotropic lineshape model. That shift is probably significant, and is a real benefit of the improved fit. More broadly, we would like to point out that about half of the samples that we have recently investigated by high resolution powder diffracometry have shown significant anisotropic strain broadening.

Clearly it is imporant to include this effect in any analysis of high resolution data. Currently, it is implemented and documented in only one Rietveld program, GSAS.

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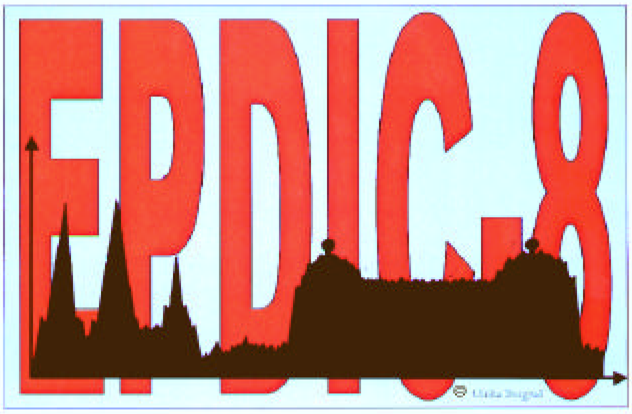

Recent developments of the program FULLPROF

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In these notes some of the most recent developments of the program *FullProf* are presented. After an introduction summarizing the most important changes we present, in more detail, few examples selected among those of more usefulness for a majority of people: a) the introduction of special form factors for treating nearly free rotating molecules, b) the use of the simulated annealing procedure for solving crystal and magnetic structures and c) the new features related to microstructural effects. The notes finish enumerating some of the projects already in course that will be publicly available soon in 2002.

```
F m 3 m                  <--Space group symbol
!Atom Typ       X         Y         Z      Biso      Occ      In Fin N_t Spc/Codes
C    SASH    0.00000  0.00000  0.1.49934  1.00000   0   0   4   0
                0.00      0.00      0.00    21.00     0.00
! Form-factor refinable parameters
!      f1      f2         f3        f4        f5      f6        f7
    3.53862 60.00000  1.00000 -0.01809  0.01335  0.00453  0.02742
      31.00     0.00      0.00     41.00    51.00    61.00    71.00
!      f8      f9         f10       f11       f12     f13       f14
   -0.01328  0.00617 -0.00220  0.02042  0.00000  0.00000  0.00000
      81.00    91.00   101.00   111.00     0.00     0.00     0.00
klj   9
    0  1    6  1   10  1   12  1   12  2   16  1   16  2   18  1   18  2
```

Fig 1: Piece of PCR file adapted for the refinement of a diffraction pattern containing C_{60} in its nearly free rotator phase.

INTRODUCTION

From the first half of 1998 profound changes have been introduced in the source code of *FullProf*. The most important was the complete transformation of the source code to the new standard Fortran 95, using the new syntax and features (suppression of COMMON statements, introduction of modules, interfaces, types, etc) [1]. This process is being continued in order to make the whole program based in a library of Fortran 95 crystallographic modules [2]. The Fourier program *GFourier* [3] is also based in this library. The new architecture of the program makes it possible to introduce new changes in a very easy way.

During the last two years the development of the program *FullProf* has continued also by improving its user friendly interface (*WinPLOTR* for Windows) and including more options. In particular dynamic allocation has been introduced in order to fit the available memory to the size of the problem to be treated. An optimization mode has also been introduced in order to speed up the calculations in simple cases.

Some examples of useful changes made on the code of *FullProf* are the following:

1. The old code generating symmetry operators from the Hermann- Mauguin symbols and the code generating reflections has been totally removed. Everything has been substituted by Fortran 95 modules able to interpret both Hermann- Mauguin and Hall symbols or generate the full space group from a small set of user-given generators [2]. These modules provide better crystallographic information to the user of the program. In particular automatic calculation of the multiplicity of each site is now performed after reading the atoms as well as the calculation of the appropriate coefficients for automatic quantitative analysis of mixture of phases.
2. The calculation of distances and angles, as well as bond valence sums can now be done automatically, without using external programs. Output files with extension *dis* contain all the relevant information for the different phases if the user is asking for this option. A byproduct of these calculations is the generation of the output files of names *dconstr*"n".*hlp* (n stands for the number of the phase) containing lines that can be directly pasted to PCR files for soft constraints on distances and angles. This makes the use of distance and angle constraints extremely easy in appropriate cases.
3. Another important modification is the handling of refinement codes. Now the user may select between the traditional mode changing by hand the numbering of codewords controlling the refinement or select the *automatic* mode. If the automatic mode is selected, a code of the type "1.00" means that the corresponding parameter should be refined. The user may combine the manual mode with the automatic mode for making the desired constraints. The program automatically renumber the codes, suppress the holes in the matrix and takes care of user-defined constraints.

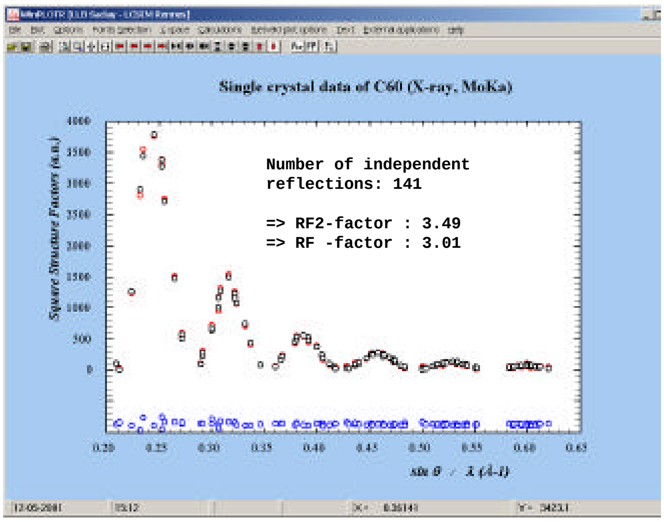


Fig 2: Plot of the observed (red) versus calculated (black) square structure factors in a region of sinθ/λ, after refining the C60 molecule using a SASH form factor.

4. A new mode for refining magnetic structures has also been included. The free parameters are then the coefficients of the basis functions of the irreducible representations of the propagation vector group. This mode can also be used with the simulated annealing optimization.
5. New functions for refinement of the background have been included. In particular the height of the linear interpolated background points that was fixed in previous versions of the program can now be refined.

Other improvements concerning special form-factors, simulated annealing and microstructural effect are discussed below in more detail.

SPECIAL FORM-FACTORS

Several types of special form factors are included in *FullProf,* among them the Symmetry Adapted Spherical Harmonics (SASH) as special form-factors are now fully implemented. The case of C_{60} is provided as an example using cubic harmonics in Figure 1.

The program knows that the user is giving a special form-factor by putting the value N_t=4 in the same line of giving the chemical species, the keyword of the form-factor and the fractional coordinates. The user must provide the type of SASH to be used (real spherical harmonics or cubic harmonics) using a particular label. In the case of C_{60} the label klj instructs the program for using cubic harmonics. The number of terms (9 in the present case) and the indices (list of pairs of integers in the line following klj) of the harmonics to be used according to the symmetry of both the site and the molecule.

```
Para-di-Iodo-Benzene (Sim.Annealing)
!
!Nat Dis Ang Pr1 Pr2 Pr3 Jbt Irf Isy Str Furth      ATZ    Nvk Npr More
   6   0   0 1.0 0.0 0.0   4   4   0   0   0         0.00   0   0   0
!
P b c a                 <--Space group symbol
!Atom Typ       x         y         z         B        Occ       P6     THETA      PHI  Spc
!      d      theta      phi        X0        Y0        Z0       CHI    P16:SAT
Pi1  I       0.17439  0.04548 -0.30989  0.00000  1.00000  1.00000  2.05548  0.06590  0
                0.00      0.00      0.00      0.00      0.00      0.00    11.00    21.00
    3.50000 -0.09100 -0.09100  0.00000  0.00000  0.00000 -2.62905  0.00000
       0.00      0.00      0.00      0.00      0.00      0.00    31.00
Pi2  C       0.06946  0.01811 -0.12342  0.00000  1.00000                                 0
                0.00      0.00      0.00      0.00      0.00
    1.39400 -0.09100 -0.09100
       0.00      0.00      0.00
. . . . . . . . . . . . . . . . . . .

! Limits for selected parameters (+ steps & BoundCond for SA):
   1      0.0000      3.1416      0.5000   1     Theta
   2     -3.1416      3.1416      0.5000   1       Phi
   3     -3.1416      3.1416      0.5000   1       Chi
! T_ini   Anneal  Accept NumTemps NumThCyc InitConf
   8.000   0.900   0.020       80        0        0
! NCyclM   Nsolu Num_Ref Nscalef  NAlgor
     200       1      71       1       1
```

Fig 3: Part of a PCR file showing the use of the simulated anneling method to determine the orientation of the molecule of $I_2C_6D_4$. The center of the molecule is at the origin and only three angles are needed to fix the position of the molecule in the unit cell.

The form-factor SASH is well adapted to nearly free molecular rotations. For a molecule with N atoms rotating around its center of mass (supposed to be in a particular crystallographic site)the molecular form factor is given by:

Where the index *s* runs from 1 to N and corresponds to N spherical shells. $j_l(x)$ is the spherical

Bessel function of order *l*. $K_{lj}(q,j)$ and $y_{lmp}(q,j)$ and are the cubic harmonics and the real spherical harmonics, respectively, as defined in [4]. b_s is the scattering length (or X-ray scattering factor). The angles used as arguments in the above expressions correspond to the spherical coordinates of the scattering vector ***Q*** with respect to a local Cartesian frame that may be the same or different as the default Cartesian frame connected with the crystallographic unit cell. In the last case a transformation matrix should be given.

The coefficients c^s_{lj} and c^s_{lmp} are free parameters. In *FullProf* the form-factor corresponds to just *one shell* (a particular value of *s*). For a complete molecule the user must provide a number of SASH objects equal to the number of spherical shells characterizing the molecule. The first parameter in the list (**f1, f2, f3, …**) corresponds to the value of the spherical shell radius: **f1**=r_s, the second parameter is the number of atoms of the chemical species given by the chemical symbol, within the spherical shell.

The coefficients (**f3, f4, f5, …f14**) correspond to the free parameters c^s_{lj} or c^s_{lmp} of the current shell in the order specified by the list. The first coefficient **f3** corresponds to the free rotator term $l = m = 0$ (or $l = j = 0$) and should, normally, be fixed to 1. The user must provide the list (*l, m, p*), or (*l, j*), in ascending order on *l* according to the local site symmetry. See Table 2 in the above reference.

Another form-factor that may be quite useful is the form-factor called: ANOM. It may be used to let refine the anomalous dispersion correction of the scattering factor of an atom showing a strong anomalous scattering. The format is similar to the general case of a special form-factor, the chemical symbol must be used as label of the atom, the real and imaginary components of the dispersion correction are stored in **f1** and **f2**.

SIMULATED ANNEALING

An option for helping to solve crystal and/or magnetic structures has been included. This is a simulated annealing module able to handle two types of algorithms: fixed and variable steps for generating new configurations. The simulated annealing technique works, at present, only with integrated intensities. A short report about the technique and the implementation in *FullProf* may be found in reference [5], here we show just some examples of using the method .

To solve a crystal or a magnetic structure a complete list of atoms with all their attributes (thermal parameters, magnetic moments, etc) should be given as if everything were known. An example of simulating annealing PCR file is given in Figure 3.

The use of codewords is totally supported so that any usual constraint may be used in the search. Of course the initial values of the parameters are arbitrary provided the hard constraints through the codewords are respected. In fact the meaning of the codewords is the same as in least square refinements, the multipliers and signs are applied to the *shifts* with respect to the previous values of the parameters. The scale factor may be treated automatically so that no codeword should be given to this parameter.

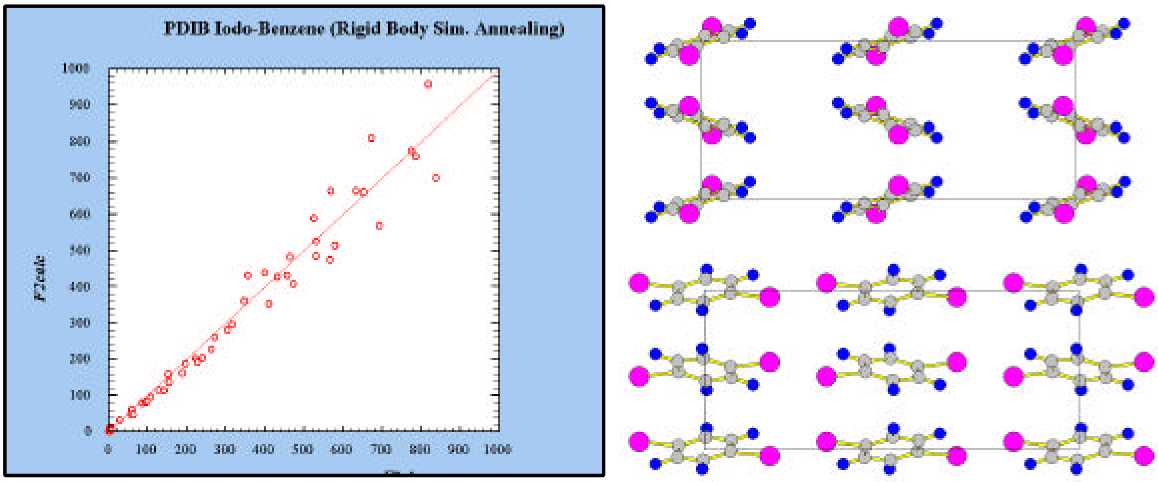
The program recognizes the use of simulated annealing by putting NRELL equal to the number of parameters to be eventually varied, and ICRYG=3 in the beginning of the PCR file (see appendix of the manual for details).

In the example above the three angles (in radians) defining the orientation of the molecule are selected as parameters 1, 2 and 3. The admissible range of values are given in a list followed by an indicator telling to the program how to treat the boundaries. The number “1” following the value of the initial step (0.5 radians) indicates that periodic boundary conditions are applied.

The flag **InitConf** is important for selecting the treatment of the initial configuration. If **InitConf** = 0 the initial configuration is totally random. If **InitConf** =1, the initial configuration is the one given by the values of the parameters in the PCR-file. This last option is useful when one tries to optimize an already good starting configuration, by controlling the box limits and the steps.

The other critical point is to select between the two algorithms. This is controlled by the value of the variable **Nalgor.** If its value is zero, the Corana algorithm is selected. This algorithm does not use fixed steps for moving the parameters defining the configuration, instead the program starts by using then whole admissible interval as initial step for all parameters and then adapt progressively their values in order to maintain an approximate rate of accepted configurations between 40% and 60%. If **Nalgor** =1 the same algorithm is used but the starting steps are those given in the file. For **Nalgor** =2, the normal SA algorithm (fixed steps) is used. The last method, used with appropriate boundary box for parameters and **InitConf** =1, is better when one tries to *refine* a configuration without destroying the starting configuration.

```
=> **** SIMULATED ANNEALING SEARCH FOR STARTING CONFIGURATION ****
=> Initial configuration cost:    77.53
=> Initial configuration state vector:
=>      Theta      Phi      Chi
=>          1        2        3
=>     1.3807   2.4672  -3.0110
=> NT:  1 Temp:  8.00 (%Acc): 23.50  <Step>:  5.2360  <R-factor>: 44.4302
. . . . . . .
=> NT:  6 Temp:  4.72 (%Acc): 30.50  <Step>:  0.3496  <R-factor>: 23.8774
. . . . . . . .
=> NT: 11 Temp:  2.79 (%Acc): 39.33  <Step>:  0.1440  <R-factor>: 13.4990
. . . . . . . .
=> NT: 21 Temp:  0.97 (%Acc): 38.50  <Step>:  0.0530  <R-factor>:  6.3417
. . . . . . . .
=> NT: 33 Temp:  0.27 (%Acc): 36.17  <Step>:  0.0179  <R-factor>:  4.3854
```



```
=>BEST CONFIGURATIONS FOUND BY Simulated Annealing FOR PHASE:        1
=> -> Configuration parameters (    71 reflections):
=> Sol#: 1 RF2=   3.928 ::
=>      Theta      Phi      Chi
=>          1        2        3
=>     0.9401   0.1464   2.7477
=>              CPU Time:    25.177 seconds
                                  ⇨      0.420 minutes
                                  ⇨
```

Fig 4: Simplified screen capture of the *FullProf* output when running in the simulating annealing mode for the example of figure 3. The first picture of the structure corresponds to the starting configuration. The final result is also displayed.

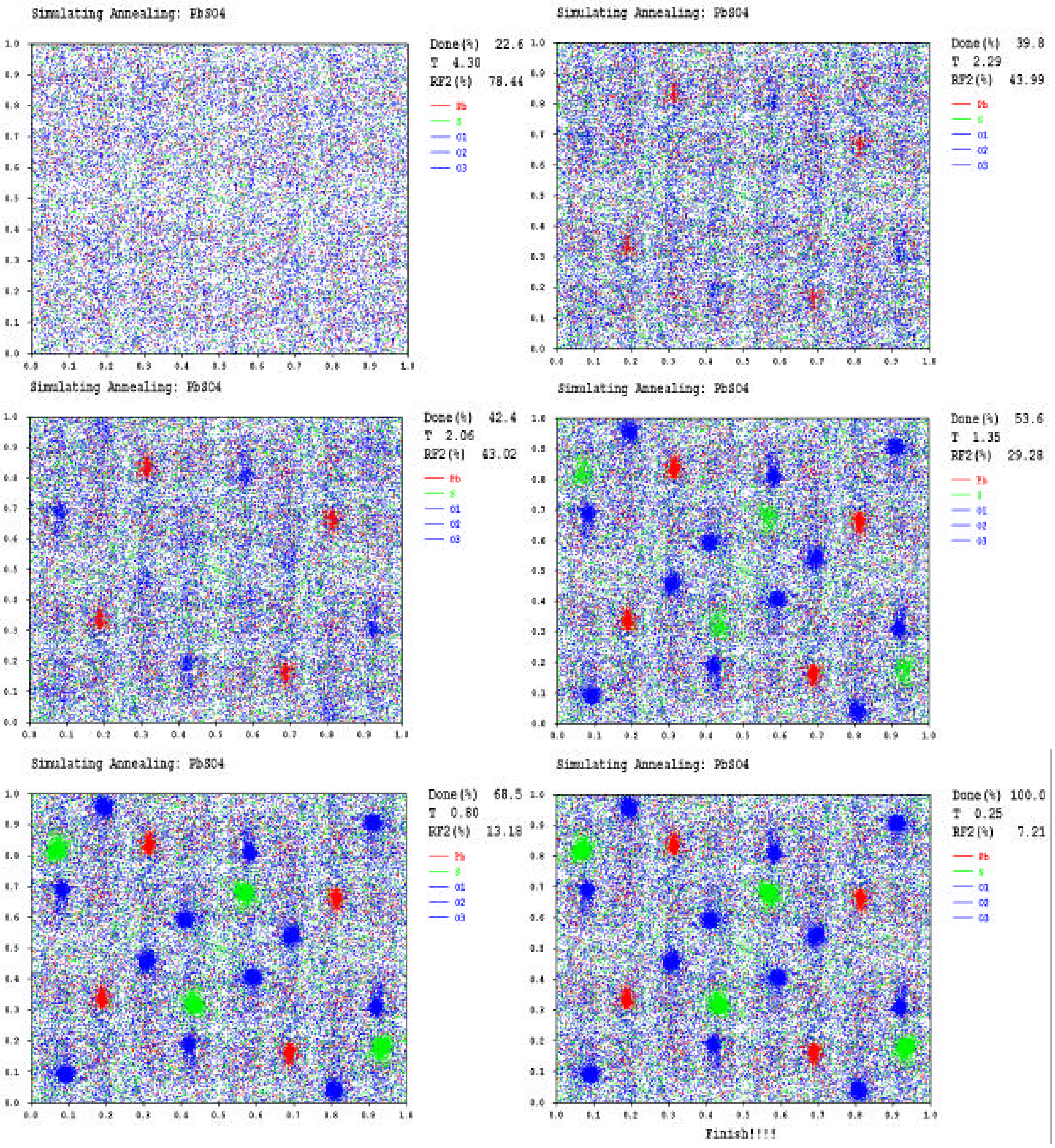


Fig 5: Different stages of the trajectories of configurations (projections in the *ab* plane) in a simulated annealing run for the determination of the structure of $PbSO_4$ from neutron powder diffraction data using overlapped integrated intensities. Lead atoms (*b*= 0.94) are found first (at 40% of the total run time), oxygen atoms (*b*= 0.58) in a second stage and finally (at about 54%) the sulphur atoms (*b*= 0.285) start to remain into their oxygen tetrahedra.

Within the distribution of *FullProf* there is a simple example of simulating annealing work using neutron diffraction data from D1A on lead sulfate $PbSO_4$. In this example the atoms are treated independently using the correct space group and an artificial constraint is used: several atoms are constrained to have the same *y* fractional coordinate. We know that all these atoms are in a special position of the *Pnma* space group (*y* should be ¼ or ¾), but the file is prepared in such a way as to illustrate the use of constraints. Starting from a random configuration for all the free parameters (including the special *y*'s) the program finds progressively the good atom positions when the appropriate values of the control parameters are used (see figure 5).

The user should experiment for each own case in order to select good control parameters. For instance the appropriate starting temperature depends strongly on the number of free parameters, the step sizes and the constraints. For solving a structure (crystallographic or magnetic) from the scratch it is important to select a temperature for which the percentage of accepted configurations is high (or the order of 80%) in order to let the procedure explore a large set of configurations. The Rietveld refinement cycles together with Fourier synthesis. For using the *GFourier* program [3], distributed in the same site that *FullProf* , it is important to use the value **Jfou**=4 in the PCR-file, to output an appropriate set of structure factors and an input file (extension *inp*) for *GFourier*.

MICROSTRUCTURAL EFFECTS

The microstructural effects within *FullProf* are treated using the Voigt approximation: both instrumental and sample intrinsic profile are supposed to be described approximately by a convolution of Lorentzian and Gaussian components. The TCH pseudo-Voigt profile function [6] is used to mimic the exact Voigt function and it includes the Finger‘s treatment of the axial divergence [7]. The integral breadth method to obtain volume averages of sizes and strains is used to output a microstructural file where an analysis of the size and strain contribution to each reflection is written. No physical interpretation is given by the program, only a phenomenological treatment of line broadening in terms of coherent domain size and strains due to structural defects is performed. The user should consult the existing broad literature to go further in the interpretation of the results. A recent book [8], gathering different articles, is a good introduction to microstructural problems.

The new file containing information about the microstructure is output only if the user provides an input file containing the instrumental resolution function (IRF, see manual for the different ways of giving resolution parameters). At present, this option works only for constant wavelength mode.

The FWHM of the Gaussian (H_G) and Lorentzian (H_L) components of the peak profile have an angular dependence given by:

$$H_G^2 = (U + (1-x)^2 D_{ST}^2(\mathbf{a}_D)) \tan^2 q + V \tan q + W + \frac{I_G}{\cos^2 q}$$

$$H_L = (X + x D_{ST}(\mathbf{a}_D)) \tan q + \frac{[Y + F(\mathbf{a}_Z)]}{\cos q}$$

If the user provides a file with the IRF, the user should fix V and W to zero, then the rest of parameters in the above formula have a meaning in terms of strains ($U, \mathbf{a}_D, X$) or size ($Y, I_G, \mathbf{a}_Z$).

The functions $D_{ST}(\mathbf{a}_D)$ and $F(\mathbf{a}_Z)$ have different expressions depending on the particular model used of strain and size contribution to broadening. The parameter x is a mixing coefficient to mimic Lorentzian contribution to strains.

The anisotropic strain broadening is modeled using a quartic form in reciprocal space. This correspond to an interpretation of the strains as due to static fluctuations and correlations between metric parameters [9].

$$M_{hkl} = \frac{1}{d_{hkl}^2} = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk = M\left(a_i; hkl\right)$$

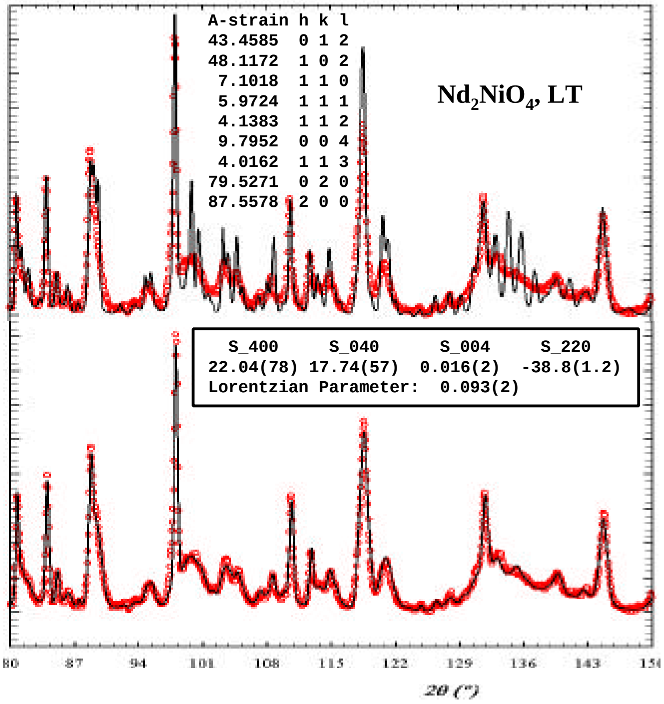
The metric parameters a_i (direct, reciprocal or any combination) are considered as stochastic variables with a correlations between metric parameters [9].

$$M_{hkl} = \frac{1}{d_{hkl}^2} = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk = M\left(a_i; hkl\right)$$

The metric parameters a_i (direct, reciprocal or any combination) are considered as stochastic variables with a Gaussian distribution characterized by the mean $\langle a_i \rangle$ and the variance-covariance matrix C_{ij}. Here we consider the set: $\{a_i\} = \{A, B, C, D, E, F\}$.The position of the peaks is obtained from the average value of M_{hkl} given by: $\langle M_{hkl} \rangle = M\left(\langle a_i \rangle; hkl\right)$. The broadening of the reflections is governed by the variance of M_{hkl}:

$$s^2\left(M_{hkl}\right) = \sum_{i,j} C_{ij} \frac{\partial M}{\partial a_i} \frac{\partial M}{\partial a_j} = \left(h^2 \quad k^2 \quad l^2 \quad kl \quad hl \quad hk\right) \begin{pmatrix} S_A^2 & C_{AB} & C_{AC} & C_{AD} & C_{AE} & C_{AF} \\ C_{AB} & S_B^2 & C_{BC} & C_{BD} & C_{BE} & C_{BF} \\ C_{AC} & C_{BC} & S_C^2 & C_{CD} & C_{CE} & C_{CF} \\ C_{AD} & C_{BD} & C_{CD} & S_D^2 & C_{DE} & C_{DF} \\ C_{AE} & C_{BE} & C_{CE} & C_{DE} & S_E^2 & C_{EF} \\ C_{AF} & C_{BF} & C_{CF} & C_{DF} & C_{EF} & S_F^2 \end{pmatrix} \begin{pmatrix} h^2 \\ k^2 \\ l^2 \\ kl \\ hl \\ hk \end{pmatrix}$$

where the non diagonal terms may be written as product of standard deviations multiplied by correlation terms: $C_{ij} = S_i S_j corr(i, j)$. This original formulation can be used with a total control of the correlation terms that must belong to the interval [-1, 1].



```
A-strain h k l
43.4585  0 1 2
48.1172  1 0 2
 7.1018  1 1 0
 5.9724  1 1 1
 4.1383  1 1 2
 9.7952  0 0 4
 4.0162  1 1 3
79.5271  0 2 0
87.5578  2 0 0
```

```
   S_400      S_040      S_004      S_220
22.04(78) 17.74(57)  0.016(2)  -38.8(1.2)
Lorentzian Parameter:  0.093(2)
```

Fig 6: High angle part of the neutron powder diffraction pattern (D2B, ILL) of the low temperature phase of Nd$_2$NiO$_4$ [11]. (top) Comparison of the observed pattern with the calculated pattern using the resolution function of the diffractometer. (bottom) Observed and calculated pattern using an anisotropic model of strains with non-null values given in the panel. A list of apparent strains (x 10^{-4}), extracted from the microstructure file, for a selected number of reflections is also given.

When using this formulation the user cannot refine all parameters (up to 21) because some of them contributes to the same term in the quartic form in reciprocal space, however this allows a better interpretation of the final results. Taking the appropriate caution one can test different degrees of correlation between metric parameters. There are several special formulations, within *FullProf*, for working with direct cell parameters instead of using reciprocal parameters.

Another formulation and a useful notation corresponding to a grouping of terms was proposed by Stephens [10] who also included a phenomenological Lorentzian contribution to the microstrains (the parameter x). The final grouping of terms simplifies to:

$$s^2(M_{hkl}) = \begin{pmatrix} h^2 & k^2 & l^2 & kl & hl & hk \end{pmatrix} [C] \begin{pmatrix} h^2 \\ k^2 \\ l^2 \\ kl \\ hl \\ hk \end{pmatrix} = \sum_{\substack{HKL \\ \{H+K+L=4\}}} S_{HKL} h^H k^K l^L$$

The Stephens' notation can also be used within *FullProf*. A maximum of 15 parameters can be refined for the triclinic case. Whatever the model used for microstrains the mixing Lorentzian parameter, x , may be used. In *FullProf* the function $D^2_{ST}(\mathbf{a}_D)$, being $\mathbf{a}_D$ the set of parameters C_{ij} or S_{HKL} , is given by:

$$D^2_{ST}(\mathbf{a}_D) = 10^{-8}\ 8\mathrm{Ln}2 \left(\frac{180}{p}\right)^2 \frac{s^2(M_{hkl})}{M^2_{hkl}}$$

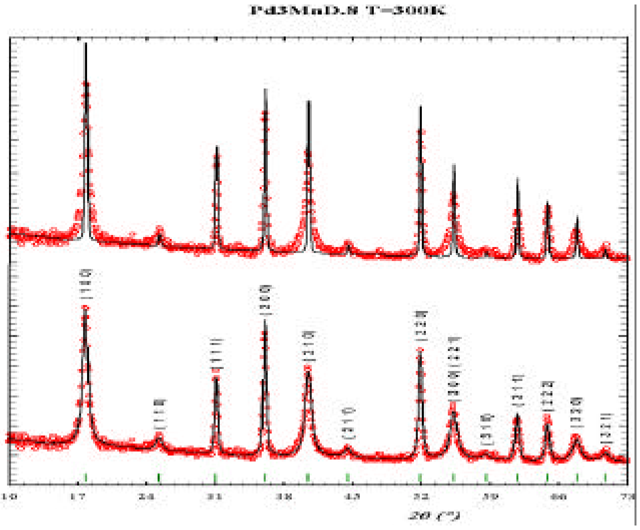


Fig 7: Portion of the neutron diffraction pattern of $Pd_3MnD_{0.8}$ at room temperature obtained on 3T2 (LLB, λ = 1.22 Å). On top, the comparison with the calculated profile using the resolution function of the instrument. Below fit using `IsizeModel`=-14. Notice that only the reflections with indices of different parity are strongly broadened. An isotropic strain, due to the disorder of deuterium atoms, is also included for all kind of reflections.

An example of anisotropic strain refined using this formulation is shown in Figure 6, where the neutron diffraction pattern of the low temperature phase of Nd_2NiO_4 is refined using the diffractometer D2B at ILL [11].

Concerning anisotropic size broadening it is possible to use a very general phenomenological model, using the Scherrer formula, that considers the size broadening can be written as a linear combination of spherical harmonics (SPH). At present the anisotropic size is supposed to contribute to the Lorentzian component of the total Voigt function. A Gaussian contribution will be introduced using a mixing parameter similar to that used for anisotropic strain. The explicit formula for the SPH treatment of size broadening is the following:

$$b_{\mathbf{h}} = \frac{l}{D_{\mathbf{h}} \cos q} = \frac{l}{\cos q} \sum_{lmp} a_{lmp} y_{lmp}(\Theta_{\mathbf{h}}, \Phi_{\mathbf{h}})$$

where $b_{\mathbf{h}}$ is the size contribution to the integral breadth of reflection **h**, $y_{lmp}(\Theta_{\mathbf{h}}, \Phi_{\mathbf{h}})$ are the real spherical harmonics with normalization as in [12]. The arguments are the polar angles of the vector **h** with respect to the Cartesian crystallographic frame. After refinement of the coefficients a_{lmp} the program calculates the apparent size (in angstroms) along each reciprocal lattice vectors if the IRF is provided in a separate file.

An important type of defects that give rise to size-like peak broadening is the presence of anti-phase domains and stacking faults. These defects produce selective peak broadening that cannot be accounted using a small number of coefficients in a SPH expansion. In fact only a family of reflections verifying particular rules suffers from broadening. For such cases there is a number of size models built into *FullProf* corresponding to particular sets of reflections that are affected from broadening. In figure 7 it is represented the case of $Pd_3MnD_{0.8}$ [13] of structure similar to Au_3Mn and showing the same kind of defects: anti-phase domains [14]. In figure 8 a portion of the final microstructural file is shown.

Other models for size broadening in *FullProf* following particular rules for each (*hkl*) are available. Moreover an anisotropic size broadening modeled with a quadratic form in reciprocal space is also available. The expression presently used in *FullProf* is the following:

$$F(\mathbf{a}_Z) = \mathrm{k_s}\ \mathrm{d}^2\ \left(a_1 h^2 + a_2 k^2 + a_3 l^2 + a_4 kl + a_5 hl + a_6 hk\right)$$

where k_s is defined as $k_s = 360/\pi^2 \times \lambda\ 10^{-3}$ for the 2θ space and $k_s = 2/\pi \times$ **Dtt1** 10^{-3} for TOF and Energy space. Simple crystallite shapes as infinite platelets and needles (**IsizeModel** = 1, -1 respectively) are also available.

Together with the size broadening models built into *FullProf* and described above, there is another way of fitting independent size-like parameters for different sets of reflections. The user may introduce his(her) own rule to be satisfied by the indices of reflections provided the rule can be written as a linear equality of the form: $n_1 h + n_2 k + n_3 l = n_4\, n + n_5$. Where n is an arbitrary integer and $n_i (i = 1,2,\ldots 5)$ are integers given by the user. A size parameter is associated to each rule (a maximum of nine rules may be given per phase) that may be refined freely or constrained using the codewords appropriately.

To access this option in *FullProf* the value of **IsizeModel** should be in the interval [-2,-9]. The absolute value of **IsizeModel** corresponds to the number of rules (independent parameters) to be given. If all n_i=0 the rule is

```
!  MICRO-STRUCTURAL ANALYSIS FROM FULLPROF (still under development!)
!  ================================================================
!  Pattern No:  1 Phase No:   1 Pd3MnD.8 - CFC
... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ...
!  Integral breadths are given in reciprocal lattice units (1/angstroms)x 1000
!  Apparent sizes are given in the same units as lambda (angstroms) …
!  Apparent strains are given in %% (x 10000) (Strain= 1/2 * beta * d)
!  An apparent size equal to 99999 means no size broadening
!  The following items are output:
... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ... ...
! The apparent sizes/strains are calculated for each reflection using the formula:
!
!  App-size (Angstroms) =  1/(Beta-size)
!  App-strain (%%) =  1/2 (Beta-strain) * d(hkl)
!
!  (Beta-size) is obtained from the size parameters contributing to the FWHM:
!          FWHM^2 (G-size) = Hgz^2 = IG/cos^2(theta)
!          FWHM   (L-size) = Hlz   = ( Y + F(Sz))/cos(theta)
!(Beta-strain) is obtained from the strain parameters contributing to the FWHM:
!          FWHM^2 (G-strain) = Hgs^2 =   = (U+[(1-z)DST]^2) tan^2(theta)
!          FWHM   (L-strain) = Hls   = (X+ z DST) tan(theta)
!
!   In both cases (H,eta) are calculated from TCH formula and then
!   Beta-pV is calculated from:
!
!            beta-pV= 0.5*H/( eta/pi+(1.0-eta)/sqrt(pi/Ln2))
!
!  The standard deviations appearing in the global average apparent size and
!  strain is calculated using the different reciprocal lattice directions.
!  It is a measure of the degree of anisotropy, not of the estimated error
 ...   betaG     betaL ...  App-size App-strain    h     k     l     twtet ...
 ...  1.4817   11.5859 ...     93.58   41.6395     1     0     0   17.7931 ...
 ...  2.0954   11.9584 ...     93.58   41.6395     1     1     0   25.2665 ...
 ...  2.5664    1.5573 ...  99999.00   41.6395     1     1     1   31.0743 ...
 ...  2.9634    1.7982 ...  99999.00   41.6395     2     0     0   36.0343 ...
 ...  3.3132   12.6973 ...     93.58   41.6395     2     1     0   40.4625 ...
 ...  3.6294   12.8892 ...     93.58   41.6395     2     1     1   44.5207 ...
 ...  4.1909    2.5431 ...  99999.00   41.6395     2     2     0   51.8786 ...
 ...  4.4451   13.3842 ...     93.58   41.6395     3     0     0   55.2849 ...
 ...  4.4451   13.3842 ...     93.58   41.6395     2     2     1   55.2850 ...
 ...  4.6855   13.5301 ...     93.58   41.6395     3     1     0   58.5562 ...
 ...  4.9142    2.9820 ...  99999.00   41.6395     3     1     1   61.7169 ...
 ...  5.1327    3.1146 ...  99999.00   41.6395     2     2     2   64.7864 ...
 ...  5.3423   13.9286 ...     93.58   41.6395     3     2     0   67.7802 ...
 ...  5.5440   14.0510 ...     93.58   41.6395     3     2     1   70.7114 ...
```

Fig 8: Portion of the microstructural file (extension *mic*) corresponding to the fitting of the neutron diffraction pattern in figure 7.

not used. To give a single rule one must put **IsizeModel**=-2 and put zeros for the last condition. This is needed in order to avoid the confusion with the case of an infinite needle. In Figure 10 we give an example using **IsizeModel** = -2 and in Figure 9 the relevant part of the PCR file is written.

Finally, a general formulation for peak shifts, due to defects or to residual stresses, has also been implemented. For **JSOL**≠**0**, the lines corresponding to shift parameters are read in the PCR file. Selective shifts can be selected when **IShif** <-1. For this option a set of up to ABS(**IShif**) (≤10) lines can be given. The lines define rules to be satisfied by reflections undergoing shifts with respect to the theoretical Bragg position due to some kind of defects (stacking and twin faults for instance). The rules are similar to those of selective size broadening discussed above. The position of the reflections satisfying the rules are displaced according to the expressions:

$$2\theta_S = 2\theta_B + 2\,\mathbf{Shift}\; d^2 \tan\theta \times 10^{-2} \quad \text{(2θ space)}$$

$$TOF_S = TOF_B - \mathbf{Shift}\; d^3\, \mathbf{Dtt1} \times 10^{-2} \quad \text{(T.O.F. space)}$$

$$E_S = E_B - \mathbf{Shift}/(2d)\, \mathbf{Dtt1} \times 10^{-2} \quad \text{(Energy space)}$$

where the index B stands for the theoretical Bragg position of the non defective material and **Shift** is the shift parameter to be refined. The shift of Bragg reflections may also be due to external stresses or residual stresses. For those cases it is more appropriate to use the following generalized model for shifts.

```
. . . . . . . . . . . . . . . . . . . . . . . . . . .
! Selective Size-Broadening:
! hkl cond.      (n1.h + n2.k + n3.l=n n4 +/- n5)   Size-par      Code
  0  0  0          0      0      1      2      3     9.61440   661.000
  0  0  0          0      0      0      0      0     0.00000     0.000
```

Fig 9: Portion of the PCR file for `IsizeModel` = -2 corresponding to the refinement in Figure 10. The first set of zeros below the text '`hkl cond.`' is not used at present.

The model is implemented for **IShif = 100+NumLaue** (with **NumLaue** the number of the Laue class according to *FullProf* manual) , and a set of parameters corresponding up to quartic form in *hkl* can be refined. The position of a reflection is displaced according to the expressions:

$$2\theta_S = 2\theta_B + 2\, S_{\mathbf{h}}\, d^2 \tan\theta \times 10^{-2} \quad (2\theta \text{ space})$$

$$\mathrm{TOF}_S = \mathrm{TOF}_B - S_{\mathbf{h}}\, d^3\, \mathbf{Dtt1} \times 10^{-2} \quad (\text{T.O.F. space})$$

$$E_S = E_B - S_{\mathbf{h}} /(2d)\, \mathbf{Dtt1} \times 10^{-2} \quad (\text{Energy space})$$

The expression used for calculating the scalar $S_{\mathbf{h}}$ for reflection **h** is given by:

$$S_{\mathbf{h}} = \sum_{\{H+K+L=2\}} D2_{HKL}\, h^H k^K l^L + \sum_{\{H+K+L=4\}} D4_{HKL}\, h^H k^K l^L$$

The free parameters for this option are the sets $D2_{HKL}$ and $D4_{HKL}$. To refine these parameters the average cell parameters of the non-stressed material should be fixed during the refinement.

NEAR FUTURE OPTIONS IN FULLPROF.

Within these notes I have given a flavor of what can be done using *FullProf* in some fields of diffraction applications. The program is in continuous change and development. Of course the future developments depend on the particular field of Science I'm personally interested: some of the forthcoming options in *FullProf* reflect my current interests.

- Treatment of polarized neutrons in the single crystal option. The refinement of coefficients to model the spin density, in terms of multipoles (linear combinations of radial functions and spherical harmonics), from flipping ratio measurements is already available and under testing but it is not documented yet.
- Extension of the above formulation for general electron density modeling and refinement.
- Size parameters corresponding to particular shape of crystallites.
- Additional linear and quadratic soft constraints (restrains) defined by the user for arbitrary parameters.
- Complete handling of crystallographic incommensurate structures. The refinement of commensurate superstructures in terms of displacements (modulation) functions is already available but no totally documented.
- New cost functions in simulated annealing mode: bond valence sums, potentials, etc.
- New description of rigid bodies and molecular geometry.

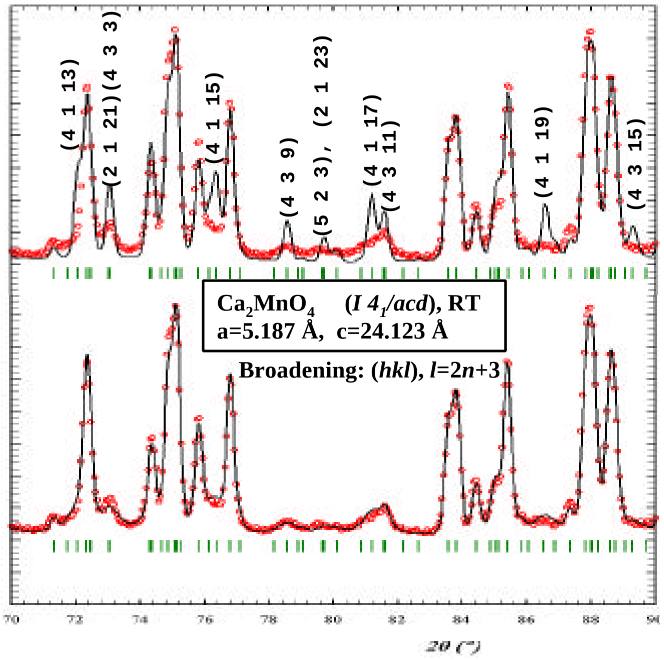


Fig 10: Selective size broadening observed by neutron diffraction at room temperature (3T2, LLB) for superstructure reflections in Ca_2MnO_4[15]. (top) Size parameter fixed to zero. (bottom) Single size parameter according to the rule (*hkl*), *l*=2*n*+3. Indices of most intense Bragg reflections affected by size broadening are also given.

A part from these development, a new GUI interface (*EdPCR*) for working with the PCR file is being prepared by Javier González-Platas and myself. This program will be useful for beginners to prepare a correct PCR file as well as for everybody to perform all kind of crystallographic calculations. The program will be working in Windows and Linux. We hope to provide a first version of this program before the summer of this year (2002).

ACKNOWLEDGEMENTS

It is a pleasure to thank here all my colleagues that have contributed with discussions, writing pieces of code, or are presently contributing with companion programs to *FullProf*: Thierry Roisnel, Javier González-Platas, Aziz Daoud-Aladine, Carlos Frontera, Vincent Rodriguez and Robert Papoular. I would like to thank many users for giving me a feedback without which the program could not be improved.

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Rietveld Refinement and Beyond

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In the past few years, there has been a distinct trend away from the "classical" applications of the Rietveld technique towards structure solution and determination. By "classical", I mean the types of problem typically encountered in traditional areas of materials science such as superconductors, magnetic systems, ferroelectrics and battery materials, in which the structure determination part of the project is frequently straightforward or even trivial, but the precise details of the refinement are all-important. It is clear that this trend has been accentuated both by the development of very elegant real-space methods of structure solution and by the availability of more user-friendly and sophisticated software for traditional methods of structure solution, especially as applied to small (and not-so-small) organic molecules, as described in the July issue of the CPD Newsletter. Another powerful driving force in my opinion has been the superb quality of the data that can be collected at second- and third-generation synchrotron sources (although this is perhaps a more controversial viewpoint not shared by everyone), but unfortunately, there still appears to be some reluctance within the powder diffraction community to exploit these sources.

In the present article, I will argue that Rietveld refinement still has an important role to play in materials science, but with a number of caveats which were previously not so apparent in the analysis of laboratory x-ray and neutron data sets, but which can no longer be ignored under the harsh glare of a high-resolution synchrotron x-ray experiment. I will focus on some of these caveats and possible pitfalls, especially in the context of some recent diffraction studies of the piezoelectric perovskite-type system $PbZr_{1-x}Ti_xO_3$ (commonly known as PZT) carried out by my colleagues Beatriz Noheda and Gen Shirane at Brookhaven, together with a number of collaborators at other institutions. PZT is well-known to exhibit very desirable piezoelectric properties under an applied electric field and is the backbone of many commercial electromechanical devices. For almost four decades, these properties have been associated with the coexistence of rhombohedral and tetragonal phases in the vicinity of the so-called "morphotropic phase boundary" (an almost vertical line on the temperature-composition phase diagram at x ˜ 0.48 separating regions with rhombohedral and tetragonal symmetry, usually called the MPB), as described in numerous laboratory x-ray and neutron powder diffraction studies. However, a surprise was in store, for in 1999 a high-resolution synchrotron x-ray study of this composition revealed the presence of a new phase with a slightly-distorted monoclinic structure[1]. Subsequent Rietveld refinement showed that the polar axis in the new phase was rotated away from the tetragonal [001] axis towards the rhombohedral [111] axis, and that the monoclinic structure could therefore be viewed microscopically as a "bridge" between these two higher-symmetry structures[2]. Since then there have been numerous experimental and theoretical studies of PZT and related systems which have provided much new insight into the relationship between this and other lower-symmetry phases and their electrical properties.

The optimization of physical properties in temperature-composition phase space is of course a very common objective in materials science, but as in the case of PZT, the problems of pseudosymmetry and phase coexistence are not always recognized, and then Rietveld refinement can at best give only some kind of average structure and at worst erroneous results. How can such pitfalls best be avoided? Clearly, high-quality samples and high-resolution synchrotron data are an excellent starting point. If, as is often advantageous, Debye-Scherrer diffraction geometry with a capillary specimen is chosen, it is important not to degrade the sample by excessive grinding, which can result in broadened peaks. To this end we routinely adopt the procedure of lightly crushing ceramic samples (or even small single crystals) and only using the fraction retained between 325 and 400 mesh sieves - large boulders by normal powder diffraction standards!

In an ideal world, a small distortion would be uniquely revealed by a definite splitting of certain types of peaks, but unfortunately the situation is often complicated by anisotropic peak broadening, which is discussed in more detail by Peter Stephens in another article in this issue. Such anisotropic broadening has a number of possible origins; in mixed systems one common cause is the sensitivity of some of the lattice parameters to the presence of small long-range fluctuations in composition. Under these circumstances, we have found that fits to selected clumps of peaks (preferably with unconstrained individual peak widths and mixing parameters) *prior to* Rietveld refinement is the best way to unequivocally establish the presence of a lower-symmetry distortion and/or phase coexistence. Although pattern-matching techniques (refinement without a structural model) are frequently employed for this purpose, it is important to remember that if anisotropic peak broadening is neglected, the choice of a lower-symmetry cell will very likely result in an improved fit, but not necessarily any better than the fit obtained with a higher-symmetry cell and a generalized model of anisotropic broadening.

It frequently happens in materials science studies that one is confronted with the problem of discriminating between less- and more-constrained structural models, involving pseudosymmetry, non-stoichiometry, mixed cation distribution and highly-anisotropic temperature factors related to static or dynamic cation disorder, to name a few. In such a situation, is it possible to make any kind of objective choice between the models? This is not a trivial question, since the existence of subtle features of this sort may have an important bearing on understanding the physical properties, but it is one that statisticians appear reluctant to address. For want of anything better, one can use to the Hamilton significance tests [3]. Of course, these require an estimate of the number of independent observations (integrated intensities or F^2 's), but several reasonable algorithms have been proposed in the literature (for example, the number of peaks or clumps of peaks separated by = 0.5 FWHM). In my experience, these tests generally work quite well if applied conservatively, even if they do not meet with the approval of the statisticians. This type of approach also allows a more realistic estimate of standard errors [4], but that is another story.

Our ability to extract accurate structural information from powder data is now further enhanced by another powerful and elegant tool, namely the combination of Rietveld refinement with Maximum Entropy Methods (MEM), which has been exploited very effectively in the past few years by Masaki Takata, Matt Sakata and colleagues at Nagoya University. This is an iterative procedure in which the features observed in the MEM electron density distribution at each step are incorporated into an improved structural model for the next stage of Rietveld refinement until the final distribution is compatible with the structural model. The application of this technique to materials science is described for a number of systems in a recent review article by Takata *et al.*[5], one beautiful example being the direct observation of orbital order in the manganite compound $NdSr_2Mn_2O_7$. This procedure avoids the guesswork involved in fine-tuning the structural model in an unbiased way, and hopefully will become standard practice in the future.

It is interesting to recall that Rietveld refinement was originally developed for structure analysis based on neutron powder data, and the powder diffraction community has a long and distinguished track-record of using neutron facilities for materials science studies. With new synchrotron sources being built or planned around the world, there are rapidly expanding opportunities to exploit high-resolution synchrotron techniques in the same way. At the same time, as outlined above, there will be many new challenges along the way.

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Accuracy In X-ray Powder Diffraction: A Comparison of Quantitative Methods

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The following paper is the summary of a poster presentation made at “Accuracy in Powder Diffraction III” (APD III), National Institute of Standards and Technology, Gaithersburg, Maryland, USA in April 2001. It is a detailed comparison of different quantitative phase analysis (QPA) techniques using the IUCr-CPD QPA round robin sample 1 as the test material. This study was prompted by the large spread of returns received from the round robin participants which lead to uncertainty in knowing whether the variability was due to the analytical methods or their application. In this work, different analytical methods were tested by the same operators using the same data sets thus reducing the number of variables for consideration.

INTRODUCTION

A comparison of commonly used methods of quantitative phase analysis (QPA) using powder X-ray diffraction (XRD) methods has been carried out. The sample mixture used for this study was that distributed by the IUCr-CPD as sample 1 in its recent round robin on QPA via diffraction methods[1]. Figure 1 shows the experimental design of the eight mixtures comprising sample 1. Figures 2 and 3 show the results returned from the round robin for CPD-supplied and participant-collected data respectively.

QUANTITATIVE METHODS USED

X-ray Fluorescence (XRF) - included as a “standard” method which in the case of these samples should be the most accurate and reproducible.

Reference Intensity Ratio[2] (RIR) - single peak (RIR1) or multi-peak (RIR2) method where RIR (I/I_c) is defined as the ratio of the strongest peak of any phase *j* to the

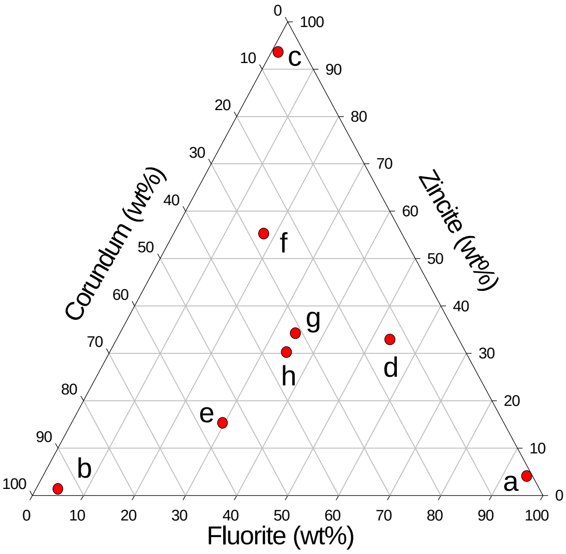


Fig. 1 Experimental design for IUCr-CPD round robin Sample 1 suite.

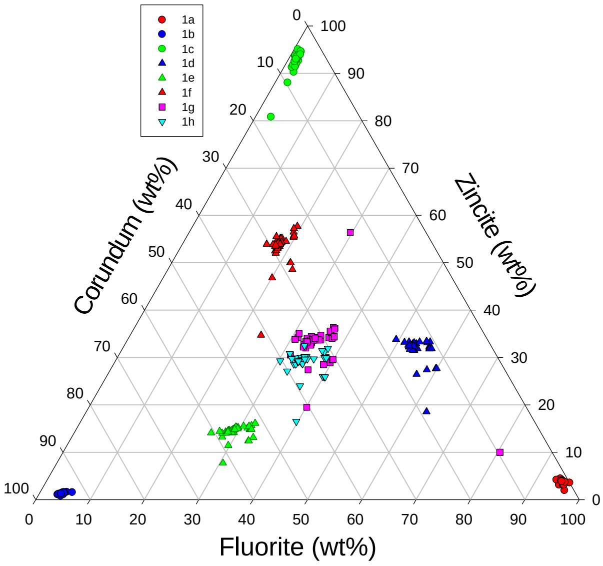


Fig 2 Analysis results - IUCr round robin, CPD-supplied data. Note the spread of results.

strongest corundum peak (113) in a 1:1 mixture (by weight). In this instance the matrix flushing method of Chung[3] has been employed thus producing a result normalised to 100wt%.

Iterative Least Squares (ILS) - single peak (Zevin1) or multi-peak (Zevin2) method where a series of simultaneous equations based upon the basic quantitative phase analysis equation (Eqn 1) are derived using all samples in the suite. In this instance, the modification of Zevin[2] has been used where the constant term *K* incorporates the mass absorption coefficient of the sample (μ_m) and the density of the phase and μ_m is iteratively calculated from the concentrations using an MS-EXCEL spreadsheet.

$$c_k = K_k I_{ik}$$

Eqn 1: *Quantitative phase analysis equation of Knudsen*[7] *where* c_k *is the concentration of phase k,* K_k *is a constant and* I_{ik} *is the intensity of the* i^{th} *peak of phase k.*

Mean Normalised Intensity[4] (MNI) - multi peak method similar to RIR where the mean normalised intensity of all peaks for a particular phase is used in place of the intensity of the strongest peak.

Rietveld Refinement - Whole pattern method where the refined scale factor of each phase is related to phase concentration via Eqn 2. This study used two software packages: Koalariet[6] (Rietveld1) and SR5[5] (Rietveld2).

$$c_k = \frac{s_k(ZMV)_k}{\sum s_i(ZMV)_i}$$

Eqn 2*: Rietveld equation where* c_k *is the concentration of phase k, s is the phase dependent, refinable Rietveld scale factor and ZMV are the number, mass and volume respectively of the formula units in each phase*[5].

RESULTS AND DISCUSSION

Results have been assessed according to a statistic based on the Kullback-Leibler distance (KLD)[8]. This value is weighted according to the concentration of a phase (Eqn 3) and may be summed to provide a single numerical assessment of the accuracy of a determination (Eqn 4).

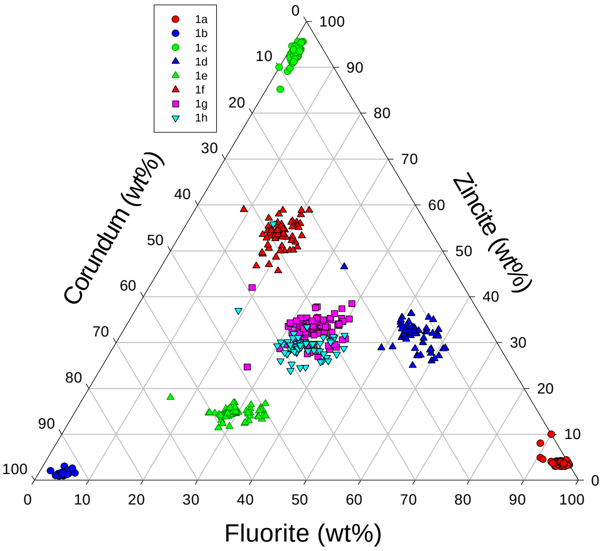


Fig. 3 Analysis results - IUCr round robin, participant-collected data. Note that the spread of results is greater than for the CPD-supplied data.

Absolute values of this figure (*AKLD*) have been used to provide a general estimate of the magnitude of the error. Averages of these $AKLD_{sum}$ values provide an estimate of the accuracy of analysis across a particular group, which is in this case, analytical method. Small values of $AKLD_{sum}$ represent the most accurate analyses. To assess the variation of *AKLD* within a group, an approximate estimate of the 95% confidence limits can be obtained by first determining the standard deviation (SD) of all values of *AKLD* in the group and calculating the uncertainty according to Eqn 5. The significance of differences between groups is based on their combined uncertainties.

$$KLD = 0.01 \times wt\%_{True} \times \ln\left(\frac{wt\%_{True}}{wt\%_{Measured}}\right)$$

Eqn 3*: Kullback-Leibler distance weighted for phase concentration.*

$$AKLD_{sum} = AKLD_{corundum} + AKLD_{fluorite} + AKLD_{zincite}$$

Eqn 4*: Sum of absolute values of Kullback-Leibler distance*

$$\text{Uncertainty} = \frac{2 * \text{SD of AKLD}}{\sqrt{\text{N}}}$$

Eqn 5*: Calculation of the uncertainty of the AKLD values where SD is the standard deviation of the group and N is the number of values in the group.*

Table 1 shows the assessment of the analytical methods considered here via the calculation of $AKLD_{sum}$ values. There is little significant difference between any of the methods and all returned a very low average $AKLD_{sum}$ value representing accurate analyses. This is borne out in Figure 4 which shows graphically the results of all analyses performed using all methods and should be compared with the spread of returns from the IUCr-CPD round robin (Figures 2 and 3). It is noteworthy that each group in Figure 4 represents 24 separate analyses (8 analytical methods, three replicates of each).

Analysis Method	**$AKLD_{sum}$**		
	Authors	**IUCr Round Robin Participants**	
		CPD Data	**Participant Data**
XRF*	0.008(1)	0.008(1)	0.008(1)
MNI	0.016(3)	-	-
Rietveld 1	0.010(3)	0.044(9)	0.044(4)
Rietveld 2	0.012(4)		
RIR 1	0.009(2)	0.046(32)	0.089(19)
RIR 2	0.011(2)		
Zevin 1	0.016(3)	-	-
Zevin 2	0.015(3)	-	-
All Methods	0.013(1)	0.044(9)	0.050(2)

Table 1. Assessment of analytical methods via measurement of $AKLD_{sum}$.

**XRF value not included in calculation of "All Methods"* $AKLD_{sum}$

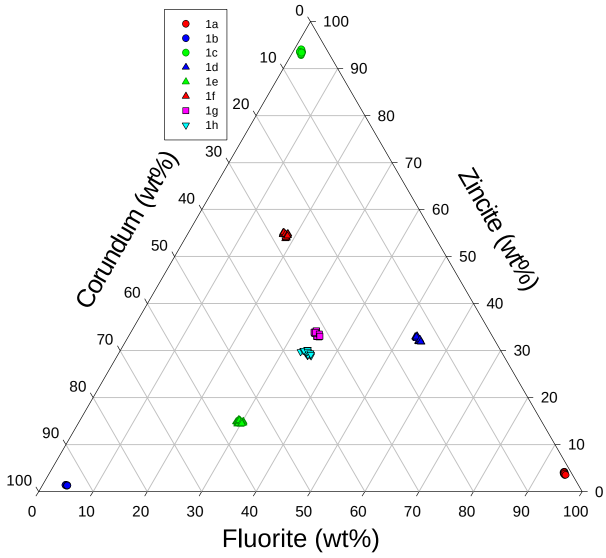


Fig 4: Analytical results - authors.

CONCLUSION

The errors reported in the IUCr-CPD round robin returns for sample 1 are largely operator induced. This study has shown that, for a simple crystalline system such as this one, many common methods of quantitative phase analysis using XRD are adequate. Differences in applicability of these methods may arise in more complex analytical systems where problems such as preferred orientation, microabsorption and presence of amorphous material may occur.

REFERENCES

1. Madsen, I.C., Scarlett, N.V.Y., Cranswick, L.M.D. and Lwin, T. (2001) “Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: Samples 1A to 1H” J. Appl. Cryst. (2001), **34**, 409-426.
2. Zevin, L.S. and Kimmel, G. (1995) “Quantitative X-ray Diffractometry” Springer-Verlag New York, Inc.
3. Chung, F.H. (1974) “Quantitative Interpretation of X-ray Diffraction Patterns of Mixtures II. Adiabatic Principle of X-ray Diffraction Analysis of Mixtures” J. Appl. Cryst. 7, 526.
4. Li, De Y. and O’Connor, B.H. (1998) “Mean-Normalized-Intensity (MNI) Method For X-ray Powder Diffraction Phase Composition Analysis” Material Science Forum Vol278-281, 57-62 Trans-Tech Publications Ltd.
5. Hill R.J. and Howard C.J. (1986) “A Computer Programme for Rietveld Analysis of Fixed Wavelength X-ray and Neutron Powder Diffraction Patterns”, AAEC (now ANSTO) Report AAEC/M112.
6. Coelho A.A., Madsen I.C. and Cheary R.W. (1997), “A New Rietveld Refinement Program Using a Fundamental Parameters Approach to Synthesizing Line Profiles”, Abstract D1-PM2, Proceedings of the 20th Conference of the Society of Crystallographers in Australia, April 2nd -5th, Queenstown, New Zealand.
7. Knudsen, T. (1981) “Quantitative X-ray Diffraction Analysis With Qualitative Control Of Calibration Samples”, X-ray Spectrometry, 10(2), 54-56.
8. Kullback, S. (1968), “Information Theory and Statistics”, Dover Publications, 1-11

Internet Available Rietveld Software

Lachlan M. D. Cranswick
Collaborative Computational Project No 14 (CCP14)
for Single Crystal and Powder Diffraction
CCP14 - School of Crystallography,
Birkbeck College,
Malet Street, Bloomsbury,
WC1E 7HX, London, UK
Tel: (+44) 020 7631 6849
Fax: (+44) 020 7631 6803
E-mail: l.m.d.cranswick@dl.ac.uk
WWW: http://www.ccp14.ac.uk -
http://ccp14.sims.nrc.ca - http://ccp14.semo.edu

There exists at present a wide genetic diversity of Rietveld programs expressing a range of ideas and approaches. Many of these software packages are also available via the Internet for the benefit of the scientific community. When up against a new structure refinement of powder diffraction data, it can be worth while exploring the available Rietveld programs to determine which may be the most appropriate to use with particular problems. Most can be immediately downloaded, tested and run. The following represents a non-comprehensive list of what can be found on the Internet, mentioning some of the functionality that is available (to exhaustively mention the entire functionality of a single Rietveld program could take quite a few pages). Nearly all the following software can be obtained via the CCP14 mirrors viewable at http://www.ccp14.ac.uk/mirror/. Suggestions on additions, missing information, corrections and elaboration on the following would be appreciated by sending an E_mail to the author so it can be included in the next edition of the CPD newsletter.

Rietveld Code of Historical Interest

Some Rietveld codes of historical interest are available on the internet. This includes the original Hugo Rietveld report containing Algol source code *(H. M. Rietveld, “An ALGOL Program for the Refinement of Nuclear and Magnetic Structures by the Profile Method by H. M. Rietveld”, Reactor Centrum Nederland, April 1969; RCN 104.)* at http://www.ccp14.ac.uk/ccp/web-mirrors/-hugorietveld/riet-report/. This webpage also links to on-line versions of the seminal Rietveld Method papers. Another example is the Hugo Rietveld & Alan Hewat Fortran source code for Rietveld/Profile Refinement viewable at http://www.ccp14.ac.uk/ccp/web-mirrors/-hewat-rietveld/.

A range of Rietveld programs available via the internet

BGMN

Fundamental parameters Rietveld for structure refinement, size-strain and quantitative analysis

Contact: Joerg Bergmann

Email: support@bgmn.de

WWW: http://www.bgmn.de

References: *J. Bergmann, R. Kleeberg, and T. Taut "A new structure refinement and quantitative phase analysis method basing on predetermined true peak profiles" Z. f. Kristallographie, Supplement issue No. 8, Europ. Cryst. Meeting 15 (1994), Book of Abstracts p. 580*

While a Graphical User Interface (GUI) version of BGMN is commercially available from Siefert, academics and student can download a free non-GUI version from the BGMN website which uses an ASCII control file. BGMN makes use of "fundamental parameters"; high stability algorithms in modeling the diffraction profile; and a macro based equation editor. This makes BGMN effective in obtaining accurate size-strain, structural and quantitative analysis results.

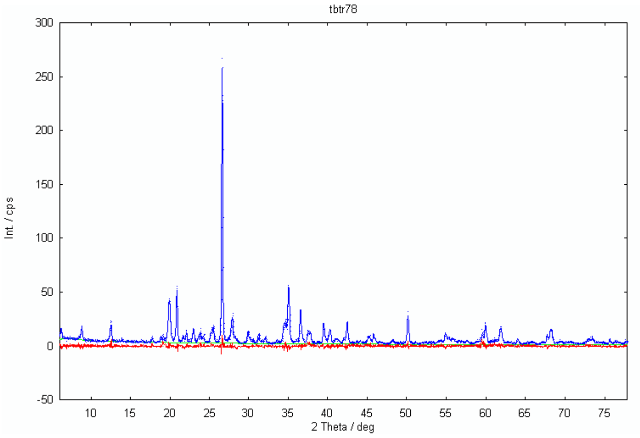


Fig 1: BGMN quantitative analysis fit to reference sample Metashale Böhlscheiben, "Bergmann, J., Kleeberg, R.,Taut, T., Haase, A., 1997: Quantitative Phase Analysis Using a New Rietveld Algorithm - Assisted by Improved Stability and Convergence Behavior. Adv. X-Ray Analysis 40 (1997)."

DBWS

Rietveld Refinement, quantitative phase analysis
and size-strain analysis.

OS: DOS/MS-Windows, SUN Solaris and Linux

Contact: Ray Young

Email: r.young@physics.gatech.edu

WWW:http://www.physics.gatech.edu/downloads/young/DBWS.html

References: *R. A. Young, A. Sakthivel, T. S. Moss and C. O. Paiva-Santos, "DBWS-9411 - an upgrade of the DBWS programs for Rietveld Refinement with PC and mainframe computers", J. Appl. Cryst., Vol. 28, 366-7; 1995*

DBWSTOOL

Graphical User Interface for creating and controling DBWS input files

OS: MS-Windows

Contact: Lucas Bleicher

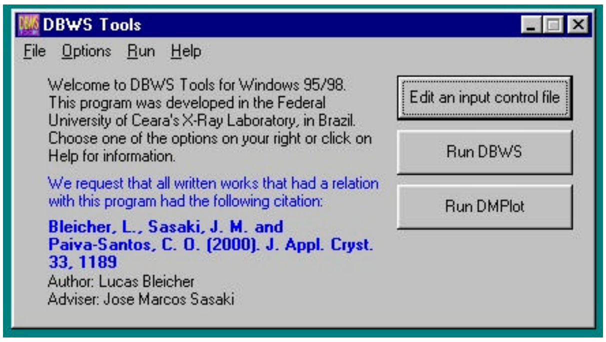
Email: sasaki@fisica.ufc.br

WWW: http://www.fisica.ufc.br/raiosx/DBWS.htm

Download FTP: http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/dbwsgui/pub/

References: *L. Bleicher, J. M. Sasaki and C. O. Paiva Santos. "Development of a graphical interface for the Rietveld refinement program DBWS" (2000). J. Appl. Cryst. 33, 1189.*

DBWS is a Rietveld program whose source code has spawned a number of variants (Fullprof, LHPM, SR5, Riet7, Rietica, etc), but still has a free-standing active existence. Applications of DBWS include structure refinement of colossal magnetoresistance materials, thermoelectrics and negative thermal expansion ceramics, quantitative analysis and crystallite size and microstrain analysis. While DBWS is normally controlled via an ASCII input file, the recently written DBWSTool can act as a Graphical User Interface (GUI) for setting up a starting ASCII input file and controlling the refinement.



Welcome to DBWS Tools for Windows 95/98.
This program was developed in the Federal University of Ceara's X-Ray Laboratory, in Brazil.
Choose one of the options on your right or click on Help for information.

We request that all written works that had a relation with this program had the following citation:

Bleicher, L., Sasaki, J. M. and Paiva-Santos, C. O. (2000). J. Appl. Cryst. 33, 1189

Author: Lucas Bleicher
Adviser: Jose Marcos Sasaki

Fig 2: Starting screen for DBWSTools; a graphical user interface for DBWS Rietveld.

Fullprof

Single crystal and powder diffraction refinement software

OS: MS-Windows, DOS, SUN Solaris and Linux

Contact: Juan Rodriguez-Carvajal

Email: juan@bali.saclay.cea.fr

WWW: http://www-llb.cea.fr/fullweb/powder.htm

Download FTP:

ftp://charybde.saclay.cea.fr/pub/divers/fullprof.2k/

References: *J. Rodriguez-Carvajal, Abstr. 15th Conf. Int. Union Crystallogr. (Toulouse, France) 1990, p. 127, Satellite Meeting on Powder Diffraction.*

The Fullprof Rietveld software can perform a variety of refinement types, including combined X-ray / Neutron; TOF neutron; fixed angle INEL PSD data, incommensurate refinement, magnetic refinement. Fullprof is normally controlled via an ASCII input file and links to a number of utility programs such as Winplotr utility software (by Thierry Roisnel and Juan Rodriguez-Carvajal), JfullProf GUI for Fullprof (by Alain Bouvet) and GFOUR Fourier software (by Javier Gonzalez-Platas and Juan Rodriguez-Carvajal). As Fullprof is the subject of a separate article in this issue of the CPD newsletter, the following will concentrate on the Winplotr software provided with Fullprof.

Winplotr for MS-Windows by Thierry Roisnel and Juan Rodriguez-Carvajal provides a wide range of functionality. This includes the ability to plot Fullprof PRF, Jana2000 PRF, Rietian2000 PAT and Debvin GRA Rietveld plot files; not only in 2-theta/TOF space, but also Q (Å^{-1}), d (Å), sinTheta/Lambda and "s" (= 1/d). Winplotr will open Fullprof, GSAS, CPI and other raw data file formats. Data analysis includes background selection, peak find (manual and automatic), peak profiling, integration, summation, averaging, background subtraction and passing peak positions to various indexing programs included with the

Winplotr distribution (WinIto, WinDicvol, WinTreor and supercel). At the termination of a successful powder indexing session, Winplotr can also create starting Fullprof PCR files.

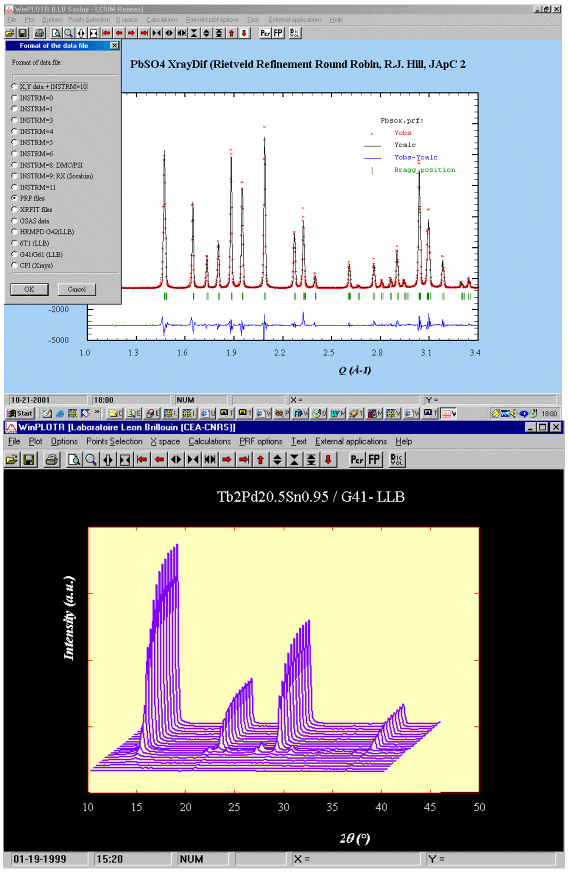


Fig 3: Winplotr (supplied with Fullprof) a) viewing a Rietveld plot file while also showing the variety of raw data file formats in can open; and b) displaying diffraction patterns in a pseudo 3D plot as described in the Winplotr tutorials at :

http://www-llb.cea.fr/fullweb/winplotr/wpl_demo.htm.

GSAS

Single crystal and powder diffraction refinement software

OS: MS-Windows, SGI IRIX and Linux

Contact: Bob Von Dreele and Alan Larson

Email: vondreele@lanl.gov

Download FTP: ftp://ftp.lanl.gov/public/gsas/

References: *A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR 86-748 (1994).*

The GSAS structure refinement suite is controlled by a menu based system, and can handle a range of structures including proteins. GSAS has a large number of restraint types; the ability to refine on single crystal and powder diffraction data. Combined refinement of X-ray / Neutron data can be performed, including TOF Neutron and Energy Dispersive X-ray data. A large number of utilities plug into GSAS or can make use of GSAS files and a list of these is available via the CCP14 website at http://www.ccp14.ac.uk/solution/gsas/. As GSAS is the subject of a separate article in this issue of the CPD newsletter, the following will concentrate on Brian Toby's EXPGUI software, which is a Graphical User Interface (GUI) for GSAS running on UNIX and Windows.

EXPGUI

Graphical User Interface for GSAS running on Windows and UNIX

OS: MS-Windows, SGI IRIX and Linux

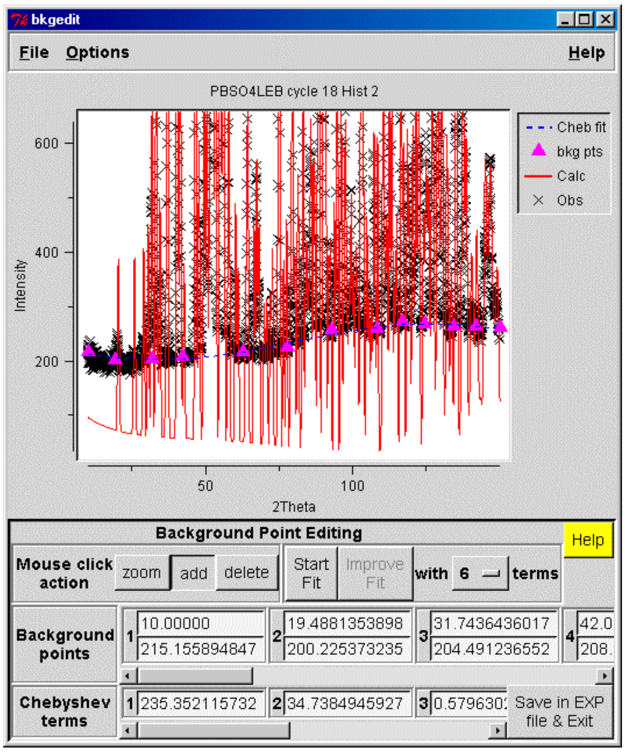
Contact: Brian Toby

Email: Brian.Toby@nist.gov

WWW: http://www.ncnr.nist.gov/programs/crystallography/software/expgui/

References: *B. H. Toby, EXPGUI, a graphical user interface for GSAS, J. Appl. Cryst. (2001). 34, 210-213.*

EXPGUI allows people familiar with Windows style graphical user interfaces to quickly and intuitively start using GSAS. EXPGUI also has extra functionality not available in the standard GSAS package. This includes the ability to graphically select a manual background (BKGEDIT) and fit it to a Chebyshev function; graphically exclude regions (EXCLEDT); and the display of "cumulative chi squared plots" *[W.I.F. David, "Beyond least-squares analysis in profile refinement"; Accuracy in Powder Diffraction-III, 2001]*. The latest versions also include the ability to set up dummy histograms and enable/disable histograms (diffraction patterns).



with 6 terms

Background points: 1 10.00000 / 215.155894847; 2 19.4881353898 / 200.225373235; 3 31.7436436017 / 204.491236552; 4 42.0 / 208.

Chebyshev terms: 1 235.352115732; 2 34.7384945927; 3 0.579630

Fig 4: The new BKGEDT function in Brian Toby's EXPGUI for manually defining the background (triangles) which can then be fitted by a Chebyshev function and saved in the GSAS EXP file. The poor difference curve is from the previous "refined" background during Le Bail fitting.

Jana2000

Single crystal and powder diffraction refinement of Standard, Modulated and Composite Structures

OS: Windows and UNIX (IRIX, Linux, etc)

Contact: Vaclav Petricek & Michal Dusek

Email: petricek@fzu.cz or dusek@fzu.cz

WWW: http://www-xray.fzu.cz/jana/jana.html

FTP Download: ftp://ftp.fzu.cz/pub/cryst/jana2000

References: *Dusek, M., Petricek, V., Wunschel, M., Dinnebier, R.E. and Smaalen, S. van (2001), J.Appl.Cryst.34, 398-404, Refinement of modulated structures against X-ray powder diffraction data with Jana2000* and *Petricek,V. & Dusek,M.(2000). The crystallographic computing system JANA2000. Institute of Physics, Praha, Czech Republic.*

A recent change in the Jana single crystal suite is the ability to now refine on powder diffraction data via an extension to the Jana Graphical User Interface (GUI). This was made possible using source code and implementation details provided by Bob von Dreele. As well as reading its own data format, Jana2000 can also read GSAS and RIETAN data file formats. In the latest beta version, Jana2000 can handle multiple phases. Other features include Le Bail fitting, modelling peak asymmetry via the Finger, Cox, Jephcoat method; and anisotropic peak broadening via the Stephens method (J. Appl. Cryst. 32, 281 (1999)). As information on powder refinement has not made it into the Jana manual, there is a web tutorial at http://www-xray.fzu.cz/jana/Jana2000/powders.html ; again with mirrors via the CCP14 websites:

UK: http://www.ccp14.ac.uk/ccp/web-mirrors/jana/jana/Jana2000/powders.html

Canada: http://ccp14.sims.nrc.ca/ccp/web-mirrors/jana/jana/Jana2000/powders.html

US: http://ccp14.semo.edu/ccp/web-mirrors/jana/jana/Jana2000/powders.html

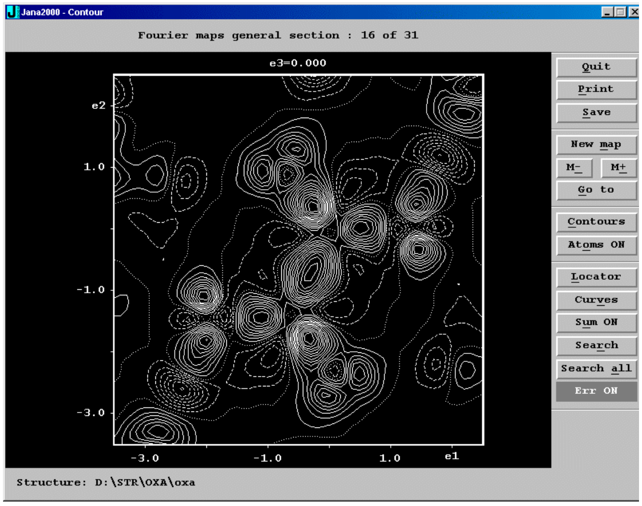


Fig 5: Fourier contour map viewing as part of Jana 2000. Powder refined structures have access to all the relevant facilities of the Jana2000 software; including Fourier map generation and viewing; charge density analysis; etc.

MAUD for Java

GPL'd materials science Rietveld for structure refinement, crystallite size-strain-shape, pole-figure and quantitative analysis.

OS: Any Java enabled platform (Mac, Windows, UNIX) as well as GPL'd source code

Contact: Luca Lutterotti

Email: Luca.Lutterotti@ing.unitn.it

WWW: http://www.ing.unitn.it/~luttero/maud/

References: *L. Lutterotti, S. Matthies and H. -R. Wenk, "MAUD (Material Analysis Using Diffraction): a user friendly Java program for Rietveld Texture Analysis and more.", Proceeding of the Twelfth International Conference on Textures of Materials (ICOTOM-12), edited by Szpunar J. A., August 9-13, 1999, Montreal, Canada. Vol. 2, 1599.*

MAUD (Material Analysis Using Diffraction) for Java is optimised for materials analysis and runs controlled by a Graphical User Interface (GUI). Capabilities include quantitative analysis (with the new ability to import an HKL file if the structure is lacking); size-strain-shape analysis; pole-figure analysis, and other materials analysis. New developments in MAUD are also being implemented to assist in structure solution from powder diffraction using genetic algorithms. Web tutorials are available via the MAUD webpage at http://www.ing.unitn.it/~luttero/-maud/tutorial/, showing how techniques such as quantitative analysis; digitising a diffraction image; and texture analysis from traditional pole figures. MAUD is distributed under the GNU Public Licence such that its source code can be freely modified. For information on the GNU General Public License, refer to http://www.gnu.org/copyleft/gpl.html.

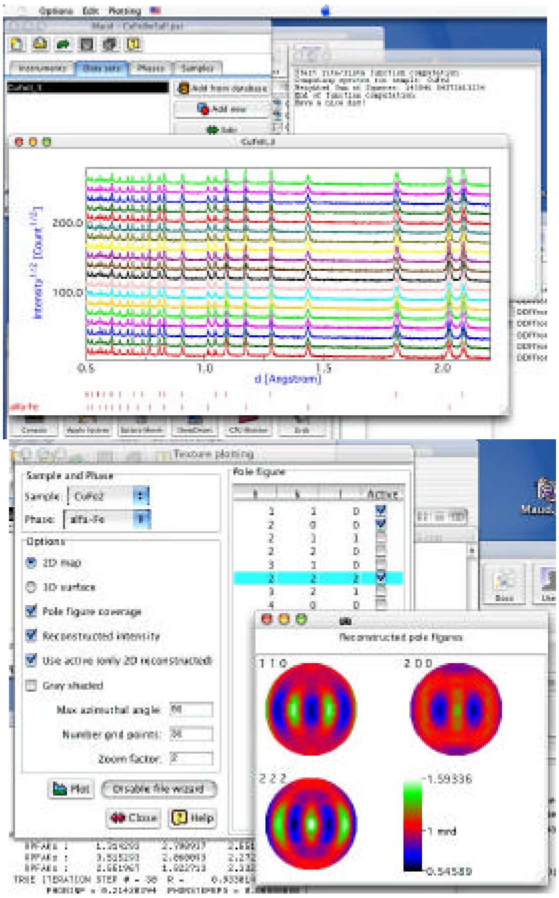


Fig 6: Screen images of MAUD for Java Rietveld software in action while performing texture / pole figure analysis as described in the tutorial at http://www.ing.unitn.it/~luttero/maud/tutorial/ODFfromPF/

Prodd

Powder diffraction refinement with the source code bundled up in the CCSL (Cambridge Crystallography Subroutine Library)

OS: DOS executable and source code available from the authors

Contact: Jon Wright and Bruce Forsyth

Email: wright@esrf.fr

WWW: http://www.ccp14.ac.uk/ccp/web-mirrors/prodd/~jpw22/

CCSL WWW: http://www.ill.fr/dif/ccsl/

References: *J P Wright & J B Forsyth "Profile Refinement of Diffraction Data using the Cambridge Crystallographic Subroutine Library (CCSL)"; Rutherford Appleton Laboratory Report RAL-TR-2000-012; Version 1.0; May 2000.*

Prodd is a new "hackers" Rietveld for those who may have structure refinement problems that are not doable in existing Rietveld binaries (thus requiring custom coding). An extra advantage is that Prodd is based around the CCSL (Cambridge Crystallography Subroutine Library). Though to learn the rest of the CCSL would result in a higher learning curve. Prodd is controlled by editing an ASCII file and supports time of flight and constant wavelength neutron data as well as synchrotron X-ray; but not (at present) laboratory X-ray data.

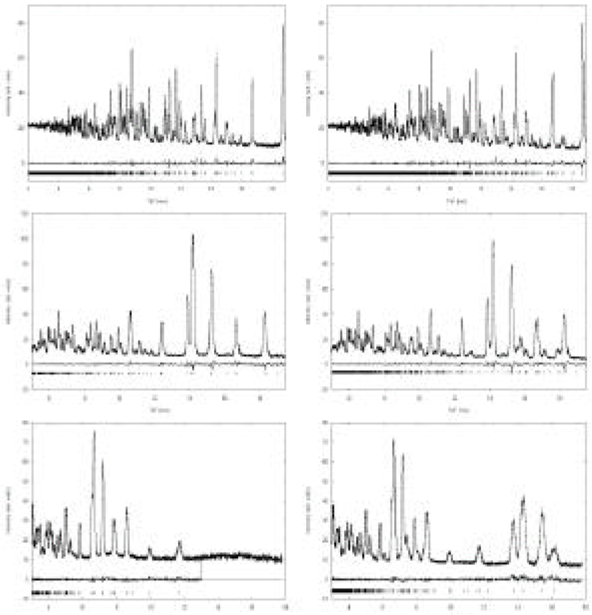


Fig 7: Two fits for FeAsO4 on POLARIS (3 detector banks, from J.P.Wright, PhD Thesis, Univ. of Cambridge). One fit has magnetic peaks, the other does not. Description of the magnetic structure in in Forsyth JB, Wright JP, Marcos MD, Attfield JP, Wilkinson C; "Helimagnetic order in ferric arsenate, FeAsO4"; Journal of Physics-Condensed Matter, 11 (6): 1473-1478 Feb 15 1999.

Profil

Rietveld that automatically handles atomic and anisotropic symmetry; and with restraints suitable for refinement of molecular compounds.

OS: DOS/Windows and VMS

Contact: Jeremy Cockcroft

Email: cockcroft@gordon.cryst.bbk.ac.uk

WWW: http://img.cryst.bbk.ac.uk/www/cockcroft/-profil.htm

FTP Download: ftp://img.cryst.bbk.ac.uk/pdpl/

References: *J. K. Cockcroft & A. N. Fitch. "The solid phases of sulphur hexafluoride by powder neutron diffraction." Zeitschrift fur Kristallographie 1988, **184**, 123-145.*

Profil is controlled by an ASCII input file, and has features relevant to complex Rietveld refinement; including the refinement of molecular compounds. Features include automatic constraints with respect to atoms on special positions and swapping between isotropic and anisotropic thermal formats. Available bond restraints include bond angle, bond length and "same" restraints. There is a newly added "multiple site chemical composition restraint" which, like the similar GSAS "total chemistry restraint", can be used as a charge balance restraint. Spacegroups are defined by symmetry operators, which Profil interprets and outputs the spacegroup symbol to the user (or an error if the symmetry operators do not describe a complete set). Thus Profil can handle quite complex (and useful) commensurate non-standard cell types relevant to materials science (e.g., F2/d monoclinic). (Refer: J. K. Cockcroft, A. Simon, H. Borrmann, & A. Obeymeyer. "The crystal structures of the low-temperature modifications of deuterium iodide - A neutron study."; European Journal of Solid State Inorganic Chemistry 1988, **25**, 471-481.).

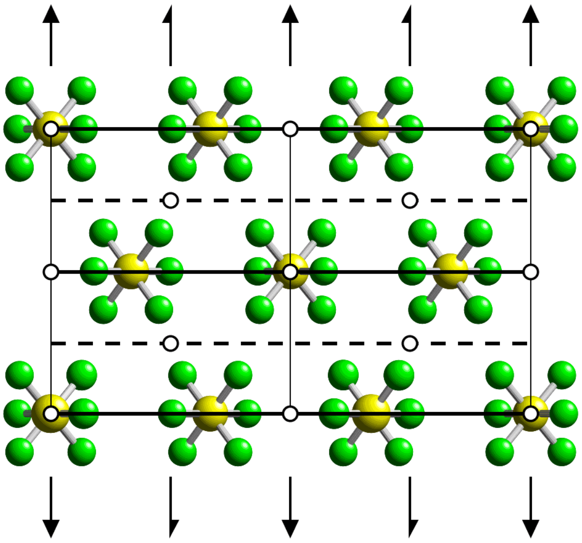


Fig 8: Structure of SF6. The Profil refinement involved making liberal use of the "same" bond-length restraint (required due to pseudo-symmetry). Cited in J. K. Cockcroft & A. N. Fitch. "The solid phases of sulphur hexafluoride by powder neutron diffraction." Zeitschrift fur Kristallographie 1988, **184**, 123-145.

Rietan

GPL'd powder diffraction refinement with MEM-based whole-pattern fitting

OS: Mac OS, MS-Windows and GPL'd source code

Contact: Fujio Izumi

Email: IZUMI.Fujio@nims.go.jp

WWW: http://homepage.mac.com/fujioizumi/rietan/angle_dispersive/angle_dispersive.html

References: *F. Izumi and T. Ikeda, Mater. Sci. Forum, 321-324 (2000) 198-203* and *F. Izumi, S. Kumazawa, T. Ikeda, W.-Z. Hu, A. Yamamoto, and K. Oikawa, Mater.Sci. Forum, 371-381 (2001) 59-64.*

As one of its features, Rietan2000 is presently the only Rietveld program which implements MEM (maximum-entropy method)-based whole-pattern fitting; making it possible to represent a crystal structure with electron/nuclear densities. It is controlled by an ASCII input file and is provided as executables and source code under the GNU Public Licence. For information on the GNU General Public License, refer to http://www.gnu.org/copyleft/gpl.html. As Rietan2000 is the subject of a separate article in this issue of the CPD newsletter, its features will not be elaborated here.

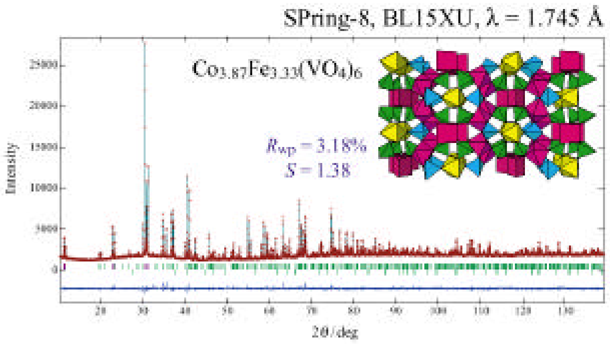


Fig 9: Example Rietveld plot and structure refined with Rietan2000.

Rietica

Sequel to the LHPM Rietveld with a complete graphical user interface

OS: MS-Windows

Contact: Brett Hunter

Email: bah@ansto.gov.au

WWW: http://www.rietica.org

FTP Download: ftp://ftp.ansto.gov.au/pub/physics/neutron/rietveld/Rietica_LHPM95/

References: *Hunter B. (1998) Rietica - A visual Rietveld program, International Union of Crystallography Commission on Powder Diffraction Newsletter No. 20, (Summer) http://www.rietica.org*

Rietica is the sequel to the LHPM Rietveld software and has a complete Graphical User Interface (while still retaining the traditional ability to edit an ASCII control file). Combined refinement can be performed on X-ray and neutron data (constant wavelength and TOF) as well as easy point and click mass Le Bail fitting. As well as the ability to import GSAS EXP and Fullprof PCR refinement files, it also includes an implementation of I. D. Brown's method for bond-valence calculation that can be used to check refined structures at the click of a menu option.

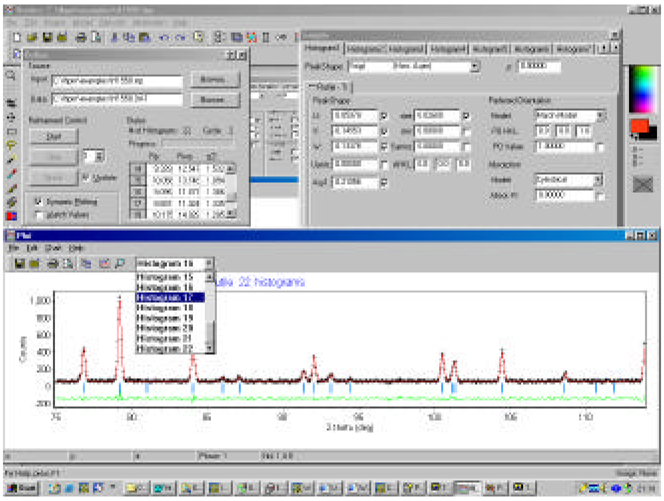


Fig 10: Screen image of Rietica running a multi-dataset refinement involving 22 powder histograms.

WinMprof

Rietveld refinement with bond restraints (including the “same” restraint) and features suitable for restrained refinement of molecular structures.

OS: MS-Windows

Contact: Alain Jouanneaux

Email: jouanneaux@univ-lemans.fr

WWW: http://lpec.univ-lemans.fr/WinMProf/

References: *A. Jouanneaux, X. Le Gonidec and A.N. Fitch "WinMProf : a visual Rietveld software" EPDIC7 : Materials Science Forum vols 378-381 (2001), pp 112-117.*

WinMprof for MS-Windows includes such functionality as: Le Bail fitting; peak asymmetry correction using the Finger, Cox, Jephcoat method ((1994) J. Appl. Cryst. 27, 892) or the Bérar & Baldinozzi function ((1993) J. Appl. Cryst. 26, 128); anisotropic peak profiling via the Anisotropic Variable method (A. Le Bail & A. Jouanneaux (1997) J. Appl. Cryst. 30, 265) and the Stephens Phenomenological method (J. Appl. Cryst. 32, 281 (1999)); as well as in-built difference Fourier calculation; and in-built bond length and angle calculation. Another feature (besides standard distance and angle bond restraints) is the ability to perform “same” bond-length restraints; which can be very useful for refinement of molecular organic structures. Other features include the ability to output to a wide variety of third party programs such as Shelxs/Shelxl, Platon WinOrtep, EXPO, Struvir, WinStruplo, WinPlotr and GFOUR Fourier software. A graphical shell for Windows, displaying Rietveld plot files and calling the various ASCII input files is included with the distribution.

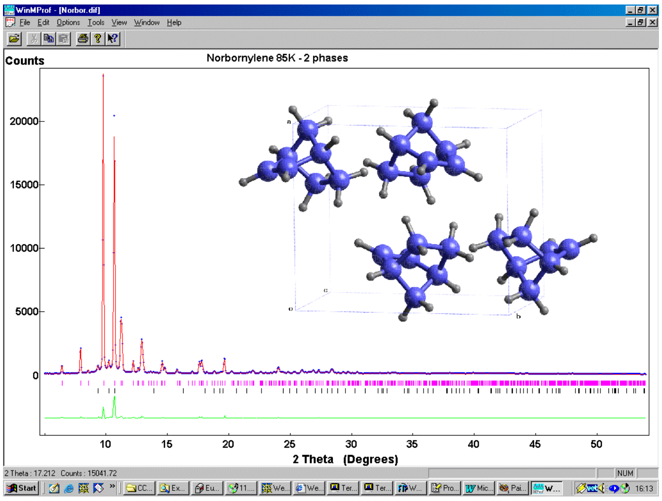


Fig 11: Example of a Norbornene Rietveld goodness of fit plot in the WinMprof MS-Windows interface overlaid with the structure of Norbornene. The refinement included the use of anisotropic pseudo-Voigt PSF (P.W. Stephens (1999) J. Appl. Cryst. 32, 281) and Bayesian constraints on distances and angles in the molecules. As cited in M. Brunelli, A.N. Fitch, A. Jouanneaux and A.J. Mora “Crystal and molecular structures of norbornene” Zeitschrift fur Kristallographie vol 216, p 51-55 (2001).

XND

Rietveld structure refinement on normal and incommensurate structures and real-time powder diffraction refinement

OS:

PC Windows, UNIX, Linux, SunOS SGI IRIX, HP-UX ("c" source code included)

Contact: Jean-Francois Berar

Email: berar@polycnrs-gre.fr

WWW: http://www-cristallo.polycnrs-gre.fr/xnd/xnd.html

Download: ftp://ftp.polycnrs-gre.fr/pub/xnd/

References: *G. Baldinozzi, D. Grebille and J-F. Bérar, Proceedings of Aperiodic' 97, World Scientific (1999) p297-301.*

The major abilities of the XND Rietveld includes the refinement of incommensurate structures; refinement of multiple datasets (Bragg-Brentano X-ray, neutron, synchrotron); and of combined refinement of a range of powder diffraction patterns changing by a parameter (such as temperature, pressure, magnetic field, electric field, time, etc). If the structure is unknown, the lattice can be modelled by the Le Bail method; and if the lattice is unknown, d-spacings can be modelled. XND can handle anomalous scattering for the analysis of multi-wavelength experiments (such as distinguishing the valences of ions in complex ferrites).

Control of the refinement is performed via the editing of an ASCII control file. Other features include the ability to handle variable step scans; modelling of parasitic wavelengths (Tungsten, K-beta, etc); and setting up equations linking together various parameters. Besides the main XND documentation, some tips on using XND are available at http://www.ccp14.ac.uk/tutorial/xnd/.

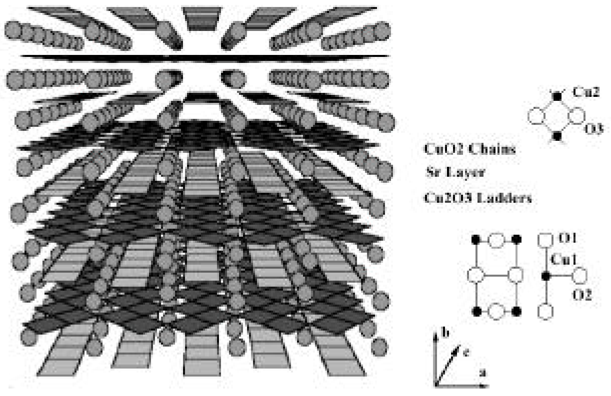


Fig 12: Example of an XND refined structure; an idealised view of the incommensurate $Sr_{14}Cu_{24}O_{41}$ type structure as cited in : S. Pachot, C. Darie, J.F. Berar, P. Bordet, C. Bougerol-Chaillout; "Refinement of incommensurate misfit compounds : $Sr_{14-x}Ca_xCu_{24}O_{41}$" EPDIC 7, Barcelona; to appear in Material Sciences Forum.

XRS-82/DLS

Rietveld structure refinement (with restraints) and distance least squares refinement

OS: UNIX, Linux, VMS, DOS, OS/2

Contact: Christian Baerlocher

Email: ch.baerlocher@kristall.erdw.ethz.ch

WWW: http://www.kristall.ethz.ch/LFK/software/

Download: http://www.kristall.ethz.ch/LFK/software/xrs/

References: *Ch. Baerlocher: The X-ray Rietveld System, XRS-82, Version of September 1982. Institut fuer Kristallographie und Petrographie, ETH Zuerich* and *Ch. Baerlocher, A. Hepp, W.M. Meier: DLS-76, a program for the simulation of crystal structures by geometric refinement. Institut fuer Kristallographie und Petrographie, ETH Zuerich.*

XRS-82/DLS is a Rietveld system primarily associated with the modelling and refinement of complex zeolitic structures. The primary interface in controlling the program is a series of ASCII files. In principle, there is no limit to the number of atoms that XRD-82/DLS can handle; as long as there are more restraints (bonds/angles) than there are variable atom co-ordinates.

For assistance in generating DLS and XRS-82 control files, Kriber by Roland Bialek can be used (http://www.kristall.ethz.ch/LFK/software/kriber/).

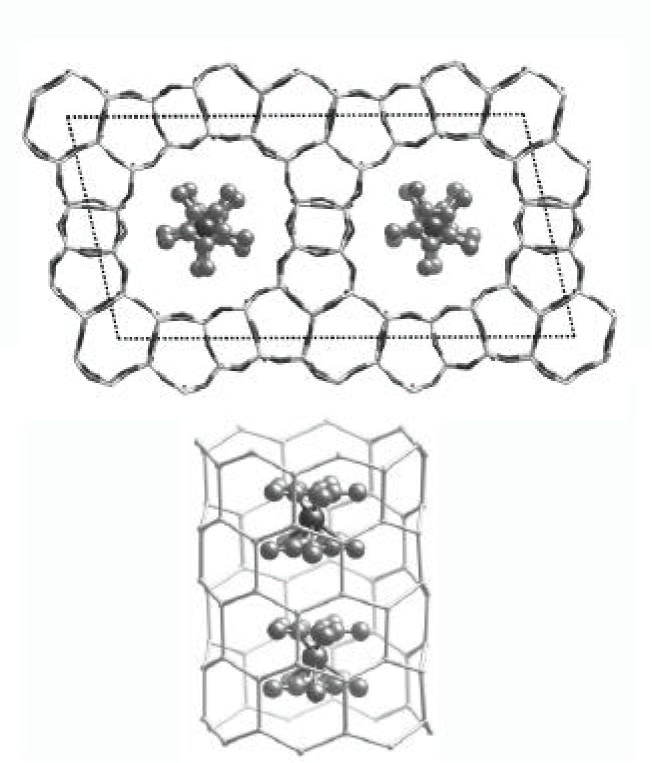


Fig 13: A 117 atom zeolite structure refined with XRS82/DLS as published in: Wessels, T., Baerlocher, Ch., McCusker L.B. and Creyghton, E.J. "An ordered form of the extra-large-pore zeolite UTD-1: its synthesis and structure analysis from powder diffraction data" (1999) J. Am. Chem. Soc., 121, 6242-6247

Dealing with unknown impurity phases

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INTRODUCTION

What do you do when you want to perform a Rietveld analysis of a particular material but have a substantial impurity phase and despite all your best attempts you can neither remove it from your sample nor index it from your diffraction pattern? Conventional wisdom would state that your chances of obtaining unbiased structural parameters are poor and that the best you can do is to manually exclude the offending impurity peaks. Standard Rietveld programs that are based upon a least-squares refinement algorithm cannot cope in an unbiased manner with an incomplete model description of the data. This is just the situation where Bayesian probability theory can come to the rescue. We can ask the question, “How do I perform a refinement on a powder diffraction pattern when I know that there is an impurity phase present but have no idea what that impurity phase may be?” This question is equivalent to stating that my diffraction pattern contains a component that I can model (known phases + background) and an additional positive, unknown contribution. It turns out that enforcing the positivity of the unknown component as an additive contribution is sufficient to produce excellent results [1].

The mathematical development of these ideas has been presented elsewhere [1,2] and results in a modified χ^2 goodness of fit function that is shown in Fig. 1. For observed data that are less than the model function, the new goodness of fit behaves essentially identically to the standard χ^2. This is to be expected since such points are unlikely to be associated with an impurity contribution. On the other hand, when the observed data value is substantially greater than the fitted model value, then the new goodness of fit brings a substantially smaller penalty (the function varies logarithmically) than the quadratic behaviour of the standard χ^2. Again this is just what is required to minimise the impact of any impurity phase. Note also that the curvature of the new goodness of fit is shallower than the standard χ^2. This means that quoted standard deviations will be higher for refinements using the new goodness of fit. This is to be expected as the allowance for an impurity phase brings a greater uncertainty into the model parameter values.

EXPERIMENTAL

Diffraction patterns of yttria and rutile were collected on HRPD at ISIS. Results from the 5% yttria : 95% rutile are shown in Fig 3. (The fitted diffraction pattern of pure yttria is shown in Fig 2 for comparison.) In order to accentuate the difference between the new goodness of fit function and standard least-squares analysis, we have chosen to refine the minority yttria phase treating the majority phase as the impurity (see Fig 3a). The excellent fit to the data for the modified χ^2 is shown in Fig 3b where we have graphically downweighted the observed points, which contribute least to the goodness of fit. This emphasizes what the algorithm is effectively doing – large positive (obs-calc)/esd values are essentially ignored. In effect, the algorithm is optimally excluding those regions that do not contribute to the model. The relative calculated peak intensities agree very well with the results for pure yttria (Fig 2).

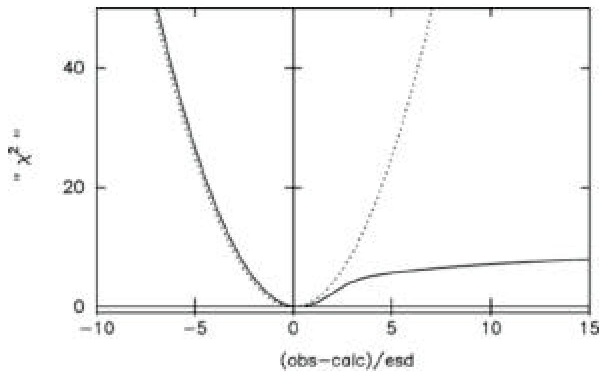

Fig. 1 The modified robust goodness of fit function (solid line) compared with the standard quadratic least-squares function.

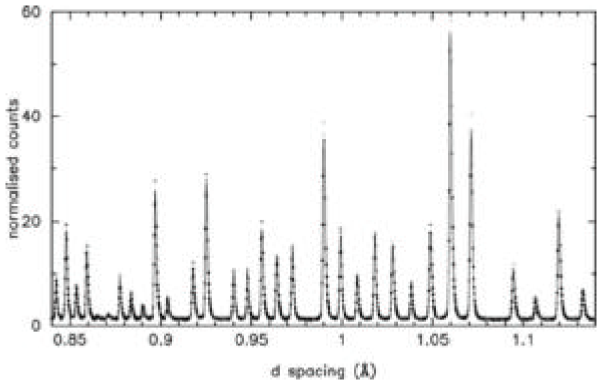

Fig. 2. The observed and calculated diffraction patterns for pure yttria determined on HRPD at ISIS

Least squares analysis (Fig 3c) produces a completely different result – all points are considered with no downweighting for possible impurities. The first obvious effect is that the refined background is too high. The reason for this is obvious since the strong impurity peaks lift up the model fit. The relative peak intensities are however also very different from the correct values suggesting that the refined structural parameters are substantially in error. This is indeed the case and is borne out by analysis of the refined zirconium and oxygen coordinates, which are shown graphically in Fig 4 as a function of yttia content. We briefly consider the other refined parameters (a fuller analysis is given in [1]). The scale factor is correct within estimated standard deviation (esd’s) for the robust analysis but behaves wildly for the standard least squares, exceeding 1000% for 25% yttria content. The least-squares analysis of the lattice constant also becomes increasingly unreliable as the refinement locks into peaks associated with rutile as well as yttria. On the other hand, the lattice constant from the robust refinement is satisfyingly stable; the esd’s increase as the yttria content decreases (the 5% e.s.d. is some five times larger than the 100% value) but all results lie within a standard deviation of the correct result.

CONCLUSIONS

Least-squares Rietveld analysis is the best and least-biased method of structure refinement from a powder diffraction pattern when the data can be fully modeled. However, when there is an unmodeled impurity contribution in the diffraction pattern, least-squares analysis gives biased results. In the example discussed in this contribution, significant deviations from the correct parameter values occur when there is as little as a 10% impurity contribution. At higher impurity levels, least-squares analysis is completely unreliable. These problems may, however, be overcome if the existence of an unknown impurity contribution is built into the refinement algorithm. While it might seem to be a logical inconsistency to build in information about an unknown contribution, Bayesian probability theory provides a framework for doing just this. Only two broad assumptions are necessary to derive an appropriate modified probability distribution function. These are (i) that the impurity contribution must be intrinsically positive and (ii) that its magnitude, *A*, is unknown and thus best modeled by a Jeffreys' prior, given by $p(A|I) \propto 1/A$ for $A > 0$ and $p(A|I) = 0$ for $A \leq 0$. This produces a modified `χ^2' function (see Fig. 1) that effectively excludes the impact of impurity peaks.

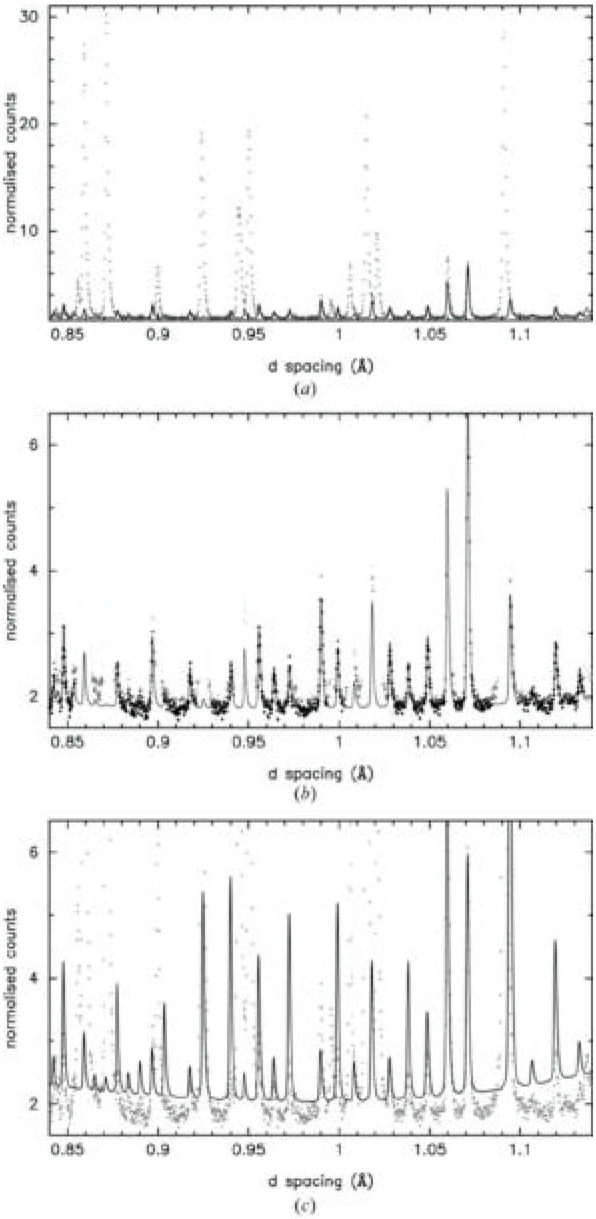

Fig 3. Observed and calculated diffraction patterns for the composition 5% yttria : 95% rutile: (*a*) robust analysis showing the full observed data range (the grey scale described in the text not used in this figure); (*b*) expanded region highlighting the successful robust refinement (the down-weighting grey scale is used in this figure); (*c*) the least-squares analysis showing the poor agreement between the observed and calculated patterns.

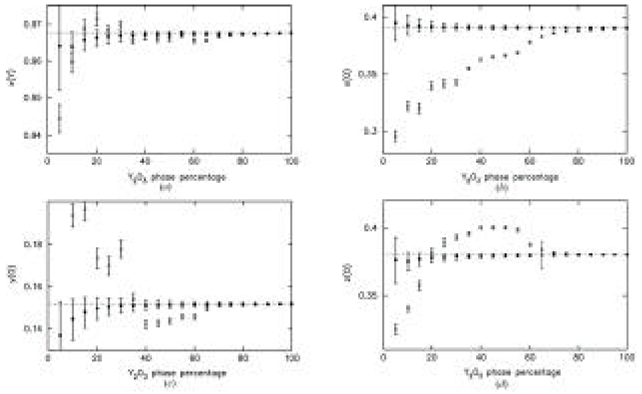

Fig 4. The refined atomic coordinates of yttria plotted as a function of yttria composition. Open circles and filled squares correspond to the least-squares and robust analyses, respectively. (*a*) The yttrium *x* coordinate. (*b*), (*c*), (*d*) The oxygen *x*, *y* and *z* coordinates. The dotted lines correspond to the correct values obtained from least-squares refinement of the pure-yttria diffraction

The results discussed in briefly in this contribution and more extensively in [1] show that the improvement over conventional least-squares analysis is dramatic. Indeed, even in the presence of very substantial impurity contributions (see Fig. 4) the refined structural parameters are within a standard deviation of their correct values.

It must, however, be stated as a final caveat that care should be taken with this approach and the use of an algorithm that can cope with the presence of impurities should be seen as a last resort. Indeed, every effort should be made to determine all the phases in a sample. It is much more desirable to include the impurity phase in a standard Rietveld refinement.

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Rietveld refinements with JANA2000

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The system of computer programs JANA2000 is designed for the refinement and analysis of incommensurately modulated structures and composite crystals as well as periodic crystals. It incorporates many different possibilities to use restrictions on the parameters, like the use of non-crystallographic site symmetry and the direct refinement of temperature factors in the TLS formalism. Here we describe the powder module of JANA2000, that allows Rietveld refinements and the LeBail fits of powder diffraction data with the full functionality of the JANA2000 system, including Rietveld refinement of incommensurate structures.

INTRODUCTION

Rietveld refinement of crystal structures against powder diffraction data has become a standard technique for the structural analysis of compounds with small unit cells. Synchrotron radiation is responsible for a very small instrumental line width. The increased resolution has pushed the limits of powder diffraction towards the analysis of more complex compounds. The much better signal to noise ratio of diffractometers based on synchrotron radiation has allowed the study of weak superlattice effects. Concomitantly, the past decade has seen the development of profile functions, that accurately describe the peculiar shapes of these high-resolution reflections. These developments are available in several extensive software packages like GSAS [1].

Incommensurately modulated structures and incommensurate composite crystals have been studied by quantitative single-crystal x-ray diffraction for the past 25 years [2]. The description of their structures and symmetries requires the superspace theory [3]. Presently, the system of computer programs JANA2000 provides the most extensive set of tools for the analysis of incommensurate structures [4]. JANA2000 has several unique features, including a great flexibility in the choice of the types of modulation functions. Many options in JANA2000 are useful for the analysis of periodic crystals too. Examples are the possibility to refine the temperature parameters in terms of rigid-body motions (TLS formalism), anharmonic temperature parameters and their modulations [5], and the possibility to apply restrictions according to non-crystallographic symmetries of molecules [6].

A powder module was introduced into JANA2000, in order to make all its features available for Rietveld refinement [4]. In this contribution we give a short introduction to incommensurate structures and we discus the specific problems that arise for the analysis of powder diffraction of aperiodic crystal structures. In the second part the importance is shown of the use of restrictions according to non-crystallographic symmetries.

INCOMMENSURATE CRYSTALS

Incommensurately modulated crystals lack 3-dimensional translation symmetry [2]. Yet their structures have perfect long-range order, as it is reflected by a diffraction pattern consisting of sharp Bragg reflections. All Bragg reflections can be indexed with four or more integers according to

$$\mathbf{H} = h\,\mathbf{a}^* + k\,\mathbf{b}^* + l\,\mathbf{c}^* + m_1\,\mathbf{q}^1 + \cdots + m_d\,\mathbf{q}^d$$

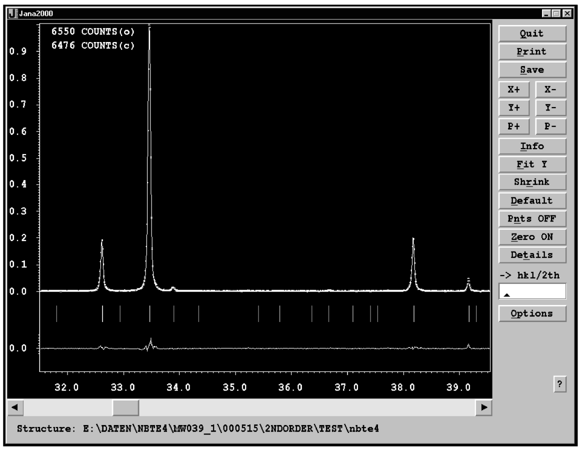
$\{\mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*\}$ form the reciprocal lattice of the basic or average structure. The modulation wave vectors $\mathbf{q}^j$ are given as a linear combination of the 3 basis vectors of reciprocal lattice of the average structure:

$$\mathbf{q}^j = s_{j1}\mathbf{a}^* + s_{j2}\mathbf{b}^* + s_{j3}\mathbf{c}^*$$

d is the dimension of the modulation; usually it is restricted to 1 or 2.

The main reflections (*h*, *k*, *l*, 0) form a reciprocal lattice. If satellites (*h*, *k*, *l*, *m*) of all orders |*m*| would be present, then they would lie dense on a line through reciprocal space. For the powder diffraction this implies, that there would be a dense set of reflections along the 2θ axis. Obviously, a full profile analysis with an infinite number of reflections is not possible. In real structures non-zero intensities are only observed up to a maximum order of the satellite index, usually up to |*m*| = 2. For applications of the Rietveld method to modulated structures it is thus required to restrict the maximum possible *m*-index to some value $|m|_{\max}$. This option has been included into the Rietveld module of JANA2000.

Figure 1 shows a screenshot of JANA2000 displaying the result of a Rietveld refinement of the incommensurately modulated structure of $NbTe_4$. The graphical user interface is visible, and the figure shows that JANA2000 offers many possibilities to vary and analyze the plot. With $|m|_{\max} = 2$ the reflections within this region of 2θ are all isolated. In Figure 2 the regions around 2θ = 31 deg. and around 2θ = 42 deg. are displayed. They show the good fit to the measured data, including relatively large intensities for some first-order satellites.



```
6550 COUNTS(o)
6476 COUNTS(c)
```

```
Structure: E:\DATEN\NBTE4\MW039_1\000515\2NDORDER\TEST\nbte4
```

Fig. 1 Screenshot of JANA2000 displaying the Rietveld plot of the incommensurately modulated structure of $NbTe_4$. With the "Plot Powder Profile" module the Rietveld plot or the result of the LeBail fit can be displayed in a great variety of ways. Information about the refinements and resulting parameters is available as a printable file.

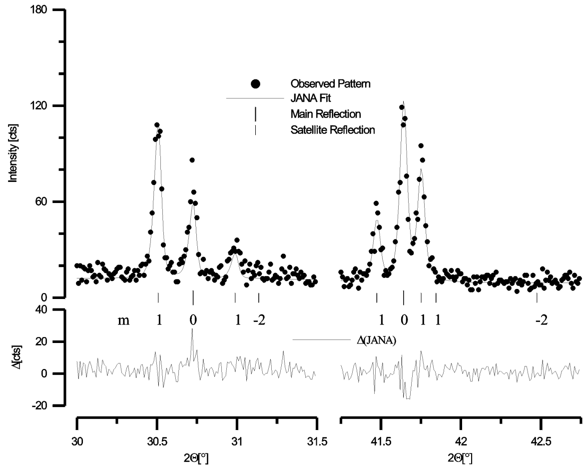


Fig. 2 .Two excerpts of the Rietveld plot of $NbTe_4$. Satellite reflections up to order $|m|_{max} = 2$ are shown.

Indeed, the Rietveld refinement resulted in basic structure parameters and modulation parameters that were equal to but less accurate than those obtained from the single-crystal refinement [4,7]. Composite crystals or incommensurate intergrowth compounds can be considered as the intergrowth of two incommensurately modulated structures. In the simplest example the first subsystem has main reflections (h, k, l, 0) while the second subsystem has main reflections (h, k, 0, m). The main reflections (h, k, 0, 0) are common to the two subsystems, while the remaining main reflections of one subsystem are satellites of the other subsystem. Reflections (h, k, l, m) with both l and m non zero are satellites of both subsystems. In order to describe all reflections with non-zero intensities, it is now necessary to restrict the minimum value of the pair ($|l|$, $|m|$) to some maximum value m_{max}. This option has been included into the powder module, and it is thus possible to perform Rietveld refinements of composite crystals with JANA2000.

NON-CRYSTALLOGRAPHIC SITE SYMMETRY

Because modulated structures are described as the sum of a basic structure with 3D translation symmetry and modulation functions, any computer program for modulated structures can also handle ordinary 3D periodic structures. In addition JANA2000 can treat many special structural features, like anharmonic temperature factors, the TLS formalism, rigid-bodies, and the non-crystallographic site symmetries. The crystal structure of CO_xC_{60} has been solved by synchrotron radiation x-ray powder diffraction at T = 25 K [8]. The C_{60} molecules form a cubic closed packed crystal with the CO molecules on the octahedral sites (space group $Pa\overline{3}$). Rietveld refinements using all 10 crystallographically independent atoms of the C_{60} molecule are not possible, because of the high correlations between these parameters. In the previous study Rietveld refinements were performed using a rigid body for the C_{60} molecule. Although anisotropic temperature parameters were used for this rigid body, the refinement led to an almost isotropic temperature tensor (Fig. 3a). The reason is, that this tensor can only describe displacements of the rigid body, and the latter are expected to be equal in all directions. Alternatively, the C_{60} molecule can be described as a molecule with icosahedral symmetry. Then there is only one independent atom.

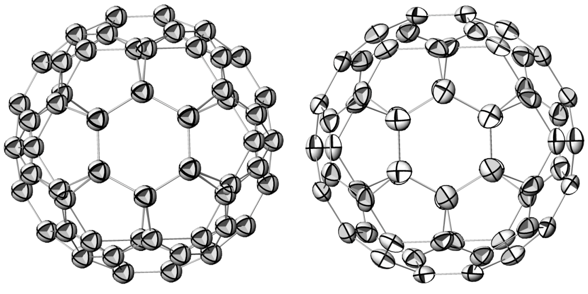


Fig. 3 The structure of C_{60} molecule in CO_xC_{60} after refinement with (left:) rigid bodies in gsas, and (right:) icosahedral site symmetry in JANA2000. Thermal ellipsoids are shown.

Refinement of its coordinates allows for the variation of the size of the molecule and the ratio of the long and short bonds. This refinement with JANA2000 lead to virtually the same geometry of the molecule as the rigid body. However, the temperature parameters were now a single temperature tensor for the independent atom. The icosahedral symmetry transplants this tensor towards all other 59 atoms, whereby the directions of the principal axes are transformed according to the point symmetry. As it follows from the refinement this description leads to an anisotropic temperature movement, that clearly reflects librations of the molecules that are larger than their translations, in accordance with the expectations (Fig. 3b). The consequence of this improved description of the electron density was a significant change in the position of the CO molecule, and a significant change in occupancy of this site from $x = 0.67$ to $x = 0.85$ in the new refinement.

CONCLUSIONS

The system of computer programs JANA2000 can be used for the LeBail fit of powder diffraction data as well as for Rietveld refinements. JANA2000 incorporates parameters for the description of modulated and composite crystals and for atypical structural features of ordinary crystals, like anharmonic temperature tensors and non-crystallographic site symmetries. All these options are available for the Rietveld refinement.

Financial support was obtained from the German Science Foundation (DFG), the FCI, and the Grant Agency of the Czech Republic (grant 202/00/0645).}

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[8] Van Smaalen, S., Dinnebier, R. E., Holleman, I., Von Helden, G. \& Meijer, G. (1998). Phys. Rev. B**57**, 6321.

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- powder diffraction pattern visualization, peak profiling and indexing software
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- Rietveld refinement packages
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Computer Corner

Updates on Freely Available Crystallographic and Powder Diffraction Software
(Suggestions, corrections, comments appreciated; especially if you know of new program features, program updates and announcements that should be mentioned here).

Lachlan M. D. Cranswick
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E-mail: l.m.d.cranswick@dl.ac.uk
WWW: http://www.ccp14.ac.uk - http://ccp14.sims.nrc.ca - http://ccp14.semo.edu

CCP14 US and Canadian full Software mirrors

Thanks to Ronald Rogge and Ian Swainson of the NRC, Chalk River, Ontaria, Canada and Marcus Bond of Southeast Missouri State University, USA, the CCP14 (Collaborative Computational Project No 14 for Single Crystal and Powder Diffraction) now has full mirrors of the main UK website in Canada and the USA.

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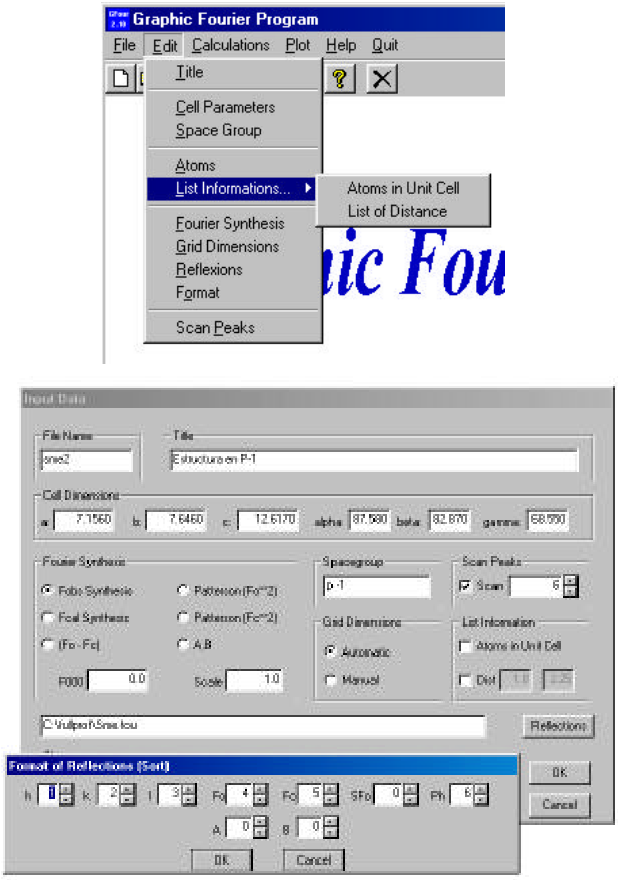
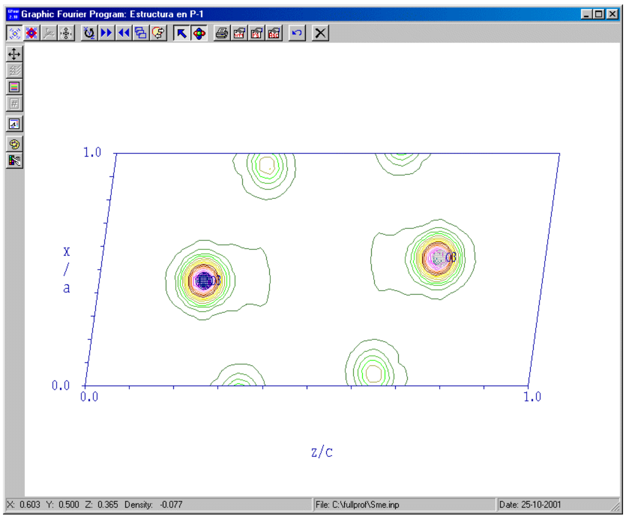
GFOUR for Windows Fourier Map Software by Javier Gonzalez-Platas and Juan Rodriguez-Carvajal

The latest GFOUR Fourier Map generation, peak find and contour map display software (updated 25th September 2001) is now available at ftp://charybde.saclay.cea.fr/pub/divers/fullprof.2k/Windows/ and CCP14 mirrors. This includes new additions and features to the Graphical User Interface (GUI) such as the ability to animate through the Fourier contour map.
While GFOUR interlinks with the Fullprof Rietveld software; it can be used by any Rietveld program that outputs files in a suitable format (the latest WinMprof Rietveld outputs GFOUR input and reflection files). GFOUR also includes the ability to define the format of the reflection file via a Graphical User Interface (GUI) anduses flexible, free format input files which will pleasantly surprise people used to programs such as the 1960's/1970's/1980's/1990's vintage Fordap input files of ones and zeros.



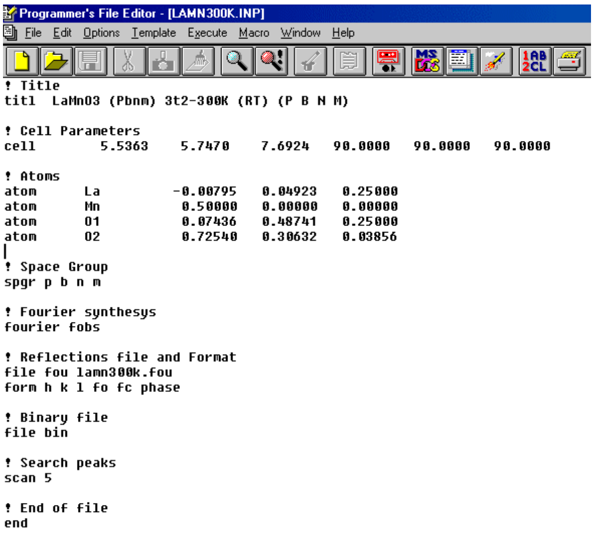
File Name: sme2
Title: Estructura en P-1
Cell Dimensions: a: 7.1560 b: 7.6460 c: 12.6170 alpha: 87.580 beta: 82.870 gamma: 68.590
● Fobs Synthesis
F000: 0.0 Scale: 1.0
Spacegroup: p -1
Scan Peaks: ☑ Scan 6
● Automatic
C:\fullprof\Sme.fou
h 1 k 2 l 3 Fo 4 Fc 5 SFo 0 Ph 6
A 0 B 0

Fig 1: *a) example of the GFOUR menu system and b) example of the "File, New" menu option including the ability to define the format of the reflection file via the GFOUR Graphical User Interface (GUI)*



X: 0.603 Y: 0.500 Z: 0.365 Density: -0.077
File: C:\fullprof\Sme.inp
Date: 25-10-2001

Fig 2: *GFOUR displaying a Fourier map; including the automatic labelling of atoms near the plane being displayed.*

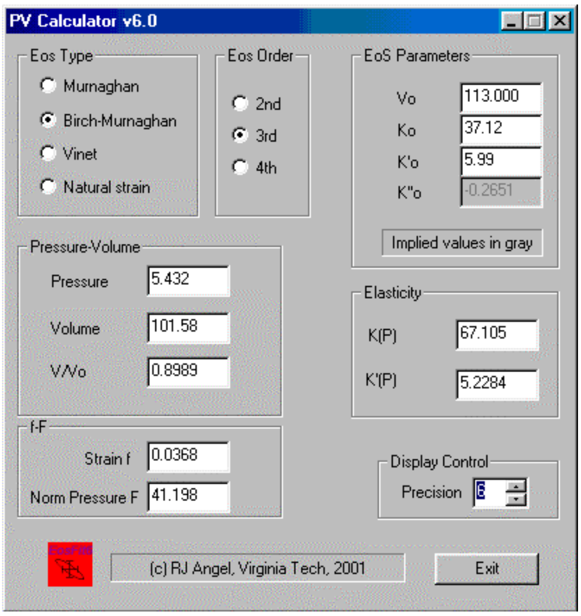


```
! Title
titl  LaMnO3 (Pbnm) 3t2-300K (RT) (P B N M)

! Cell Parameters
cell        5.5363    5.7470    7.6924   90.0000   90.0000   90.0000

! Atoms
atom      La        -0.00795   0.04923   0.25000
atom      Mn         0.50000   0.00000   0.00000
atom      O1         0.07436   0.48741   0.25000
atom      O2         0.72540   0.30632   0.03856

! Space Group
spgr p b n m

! Fourier synthesys
fourier fobs

! Reflections file and Format
file fou lamn300k.fou
form h k l fo fc phase

! Binary file
file bin

! Search peaks
scan 5

! End of file
end
```

Fig 3: *Example GFOUR input file viewed via the freeware PFE (Programmer's File Editor) for Windows (http://www.lancs.ac.uk/people/cpaap/pfe/).*

Ross Angel Equation of State software (EOSFIT, P-V Calculator) software

Software for Equation of State analysis by Ross Angel at Virginia Tech is now available on the web at http://vtso.geol.vt.edu/rja/soft/. EosFit5.2 for DOS (it also runs under a DOS box in MS-Windows) handles Pressure-Volume-Temperature data; Pressure-Volume data; and fits Murnaghan, Birch-Murnaghan, natural strain and Vinet equations of state. The P-V Calculator version 6 for Windows performs Pressure-Volume calculations, and provides f, F, and K and K' at pressure. This software can be useful during these types of experiments during diffraction beamtime at synchrotron facilities.



Eos Type: ○ Murnaghan ● Birch-Murnaghan ○ Vinet ○ Natural strain

Eos Order: ○ 2nd ● 3rd ○ 4th

EoS Parameters: Vo 113.000; Ko 37.12; K'o 5.99; K"o -0.2651

Pressure-Volume: Pressure 5.432; Volume 101.58; V/Vo 0.8989

Elasticity: K(P) 67.105; K'(P) 5.2284

f-F: Strain f 0.0368; Norm Pressure F 41.198

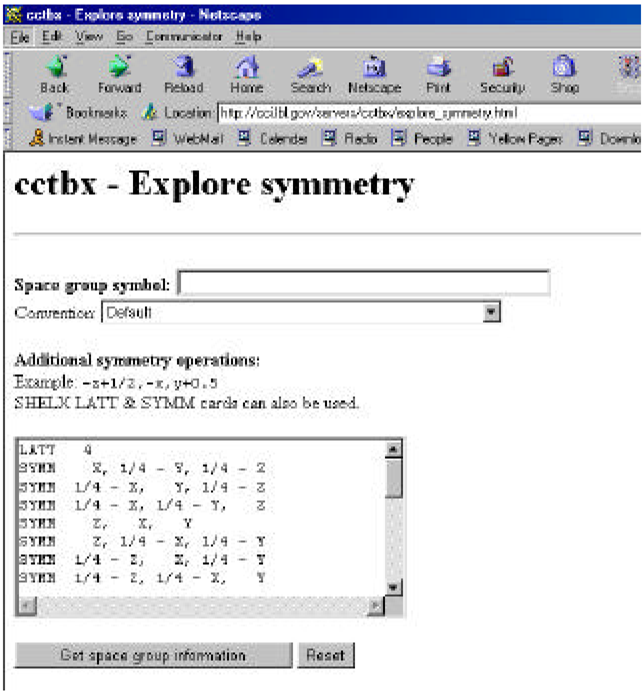
Precision 6

(c) RJ Angel, Virginia Tech, 2001

Fig 4: *Screen images of P-V (Pressure, Volume) Calculator 6.0 for Windows by Ross Angel*

Computational Crystallography Toolbox (CCTBX) by the Computational Crystallography Initiative (CCI)

The CCTBX is an Open Source project for those interested in crystallographic software development. Organized as a set of ANSI C++ classes with Python bindings, it presently has a unit cell toolbox (uctbx), a space group toolbox (sgtbx) and an element toolbox (eltbx) for the handling of scattering factors and other element properties. The CCTBX can be downloaded at its homesite at: http://cctbx.sourceforge.net/ or CCP14 mirrors.



Location: http://cci.lbl.gov/servers/cctbx/explore_symmetry.html

cctbx - Explore symmetry

Space group symbol:

Convention: Default

Additional symmetry operations:
Example: -z+1/2,-x,y+0.5
SHELX LATT & SYMM cards can also be used.

```
LATT    4
SYMM     X, 1/4 - Y, 1/4 - Z
SYMM  1/4 - X,     Y, 1/4 - Z
SYMM  1/4 - X, 1/4 - Y,     Z
SYMM     Z,     X,     Y
SYMM     Z, 1/4 - X, 1/4 - Y
SYMM  1/4 - Z,     X, 1/4 - Y
SYMM  1/4 - Z, 1/4 - X,     Y
```

Fig 5: *CCTBX web interface for determining spacegroups from symmetry operators and visa-versa at: http://cci.lbl.gov/servers/cctbx/explore_symmetry.html. It can also handle Shelx style input for discovering the spacegroup from symmetry operators. Refer "Algorithms for deriving crystallographic space-group information", R. W. Grosse-Kunstleve Acta Cryst. 1999, A55:383-395*

ObjCryst++ "open source" crystallographic source code library and FOX "real space" structure solution software byVincent Favre-Nicolin

A new resource for crystallography and powder diffraction software development is Vincent Favre-Nicolin's ObjCryst++ crystallographic source code library whose homesite is at http://objcryst.sourceforge.net/ (with mirrors at the CCP14). The library presently concentrates on source code for the global optimisation of crystal structures from diffraction data. This has been released under the "The Artistic License" (described at: http://www.gnu.org/philosophy/license-list.html#ArtisticLicense).

A further development from ObjCryst++ is FOX (Free Objects for Xtallography) for Linux, MS-Windows and source code. FOX can be used both for educational purposes as well as to solve crystal structures from powder diffraction data using global optimisation methods. Objects or components of a crystal structure can be described as a) atoms, b) organic molecules using a Z-Matrix description, c) or inorganic polyhedra.

Of the many notable FOX attributes, one is the ability to overpopulate your cell with atoms or polyhedral objects combined with a "Dynamical Occupancy Correction". Thus during global optimisation, FOX can merge atoms on shared and special positions using "Dynamical Occupancy Correction". These features make FOX attractive for solving inorganic structures where it is not known (or not possible to guess) which atoms are on general or special positions; and/or you are not sure of the connectivity between different polyhedral objects. A step-by-step HOWTO web tutorial on using FOX to solve structures is viewable at
http://objcryst.sourceforge.net/Fox/quickstart.html
and CCP14 mirrors.

Because FOX is supplied with source code as part of it being an "open source" project, it is possible for users to build on the existing algorithms in FOX and expand its functionality and optimisation criteria.

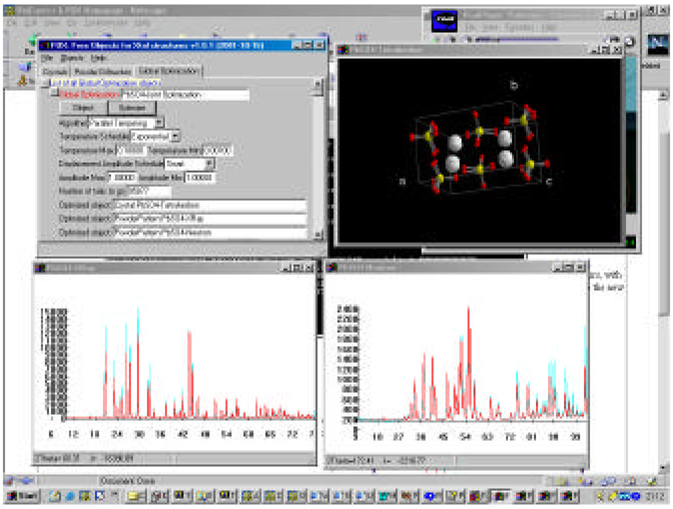


Fig 6: *Screen image of FOX solving an inorganic structure (Lead Sulphate) by simultaneous fitting to Neutron and X_ray diffraction data. The data and structure are being simultaneously displayed and updated in real time during the structure solution process. In the crystal structure display (top right), you can visually see the "Dynamical Occupancy Correction" combining atoms and sulphate groups (defined as tetrahedra) at the special positions.*

Freely available polyhedral structure viewing software

There are many programs are available for generating ORTEP structure diagrams and ball and stick structure drawing suitable for chemical crystallography. However, as freely available polyhedral structure drawing software is not so obvious to find, following is a list of software. It should be noted that commercial programs exist with this functionality; including Atoms for Windows (http://www.shapesoftware.com), Carine for Mac and Windows (http://www.esm-software.com/carine/) CrystalMaker for Mac (http://www.crystalmaker.com/) and Diamond for Windows (http://www.crystalimpact.com/diamond/).

Balls and Sticks for Windows by Sung J. Kang & Tadashi C. Ozawa

A newly announced program for the visualisation and animation of crystal structures including polyhedral structures and a mixture of polyhedral and ball and stick structures (with the emphasis on *"ease of use"*) is the "Balls and Sticks" software by Sung J. Kang and Tadashi C. Ozawa. Its website is viewable via
http://www.toycrate.org/. "Balls and Sticks" will import CIF files, then polyhedra and bonds can be defined using point and click on the mouse. All options are implemented via the Graphical User Interface (GUI)

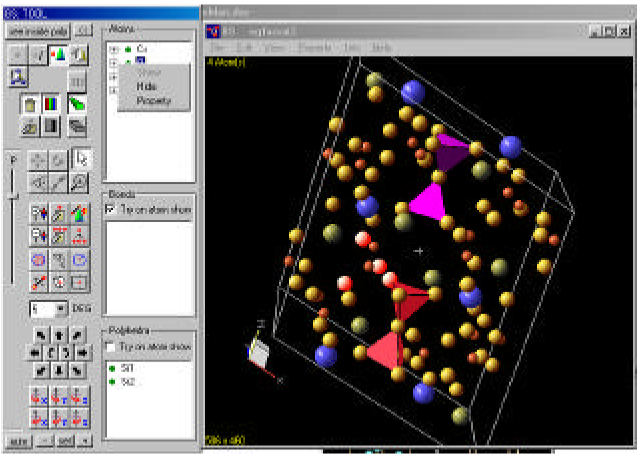


Fig 7: *"Balls and Sticks" interface where new polyhedra are defined by pointing and clicking on the vertices atoms ([CONTROL] button is used to select multiple atoms). Ball atom display can be resized individually or en-masse by right clicking in the Atoms dialog and selecting properties.*

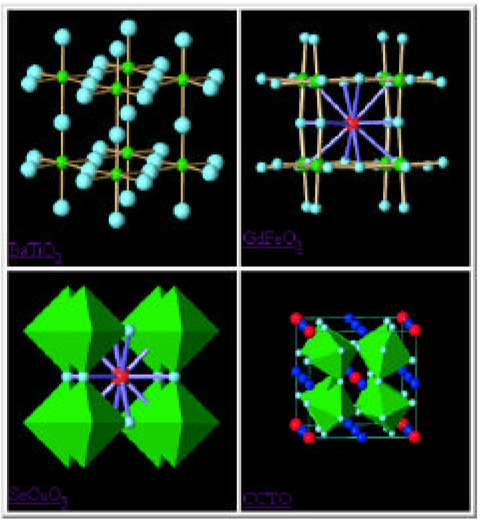


Fig 8: *Static screen capture of crystal structure GIF animations generated by Balls and Sticks as viewable on the Balls and Sticks website via http://www.toycrate.org/.*

DrawXTL for Windows, Mac, UNIX and C source code by Larry Finger and Martin Kroeker

DrawXTL version 3 is downloadable off the web at http://www.lwfinger.net/drawxtl/ and CCP14 mirrors. It will render ball and stick structures; ORTEPs, and structures in polyhedra of any desired shape. Besides its own native format, DrawXTL can read CIF, CSD, GSAS, SCHAKAL, and SHELX formats. Structures can be rendered in VRML1, and structure animations created in VRML 2 format (requiring a VRML2 viewer to see the animations)

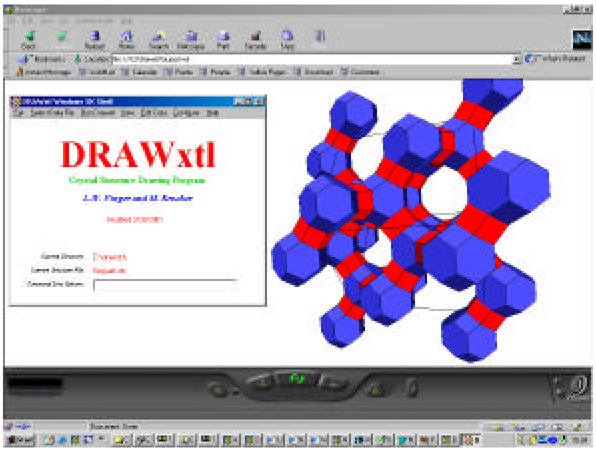


Fig 9: *Drawxtl Shell for Windows on the left overlaid with VRML structure displayed in the interactive COSMO VRML viewer (installed as a "plugin" within Netscape).*

Struvir by Armel Le Bail

Struvir is an Armel Le Bail port of the original Reinhard Fischer's Struplo code (R.X. Fischer, J. Appl. Cryst. 18 (1985) 258-262). The software modification history is somewhat more complicated, involving modifications or documentation by: A. Le Lirzin, D. Kassner, Tim McCarthy, Donald L. Ward, Donald L. Ward, W. H. Baur and Mark Koennecke. Structures can be outputted in VRML format (Virtual Reality Modelling Language), Povray files (http://www.povray.org), as well as the traditional HPGL and Postscript (via the PSPLOT program included with the distribution). Traditional Struplo91 ASCII files are used for input.

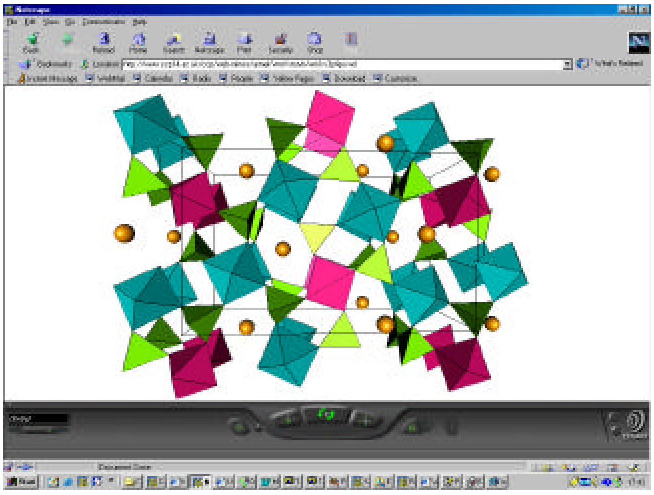


Fig 10: VRML *Structure generated by Struvir and displayed in the interactive COSMO VRML viewer (installed as a "plugin" within Netscape).*

GUI WinStruplo by Louis Farrugia

GUI WinStruplo is a port of Armel Le Bails Struvir code implemented by Louis Farrugia. Louis has added a graphical user interface with point and click operation, and the ability to import a large variety of file formats. File formats include CIF, Shelx, GSAS, Fullprof and GSAS and it is available via Louis Farrugia's site at Glasgow University, http://www.chem.gla.ac.uk/~louis/software/.

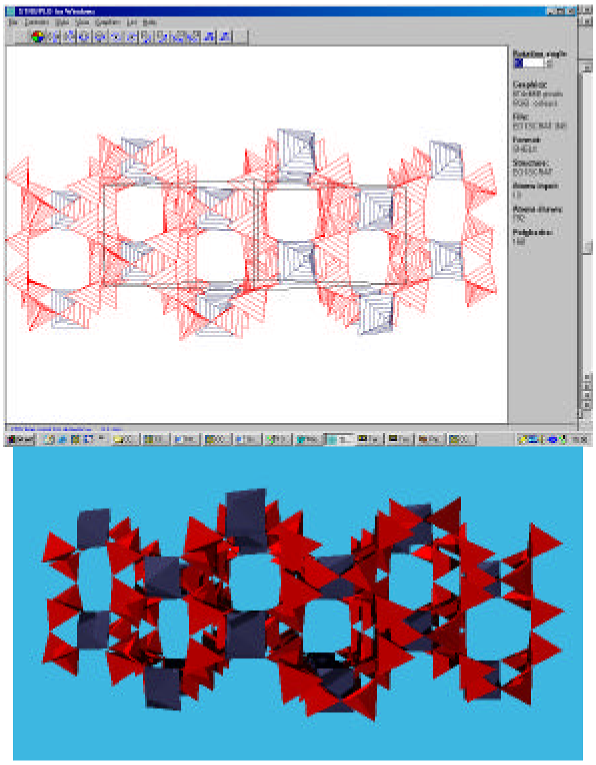


Fig 11: a) *GUI WinSTRUPLO importing a structure ready for output to supported formats such as HPGL, Postscript, VRML or Povray (freeware photorealistical rendering software – http://www.povray.org). b) Structure rendered by Porvay.*

Glassvir by Armel Le Bail for polyhedral viewing of glass models generated by RMC (Reverse Monte Carlo)

Glassvir by Armel Le Bail is available at http://sdpd.univ-lemans.fr/glasses/glassvir.html and is designed for the generation of interactive wire-frame and polyhedral VRML views of glasses modelled by RMC; with the input being that of the RMC config file (.cfg). Some available RMC (Reverse Monte Carlo) modelling software includes that of Robert McGreevy's; described at http://www.studsvik.uu.se/software/rmc/rmc.htm and downloadable via ftp://www.studsvik.uu.se/pub/rmc_mcgr/.

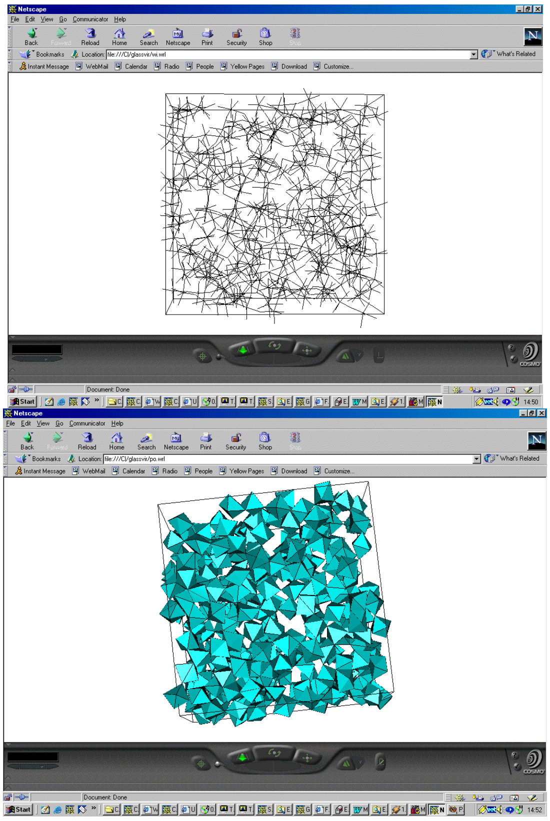


Fig 12: a) Glassvir generated *"wireframe" structure of a RMC modelled glass in VRML format as viewed interactively in the COSMO VRML viewer (in this case installed as a Netscape plugin) and b) polyhedral view of an RMC modelled glass in VRML format.*

Xtaldraw (Shareware) by Kurt L. Bartelmehs and Bob Downs

The Xtaldraw shareware software has its webpage at http://www.infotech.ns.utexas.edu/crystal/ and CCP14 mirrors. Crystal structure information is entered into a free format ASCII control file followed by running Xtaldraw. Keyboard and mouse control can then be used to generate the required view for rendering as a GIF file. Spheres, ellipsoids, bonds and polyhedra can be rendered by Xtaldraw.

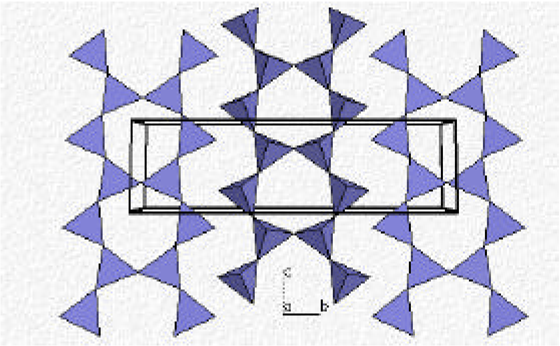
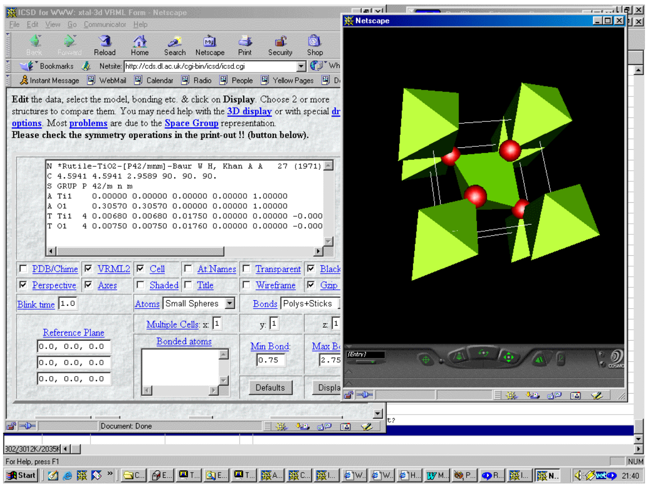


Fig 13: *Silicate as rendered by XtalDraw.*

Xtal-3d by Marcus Hewat (also part of Alan Hewat's ICSD for WWW)

Xtal3D by Marcus Hewat is available at http://barns.ill.fr/dif/icsd/xtal-3d.html and will render the structure into the interactive VRML (Virtual Reality Modelling Language). It can be used as a standalone command line or GUI based program; as well as via a web interface. Xtal3D is also included with Alan Hewat's "ICSD for Web" which has its master website at http://barns.ill.fr/dif/icsd/.



Netsite: http://cds.dl.ac.uk/cgi-bin/icsd/icsd.cgi

Edit the data, select the model, bonding etc. & click on **Display**. Choose 2 or more structures to compare them. You may need help with the 3D display or with special dr options. Most problems are due to the Space Group representation.
Please check the symmetry operations in the print-out !! (button below).

```
N *Rutile-TiO2-[P42/mnm]-Baur W H, Khan A A   27 (1971)
C 4.5941 4.5941 2.9589 90. 90. 90.
S GRUP P 42/m n m
A Ti1     0.00000 0.00000 0.00000 0.00000 1.00000
A O1      0.30570 0.30570 0.00000 0.00000 1.00000
T Ti1   4 0.00680 0.00680 0.01750 0.00000 0.00000 -0.000
T O1    4 0.00750 0.00750 0.01760 0.00000 0.00000 -0.000
```

☐ PDB/Chime ☑ VRML2 ☑ Cell ☐ At.Names ☐ Transparent ☑ Black
☑ Perspective ☑ Axes ☐ Shaded ☐ Title ☐ Wireframe ☑ Gzip
Blink time 1.0
Atoms Small Spheres
Bonds Polys+Sticks
Multiple Cells: x: 1 y: 1 z: 1
Reference Plane 0.0, 0.0, 0.0 / 0.0, 0.0, 0.0 / 0.0, 0.0, 0.0
Bonded atoms
Min Bond: 0.75
Max Bo 2.75

Fig 14: *A polyhedral view of rutile as rendered into VRML by Xtal3D within the ICSD for WWW database.*

Updated Gretep (Grenoble Thermal Ellipsoids Plot Program) by Jean Laugier and Bernard Bochu

The latest version of Gretep for ball and stick structure plotting allows for i) creating Metal-Ring bonds ii) bond labels horizontal or oblique to the bond and iii) custom bond colours. While using these features are quite elementary via the Gretep Graphical User Interface (GUI), there are also web tutorials via the Gretep website at http://www.ccp14.ac.uk/tutorial/lmgp/#gretep and can be downloaded at:
http://www.ccp14.ac.uk/ccp/web-mirrors/lmgp-laugier-bochu/.

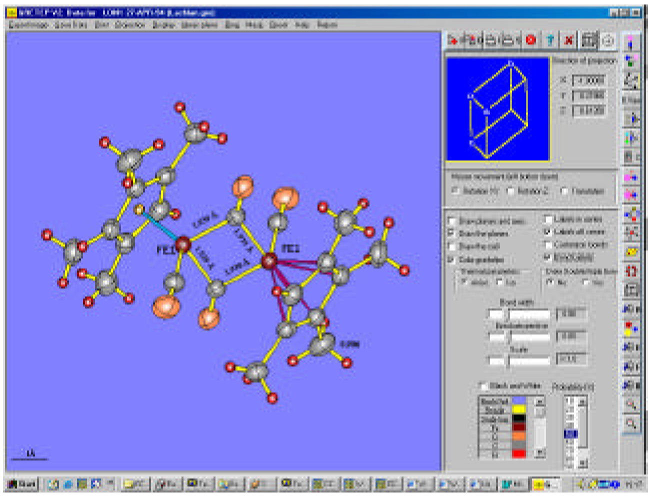


Fig 15: *Gretep screen image showing Metal-atom bonds; bond labels and custom bond colours (not evident in a black and white newsletter).*

Crysfire by Robin Shirley and Chekcell by Jean Laugier and Bernard Bochu powder indexing software updates

It can be useful to regularly check for software updates, bug fixes and new features; Crysfire and Chekcell being no exceptions. Both the Crysfire powder indexing suite and Chekcell have had miscellaneous bug fix updates since the time of the last CPD newsletter. The Crysfire webpage is at http://www.ccp14.ac.uk/tutorial/crys/ and with the Chekcell homepage at http://www.ccp14.ac.uk/tutorial/lmgp/#chekcell.

Updates in the "EFLECH" automatic fundamental parameters peak hunting and profile fitting program and "Index" powder indexing software by Jörg Bergmann

Eflech and Index have undergone miscellaneous improvements and are available at http://www.bgmn.de/related.html and CCP14 mirrors. Traditionally, Eflech will automatically hunt for peaks in a powder diffraction pattern using the fundamental parameters peak profiling model to generate a peak listing with a covariance matrix. As using "fundamental parameters" fitting is almost akin to running the sample on an "ideal" diffractometer, properly modelled peak positions can be of very high accuracy. The "Index" program will then attempt to index the Eflech determined powder peaks while making use of the covariance matrix also generated by Eflech. Recent improvements include fixing a bug for the triclinic search algorithm; changing some internal searching algorithm constants; and a new feature which will output a variety of trial cells (in cases where the information is not sufficient for a lone unambiguous solution). The latest EFLECH/Index combination is also distributed for Linux (compiled on SuSE Linux 7.2), as well as the traditional DOS, Windows and OS/2 binaries.

Rietveld Software Updates (as of late October 2001):

Hugo Rietveld website:
    http://home.wxs.nl/~rietv025/
BGMN (15th September 2001)
    http://www.bgmn.de/
DBWS (22nd February 2000)
    http://www.physics.gatech.edu/downloads/young/download_dbws.html
Debvin (25th May 2001)
    ftp://ftp.cc.uniud.it/DEBVIN/
GSAS (25th October 2001)
    ftp://ftp.lanl.gov/public/gsas/
Jana (31st May 2001) (Email authors for latest Beta test versions)
    http://www-xray.fzu.cz/jana/jana.html
LHPM-Rietica (7th December 2000)
    ftp://ftp.ansto.gov.au/pub/physics/neutron/rietveld/Rietica_LHPM95/
MAUD for Java (GPL'd) (2nd August 2001)
    http://www.ing.unitn.it/~luttero/maud/
Prodd (3rd April 2001)
    http://www.ccp14.ac.uk/ccp/web-mirrors/prodd/~jpw22/
Profil (24th May 2001)
    ftp://img.cryst.bbk.ac.uk/pdpl/
Rietan 2000 (GPL'd) (6th September 2001)
    http://www.ccp14.ac.uk/ccp/web-mirrors/prodd/~jpw22/
Winplotr/Fullprof (27th August 2001)
    http://www-llb.cea.fr/winplotr/winplotr.htm
    ftp://bali.saclay.cea.fr/pub/divers/fullprof.2k/
Winmprof (21st June 2001)
    http://lpec.univ-lemans.fr/WinMProf/
XND (6th July 2001)
    http://www-cristallo.polycnrs-gre.fr/xnd/xnd.html
    ftp://old-labs.polycnrs-gre.fr/pub/xnd/

All the above Rietveld programs are also available via the CCP14 based mirrors in UK, USA and Canada (http://www.ccp14.ac.uk/mirror/).

Summary lists of some software available via the EPSRC funded CCP14 website:

Anharmonic Thermal Refinement Software
    http://www.ccp14.ac.uk/solution/anharmonic/
Data Conversion for Powder Diffraction
    http://www.ccp14.ac.uk/solution/powderdataconv/
Image Plate Software
    http://www.ccp14.ac.uk/solution/image-plate/
Incommensurate Structure Software
    http://www.ccp14.ac.uk/solution/incomm.htm
Indexing Software for Powders
    http://www.ccp14.ac.uk/solution/indexing/
LeBail Method for Intensity Extraction
    http://www.ccp14.ac.uk/solution/lebail/
Pawley Method for Intensity Extraction
    http://www.ccp14.ac.uk/solution/pawley/
PDF, High Q Powder diffraction Analysis Software
    http://www.ccp14.ac.uk/solution/high_q_pdf/
Peak Find/Profiling Software for Powder Diffraction
    http://www.ccp14.ac.uk/solution/peakprofiling/
Pole Figure and Texture Analysis Software
    http://www.ccp14.ac.uk/solution/pole_figure/
Powder Diffraction Data Visualisation
    http://www.ccp14.ac.uk/solution/powder_data_visual/
Search-Match Phase Identification Software
    http://www.ccp14.ac.uk/solution/search-match.htm
Single Crystal Structure Solution Software relevant to Chemical Crystallography
    http://www.ccp14.ac.uk/solution/xtalsolution/
Single Crystal Structure Refinement Software relevant to Chemical Crystallography
    http://www.ccp14.ac.uk/solution/xtalrefine/
Single Crystal Suites linking to multiple programs relevant to Chemical Crystallography
    http://www.ccp14.ac.uk/solution/xtalsuites/
Spacegroup and Symmetry operator determination software and source code
    http://www.ccp14.ac.uk/recomm/sym_operators_to_spacegroups.html
    http://www.ccp14.ac.uk/recomm/spacegroups_to_sym_operators.html
Spacegroup and Structure Transformation Software
    http://www.ccp14.ac.uk/solution/transform/
Structure Conversion and Transformation
    http://www.ccp14.ac.uk/solution/structconv/
Structure Drawing and Visualisation
    http://www.ccp14.ac.uk/solution/structuredrawing/
Unit Cell Refinement of Powder Diffraction Data
    http://www.ccp14.ac.uk/solution/unitcellrefine/

MEETING AND SCHOOL REPORTS

3rd Size-Strain Conference, Trento (Italy), 2-5.12.2001

Paolo Scardi
Dipartimento di Ingegneria dei Materiali
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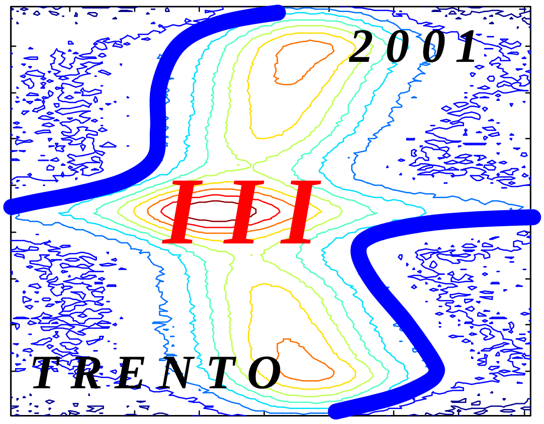
Tel: +39 0461 882417/67
Fax: +39 0461 881977
e-mail: Paolo.Scardi@ing.unitn.it
Web-site: http://www.ing.unitn.it/~scardi/



The third Size-Strain conference (SS-III) “Analysis of microstructure and residual stress by diffraction methods” was is intended as a continuation of the successful series of Size-Strain conferences initiated in 1995 (Liptovsky Mikulas, Slovakia) and continued in 1998 (Freiberg, Germany). The conference was organised under the supervision of a Technical Programme Committee (*R. Cheary, J. Cline, R. Delhez, P. Klimanek, D. Louer, E. Mittemeijer, P. Scardi, B. Scholtes, V. Valvoda*) and an International Advisory Board (*C. Hubbard, A. Kern, E. Mittemeijer, P: Munk, P. Scardi, R. Snyder*). The Local Committee (chaired by *M. Leoni*) provided an indispensable support to the many practical and logistic issues.

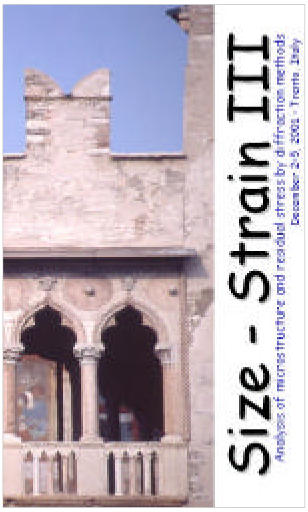
This event was made possible by the generous financial support of the European Commission (the conference was also included in the list of High-level Scientific Conferences) and the Regione Autonoma Trentino Alto Adige-Südtirol. Further important sponsorships by the International Union of Crystallography, Philips Analytical, Bruker, ICDD, Osmic, XOS, Bede and Rich-Seifert were essential for the organisation and to support the participation of young scientists and colleagues from less-favoured countries.

The general conference topics concerned materials microstructure and properties, as they can be studied by diffraction methods. In addition, applications of diffraction techniques to polycrystalline and amorphous materials were also discussed. Following the tradition of the previous Size-Strain conferences main themes were methodologies for the study of lattice defects, residual stress and texture in thin films and surfaces, line profile fitting/modeling based on fundamental parameters, simulation of materials microstructure and defects related to diffraction profiles. Particular emphasis was given to materials science applications, including e.g., phase analysis with amorphous fraction, highly defective and nanocrystalline materials, residual stress gradients and stress mapping in thin layers and coating systems.

The conference was organized around the topics of 13 invited talks (*A. Kern, I. Groma, J.-D. Kamminga, N. Armstrong, A. Ustinov, P. Scardi, J. Cline, R. Birringer, M. Leoni, C. Genzel, U. Welzel, P: Riello*), including the honor lecture by *Ian Langford* who presented an overview on the history of powder diffraction and line profile analysis methods in the past century. 15 contributed talks and two sessions dedicated to posters completed an intensive and interesting program.

One of the targets of the conference was to get together most of the experts in the main areas of interest and to encourage a free exchange of information and discussion among attendees. From this point of view the conference was a real success: long and animated discussions followed most of the presentations, thus providing a real insight into the current research activity.

Front cover of the conference proceeding booklet



Participants enjoyed the local hospitality, as also demonstrated by the high popularity of the archeological tour (visit to the underground Roman site) and especially of the social dinner and ‘wine’ tour.

Conference proceedings are collected in a booklet of extended abstract of all the presented contributions (orals and posters) which is available on request. Abstract are also displayed in electronic format on the IXAS web site (http://www.ixas.org). A book, containing full chapters dedicated to the most significant and pertinent contributions is currently being edited by the conference Chairs (*P. Scardi and E. Mittemeijer*) and should be published within one year from the conference.

Beyond the scientific program, the conference was also a nice opportunity to celebrate the long and fruitful carrier of *Ian Langford*. Even if he formally retired less than two years ago, he is very active and we all hope Ian will continue to significantly contribute to the progress in Powder Diffraction in future.

As a final remark, it is not to early to think of candidates to the organization of a 4th Size-Strain conference. Proposal and suggestions will be very welcome.

News from the International Centre for Diffraction Data (ICDD)

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http://www.icdd.com

IXAS Web Site Launched

In the last CPD newsletter, it was announced that an agreement was reached to have the ICDD provide web services for the International X-ray Analysis Society (IXAS). The IXAS web site is now on-line at www.ixas.org. Membership is free and open to the global scientific community—to join, register at the web site. The web site provides on-line access to *Advances in X-ray Analysis*, Volumes 42 and 43 (proceedings of the 1998 and 1999 Denver X-ray Conferences), as well as recent abstracts from the Size Strain III—Analysis of Microstructure and Residual Stress by Diffraction Methods Conference, held in Trento, Italy, 2–5 December 2001.

The IXAS is a not-for-profit, scientific association that focuses on the use of X-rays, neutrons, and electrons in materials characterization. The purpose of the Society is to serve professionals working in the field of materials analysis by: (a) fostering interaction among materials scientists, chemists, physicists, geologists, and others engaged in the use of X-rays and other radiations, including neutrons and electrons, for materials analysis; (b) sponsoring meetings of interest to those in the field of materials analysis; and (c) disseminating information of interest to the materials analysis community.

The 50th Annual Denver X-ray Conference

The Denver X-ray Conference (DXC) celebrated its 50th anniversary in the majestic mountains of Steamboat Springs, Colorado. The conference was held 30 July–3 August 2001 and attracted approximately 350 attendees and over 200 exhibit personnel. Conference week began with 15 tutorial workshops, followed by 16 special sessions.

The Plenary session, “Fifty Years of the Denver X-ray Conference”, gave attendees the opportunity to learn the history of what has grown to become the single most important U.S. meeting in the X-ray analysis community. The session included presentations from the pioneers of the DXC—William Mueller, Colorado School of Mines; John B. Newkirk, Colorado Sports Equipment, Inc.; Clay Ruud, The Pennsylvania State University; Paul Predecki, The University of Denver; and Ron Jenkins, (Emeritus) ICDD. Each speaker highlighted a particular era of the conference, describing the significant endeavors of the time and how those events influenced the DXC. The lectures and lecturers were immensely entertaining and often humorous. The experience was nostalgic for some, enlightening for others, and impressive to all.

Several awards were presented at the conference:

The ***2001 Barrett Award***, established for excellence in the powder diffraction field, was presented to David E. Cox, (Emeritus) Brookhaven National Laboratory. P.K. Predecki, The University of Denver, presented the award.

Newly established in 2001 to recognize scientists for their lifetime achievement in the advancement of X-rays for materials analysis, the ***Jenkins Award*** was presented to Ron Jenkins, (Emeritus) ICDD by R.L. Snyder, The Ohio State University.

C.R. Hubbard, Oak Ridge National Laboratories, presented the ***2001 Hanawalt Award*** to Raymond P. Goehner and Joseph R. Michael, Sandia National Laboratories. This award is given in recognition of an important, recent contribution to the field of powder diffraction. The Hanawalt Award Lecture, “Phase Identification Using Electron Backscatter Diffraction in the SEM: A Powerful Tool for Materials Science” was presented at the plenary session.

Ron Jenkins, (Emeritus) ICDD, received the ***Distinguished Fellows Award*** for his long and meritorious service to the ICDD. Julian Messick, ICDD, presented the award.

Annual Spring Meeting Dates

The ICDD Annual Spring Meetings will be held at ICDD Headquarters, 18–22 March 2002.

ICDD Welcomes its New Executive Director, Dr. Tim Fawcett

The ICDD is pleased to announce that Dr. Tim Fawcett has joined the ICDD as its new Executive Director. Dr. Fawcett is a long time ICDD member, ICDD Fellow, and served on the Board of Directors from 1986–1988. He brings to the ICDD outstanding experience in management and R&D for product development, as well as an exceptional background in X-ray diffraction.

Dr. Fawcett received his B.S. degree with honors from the University of Massachusetts, and his Ph.D. in Inorganic Chemistry from Rutgers University in 1979. After graduation, Dr. Fawcett joined Dow Chemical Co., worked in the X-ray diffraction facility, and then managed the inorganic analysis laboratories of Dow's Analytical Sciences Department. From 1989 to 1996, he managed several groups in Dow's Ceramics and Advanced Materials Laboratories. Dr. Fawcett was promoted to Sr. Research Manager and managed Dow's Advanced Technologies and Inorganic Coatings Group, the Interfacial Sciences Discipline, and most recently, two of Dow's new product development areas which involved a portfolio of projects leading to advanced materials products.

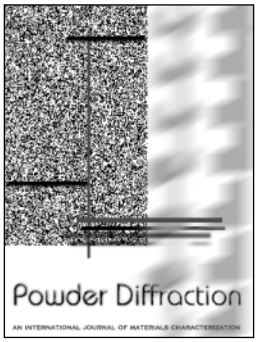
New Products

The ICDD introduces a new product line! The new database products, PDF-4s, are organized in a relational database format, which provides extensive data mining in quick time. The PDF-4 products feature a powerful user interface, PCPDFWIN™, with query sorting capabilities and integrated viewing software. PDF-4/Minerals 2001 and PDF-4 Metals and Alloys 2001 are now available with PDF-4/Full File scheduled to be released in the Spring 2002.

Our new products include the updated Mineral Powder Diffraction File™ Data Book and Search Manual, a hardcover edition featuring Sets 1–50 of the PDF®. A special combination price is available on the purchase of this edition along with our new PDF-4/Minerals 2001. Additional pricing incentives include a Multiyear License Renewal Program as well as an expanded Site License Program. The Multiyear License Renewal Program provides savings on the purchase of multiyear license renewals for the PDF-2 and PDF-4/Full-File.

In celebration of our "Sixtieth Anniversary", the ICDD is introducing special "Anniversary" pricing that offers savings up to 45% off the list prices for a PDF-2 license renewal. Now containing over 136,000 patterns, the PDF® has more than doubled in size in the past five years with the addition of calculated patterns from the Inorganic Crystal Structure Database, maintained by Fachsinformationzentrum in Karlsruhe, the continuous addition of patterns of important new materials from the ICDD's Grant-in-Aid program, as well as patterns located by the ICDD's bibliographic staff. Anniversary pricing provides a valuable opportunity for noncurrent users to update their PDF® and significantly improve the quality, accuracy, and coverage of their work.

The ICDD's quarterly journal, *Powder Diffraction*, has a new up-to-date look, featuring the lead article on the cover. Along with this new look, the journal has been updated to include on-line subscriptions. Subscribers may obtain the journal in print, on-line, or in print and on-line together



Further Information

To learn more about the ICDD, its products and services, please visit our web sites: www.icdd.com and www.dxcicdd.com.

IXAS NEWS

A few years ago the Denver X-ray Conference organizing committee established an international committee that met in Barcelona in May 2000 and founded the International X-ray Analysis Society. The By-Laws for this fully electronic and completely dues-free organization provided for the phasing in of an Executive Council and the establishment of a web site and focus groups. The last of the elections establishing the Executive council has just been held and the first complete council is now in place. The officers are:

Bob Snyder (President)
George Havrilla (Vice-President, President-Elect)
Greg McCarthy (Secretary-Treasurer)

The latest members of the Council are:

Jimpei Harada (Japan)
Scott Misture (USA)
Silvana Simabuco(Brazil)
Szabina Torok (Hungary)

They join the previously elected Council members:

E. Antipov (Russia)
R. vanGrieken (Belgium)
B. Holynska (Poland)
B O'Connor (Australia)
P. Scardi (Italy)
H. Toraya (Japan)
P. Wobrauscek (Austria)

IXAS will conduct the first full membership election this spring for the President-Elect at which time Snyder will become Past-President and Havrilla will become President. Our new web page is now in place with the full proceedings of the last two editions of Advances in X-ray Analysis and all of the latest information on the world's X-ray conferences. Software is now in place implementing discussion groups among all of the Analysis area interest groups. Visit www.ixas.org to see the developments.

WHAT'S ON

The following web-site contains an up-to-date and semi-exhaustive list of conferences and workshops in crystallography and related areas
http://www.iucr.org/cww-top/mtg.date.html

20 – 23 January 2002 (! new date !)

SECOND ISPD--2001

Calcutta and Bangalore, India

Second International School on Powder Diffraction (ISPD--2001)will be held in Jadavpur, Calcutta, India from 2ß –23 January, 2002. Lecture sessions include contemporary topics in powder diffraction by X-ray, electron, neutron and synchrotron radiation, given by experts with hands-on computer sessions for young and active researchers in institutes, universities, and companies. The meeting is sponsored by IUCr, ICDD and other organizations.

For further information contact:
For ISPD 2001: Prof S P Sen Gupta,
E-mail:msspsg@mahendra.iacs.res.in,
Fax: 91-33-473 2805
Web-site: www.iacs.res.in/ispd.html

11 – 15 February 2002

AXAA 2002

Newcastle, NSW, Australia

The schools program aims to provide training for early career professionals. The conference provides an opportunity for professionals with an interest in x-ray and surface analysis to come together over five days. The conference aims to: Recognise progress and highlight future directions for X-ray and surface analysis; develop knowledge and expertise in X-ray analysis practice and management; motivate participants to contribute to effective x-ray fluorescence, diffraction and surface analysis programs.

For further information contact:
Jane Yeaman
AXAA 2002 Conference
Tulips Meetings Management
PO Box 116, Salamander Bay, NSW, 2317 Australia
Tel 02 4984 2554
Fax 02 4984 2755
Email: axaa@pco.com.au
Web-site: www.pco.com.au/axaa2002/

8-12 April 2002

ADVANCED X-RAY DIFFRACTION FOR PHARMACEUTICAL APPLICATIONS TRAINING SEMINARS

The Eden Resort Inn & Conference Center, Lancaster PA, USA.

Application of X-ray powder diffraction, in particular its capability of solving structures from powder data in the pharmaceutical area.

For further information contact:
assainternational Inc.
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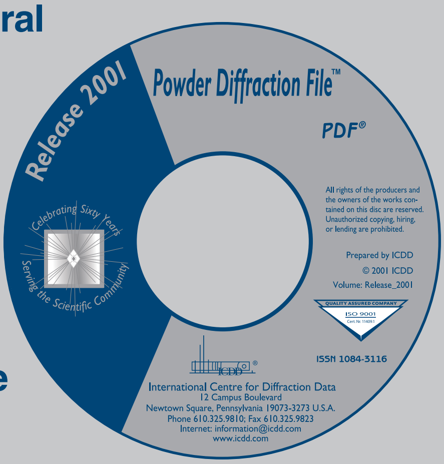
Danbury, CT 06811, USA
Tel: (203).312.0682
Fax: (203).312.0722
E-Mail: info@assainternational.com
Web-site: www.assainternational.com/home.htm


Release 2001
Powder Diffraction File™
PDF®
Celebrating Sixty Years
Serving the Scientific Community
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www.icdd.com

29 April - 3 May 2002

PRACTICAL X-RAY FLUORESCENCE SPECTROMETRY

ICDD, Newtown Square, Pennsylvania, U.S.A.

Covering basics of X-ray spectra, instrumentation design, methods of qualitative and quantitative analysis, specimen preparation, review of mathematical matrix correction procedures, applications for both wavelength and energy dispersive spectrometry and new developments in XRF.

23 – 26 May 2002

EPDIC 8

Uppsala, Sweden

The *scientific* programme for the three-day conference will include invited plenary lectures, contributed talks and poster sessions. A commercial exhibition will also be organised.

The Programme will cover the topics:

1. Methods and techniques
2. Instrumental development
3. New or improved software
4. Databases
5. Materials Sciences
6. Dynamic studies
7. Studies under non-ambient conditions
8. Industrial processes and applications
9. New research fields

Other contributions relevant or complementary to powder diffraction are welcome.

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EPDIC-8**,** Dept. of Materials Chemistry,
The Ångström Laboratory
Box 538, SE-751 21 Uppsala, Sweden

3-7 June 2002

FUNDAMENTALS OF X-RAY POWDER DIFFRACTION

ICDD, Newtown Square, Pennsylvania, U.S.A.

Covering instrumentation, specimen preparation, data acquisition, and qualitative phase analysis.

10 – 14 June 2002

ADVANCED METHODS IN X-RAY POWDER DIFFRACTION

ICDD, Newtown Square, Pennsylvania, U.S.A.

Emphasizing computer-based methods of data collection and interpretation, both for qualitative and quantitative phase analysis.

For further information on all ICDD meetings 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/

29 July to 2 August 2002

THE 51ST ANNUAL DENVER X-RAY CONFERENCE

Colorado Springs, Colorado, U.S.A.

The 51st Denver X-ray Conference will be held at the Adams Mark Hotel (formerly Antlers Doubletree Hotel) in Colorado Springs, Colorado. The *Call for Papers* is now available in hardcopy form and on the website.

For further information contact:
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Tel: +(610) 325-9814
Fax: +(610) 325-9823
E-mail: dxc@icdd.com
Web-site: www.dxcicdd.com

6 – 14 August 2002

XIX CONGRESS AND GENERAL ASSEMBLY OF THE INTERNATIONAL UNION OF CRYSTALLOGRAPHY

Geneva, Switzerland

A large-scale conference that will address all the main issues in crystallography during a long and interesting programme. Even if Powder Diffraction sessions are not specifically included, a number of microsymposia will be devoted to several aspects of powder diffraction and materials science. The second circular with the preliminary programme is now available and can be downloaded from the web.

For further information contact:
Joel Bernstein Chairperson, Organizing Committee
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e-mail: Kaftory@techunix.technion.ac.il

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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

Companies

If you would like to advertise in this twice-yearly newsletter, please contact

Paolo Scardi on e-mail: Paolo.Scardi@ing.unitn.it
Tel: +39 0461 882417/67
Fax: +39 0461 881977

Call for contributions to the next CPD Newsletter (No 27)

The next issue of the CPD Newsletter will be edited by *Gert Kruger*, to appear in summer of 2002. Gert 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 27 (addresses are given below)

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