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XRD Line Profile Analysis

(Paolo Scardi, Editor)

Powder Diffraction Line Profile Analysis:

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CPD Chairman's Message

As the new chairman of the commission on powder diffraction, it is my pleasure to express my deepest thanks to the previous chairman, Paolo Scardi who has put in a tremendous amount of highly successful work in the commission, and in particular regarding the improvement of our newsletter which has considerably increased in size, quality and the number of subscribers. Support was given to a variety of conferences, schools and workshops and several projects such as the development of Rietveld guidelines, the QPA-, and the size-strain round robin were accomplished. For the next three years, Paolo will act as a consultant to the CPD and his shared knowledge and experience will be of great help for the entire commission. I will try my best to continue the work in the tradition of the previous chairman.

I would like to cordially welcome our new members, Miguel Delgado, Camden Hubbard, Ian Madsen and Norberto Masciocchi. Following our tradition, they all will be guest editors of upcoming CPD newsletters. In turn, several members have left the CPD and I am grateful to Sen Gupta, Robert Von Dreele, Helmar Fjellvåg for their valuable contributions during the past triennium.

The newsletter has now reached a size, which creates some logistical and financial problems. In an attempt to keep production costs as low as possible, this will be the first newsletter which is printed and distributed from Venezuela. Special thanks to Miguel Delgado who voluntarily offered his help in this matter. Paolo has almost finished his task to transfer all CPD Newsletters from paper to electronic format, which will be made available online and distributed on CD-ROMs soon.
New round robins and the development of new powder diffraction standards are necessary for the benefit of the entire community. In addition to the ongoing round robins, one of the tasks in progress is the development of an organic standard for Rietveld refinement.

In general, I am pleased to see that powder diffraction is becoming more and more popular. This accelerated activity is visible in a number of ways. One certainly is the increasing demand for synchrotron beamtime for powder diffraction. A quick check on the NSLS website reveals that there are currently 11 Beamlines mainly or partly dedicated to powder diffraction and there will soon be a consortium of powder beamlines for the benefit of the user. A large upgrade at the ESRF took place last year with the movement of Andy Fitch's high resolution powder beamline from a bending magnet (BM16) to the much more powerful insertion device ID31 with state of the art equipment, and at the APS, at least 5 beamlines are mentioned at which powder diffraction experiments are possible. In particular, the use of high energy beamlines for powder diffraction is becoming more and more popular due to the many advantages for experiments in transmission geometry.

For this year, we are looking forward to the ECM21 which will, for the first time, take place in South Africa. There will be at least 6 microsymposia containing the word "powder diffraction" in the title, again reflecting the large public interest in this field.

Recent important developments in powder diffraction deal with microstructural effects, nano-materials, maximum entropy, and the use of the pair distribution function, just to name a few. Some of these "hot" topics are addressed in the current newsletter, edited by Paolo Scardi.

I am looking forward to an exciting time in an active commission.

Robert Dinnebier

CPD projects

QUANTITATIVE PHASE ANALYSIS ROUND ROBIN

The first part of the study is reported in a publication by I.C. Madsen *et al.* (J. Appl. Cryst. 34 (2001) 409-426), distributed as a free offprint together with the CPD Newsletter No 25. The second part was published afterwards by N.V.Y. Scarlett *et al.* (J. Appl. Cryst. 35 (2002) 383-400). The reprint was distributed with the previous Newsletter (No 27). Readers can refer to these papers for an exhaustive discussion on the outcomes of the QPA Round Robin .
First and second (enclosed) parts can be freely downloaded from the CPD web-site (http://www.iucr.org/iucr-top/comm/cpd/), where additional information and original data files can be found. We wish to thank again the IUCr Editorial Office for giving us permission to include the reprint from the Journal of Applied Crystallography (JAC) in the Newsletter and for allowing free downloading of offprints from the Web.

SIZE-STRAIN ROUND ROBIN

The preliminary report and analysis of results are still available at http://www.boulder.nist.gov/div853/balzar, CPD and CCP14 Web-sites. A paper has been recently submitted for publication on the Journal of Applied Crystallography. The present issue includes a summary of this work, presented by D. Balzar and N.C. Popa.

From the Editor of Newsletter 28

Since the introduction of the Scherrer formula in 1918, the study of diffraction line profiles (frequently referred to as Line Profile Analysis) has become an important research field in Powder Diffraction. After the fundamental contributions of Wilson and Warren in the ‘40s and ‘50s, important developments have been produced in the ’60s by the school of Krivoglaz and by Wilkens. Since those early days, applications of LPA in scientific and technological studies have increased steadily, even if the methodology did not basically evolved in the last forty years.

In more recent years we are assisting to a renaissance in this field, mostly driven by the availability of fast computers (as in so many other disciplines), but also due to the growing awareness that a better modelling of diffraction line profiles is possible on the basis of a deeper understanding of the various mechanisms responsible for line broadening. Moreover, better statistical approaches are being devised for line profile modelling, as well as methods for the modelling of the whole powder diffraction pattern. In the present issue of the CPD Newsletter some of these innovations and current activity in LPA are briefly present, including a short report on the CPD Size-Strain Round Robin.

Even if not exhaustive, this collection of short scientific articles can be considered as a good basis to stimulate reader’s curiosity to further readings. It is worth reminding here that a further help to assess the state of the art in LPA should be given by the book produced after the Size-Strain III conference (Trento (I); Dec. 2001), which is now close to the published by Springer-Verlag under the title: “Diffraction Analysis of the Microstructure of Materials” (edited by P. Scardi and E.J. Mittemeijer).

Methods, results and opinions expressed by the various authors contributing to this Newsletter can be quite different, even conflicting in some cases. This is not totally unintentional: authors were selected trying to present a variety of approaches and different views of LPA. Unlike typical scientific journals and textbooks, where an orthodox view of scientific disciplines is usually proposed, the CPD Newsletter can present a different point of view. The Newsletter provides a Forum where new ideas can be freely confronted and judged, with the further advantage of a rather short editorial process (i.e., rapid publication and distribution). I hope readers as well as future Editors will share this opinion on the role of the CPD Newsletter as a free space for open discussion and fast communication of developments concerning Powder Diffraction.

The editing of the present issue is the last act after a long and fruitful personal involvement in the CPD. It is a particular pleasure for me to quit after producing a Newsletter so deeply related to my main research interests, and I look forward to future opportunity to collaborate again with the CPD/IUCr.

I like to conclude this brief introduction to the present issue reporting the text of a letter I recently received from Nils O. Ersson, from Uppsala, Sweden. Beyond the specific case proposed by Nils (I hope he will receive some useful answer through the Newsletter), this letter perfectly illustrates a typical paradox of our times. As we would say in Italy, the risk is, when changing the water in a bathtub, to through away the baby together with the dirty water. Is Progress running always in the correct direction?

Paolo Scardi

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Professor Paolo Scardi
Università di Trento

Uppsala 2003-01-07

Concerning Film material for X-ray Cameras.

Dear Professor Scardi!

This is a problem I should have tried to discuss with you at your stay at Uppsala at the EPDIC-8 conference, as it was a problem already at that time.

We are extensively using the Guinier cameras, built during the time Professor Gunnar Hägg still was active. As the geometry not permits the use of double coated emulsion layers on the film base, we in the “early days” had to remove one layer from a standard, commercial X-ray film. It was a great advantage when the Swedish factory CEA made a high sensitive, single coated film (the REFLEX -15 film, much by the aid from Professor S. Abrahamsson).

A few years ago CEA was bought by AGFA and all production in Sweden was stopped, including the REFLEX -15. I have tried to find other film brands, making single-coated films. There are, of course, a number of them, intended for medical use. Films for mammographical use have a very low background, but show serious drawbacks (I compare to REFLEX -15): They have a sensitivity for X-ray radiation of only 20% but show a much higher sensitivity to normal day-light, so they are much more difficult to handle at exposure and in darkroom. (Still they are to recommend in some cases, e.g. for recording data for Rietveld refinement)

So far I have tried AGFA CURIX and KODAK BIOMAX MR films, as well as a film from CEA (no longer available). They all behave as described. At the moment we use REFLEX-15 that still are in store, but they give a background that is far too high to be accepted– besides the number of films in the store is rapidly decreasing.

This is of course not a problem only for our laboratory, but for all users of the Guinier technique. The problem is most serious for labs in poor universities, where diffractometers not are used (I have an example: The Eritrean Asmara University, to which we sent a Guinier camera equipment two years ago).

The demand of this type of films is very small, but I think that still one of the large factories could try to use the concept for the REFLEX-15. This film was much more expensive than the standard doublecoated, medical films, but was still affordable as so little was used for each exposure. (A 18x24 cm film at a price of 4 € was cut to 11 film strips for our cameras.)

The best way to convince a big firm like AGFA or KODAK must be if there is a demand from an international organisation, and of these the IUCr Powder Committee of course is the expert one. This is why I send this request to you! I hope you can help us, all of us users of the traditional, but very efficient Guinier Camera Technique!

Sincerely yours

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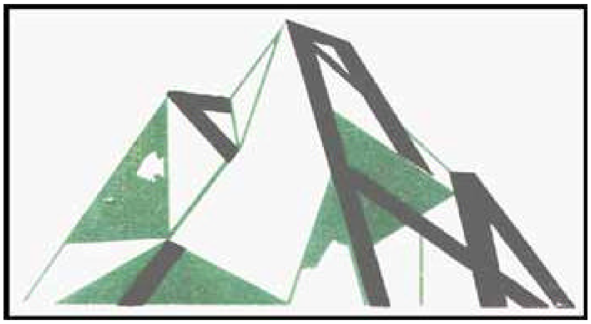
Structure Solution from Powder Diffraction Data

SSPD'03

September 14-19, 2003

CONGRESS CENTER ACADEMIA, STARA LESNA, SLOVAKIA



The purpose of this conference is to assess the progress made in the theory and techniques of structure solution based on powder diffraction data and to point to areas where further work is needed. Special attention will be paid to structure prediction done by energy minimization, because its results are frequently checked by Rietveld refinement. It is believed that a combination of these two methods will in a near future become a standard tool.

The scientific program will include both invited and contributed lectures, micro-symposia and poster sessions. A commercial exhibition will be also organized.

The main topics of the conference are :

1. optimal data collection strategies, autoindexing, space group determination,
2. Patterson & direct methods,
3. structure determination by global minimization methods,
4. structure prediction & modeling,
5. structure determination & refinement from neutron data,
6. accuracy of structure solutions,
7. influence of "real" structure,
8. applications to pharmacology & biology,
9. industrial applications,

More information can be obtained from: www.sspd-03.sav.sk

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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/

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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Whole Powder Pattern Modelling for the study of Anti-Phase Domains

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INTRODUCTION

Anti-Phase Domains (APDs) are known to form in several intermetallic systems undergoing disorder-order transformations (e.g., Cu_3Au [1]), but also in several ceramics (e.g., spinels [2], GaAs [3]) and quasicrystals [4].

In the case of Cu_3Au the high temperature (disordered) structure is *fcc*, whereas the ordered state is simple cubic ($L1_2$ structure). As a consequence of the lowering of symmetry, the disorder/order transformation in *fcc* phases is accompanied by the appearance in the diffraction pattern of the so-called superstructure reflections (Miller indices with mixed parity: 100, 110, 210, …) in addition to the fundamental lines (Miller indices with the same parity: 111, 200, 220…).

The intensity of the superstructure (s) lines is much weaker than that of the fundamental (f) ones, in that the structure factors are given respectively by [5]:

$$|F_s| = f_{Au} - f_{Cu} \qquad (1a)$$

and

$$|F_f| = f_{Au} + 3f_{Cu} \qquad (1b)$$

where f_{Au} and f_{Cu} are the atomic scattering factors of gold and copper, respectively.

Several mechanisms have been proposed for the formation of APDs. For instance, during the formation of an ordered phase from a disordered parent phase (like in the case of Cu_3Au), the change from a random site occupation to an ordered disposition of Au and Cu atoms can start at different sites. When two ordered domains grow and finally meet, it is possible that they do not merge because the ordering process in the two domains started in non-equivalent Cu and Au sites. As a consequence APDs are formed.

In principle Anti-Phase Boundaries (APBs), limiting different APDs, can occur along any direction. In Cu_3Au, APBs tend mostly to form along {100} planes as conservative boundaries [6], i.e., in such a way to avoid gold atoms to come into contact.

LINE BROADENING EFFECTS OF APDs

The presence of APDs gives a line broadening with a specific *hkl* dependence, where only superstructure reflections are broadened. Wilson's theory in 1943 [7] was the first attempt to describe this effect, leading to simple expressions for the integral breadth (*b*) of superstructure lines, which in the case of conservative boundaries along {100} planes in Cu_3Au reads:

$$b\left(s\right) = \frac{g\left(|h|+|k|\right)}{d_{hkl}\left(h^2+k^2+l^2\right)} \qquad (2)$$

where s is the reciprocal space variable, l the wavelength, d_{hkl} the interplanar distance and g the APB probability. Integral breadth methods, however, have several limitations (e.g., difficulties in measuring the integral breadth of overlapping profiles and in separating different line-broadening sources) which make it difficult to obtain reliable quantitative information.

Whole Powder Pattern Modelling (WPPM) [8-10] is a viable solution to incorporate several line broadening models, related to different sources, in a single refinement procedure, without arbitrary assumptions on profile shape. Each diffraction profile *I(s)* can be described in terms of the Fourier Transform *C(L)* as:

$$I\left(s\right) = k\left(s\right)\int C(L)\,e^{2piLs}\,dL \qquad (3)$$

where *k(s)* is a known function of *s*, including terms not related to the microstructure of the sample (e.g., the Lorentz-polarization factor, $|F|^2$, etc.) . The advantage of this approach is that the convolution between the effects of different line broadening sources can be treated by multiplying the corresponding Fourier terms:

$$C\left(L\right) = T^{IP}\left(L\right) A^S(L) < e^{2pi\cdot y(L)} >< e^{2pi\cdot f(L)} >< e^{2pi\cdot c(L)} > .... \qquad (4)$$

where are explicitly considered (from left to rigth): instrumental broadening, domain size, dislocations, twin and deformation faults (expressions are reported in [10]), APDs. The Fourier term for the latter effect can be written as [7]:

$$< e^{2pic(L)} > = e^{\frac{-2g\left(|h|+|k|\right)\cdot L}{d_{hkl}\left(h^2+k^2+l^2\right)}} \qquad (5)$$

in the case discussed before (cf. Eq.(2)).

Analogous expressions hold for APDs delimited by differently oriented APBs [7,11]: in any case the FT for APDs is an exponential of the Fourier length, *L*, and the

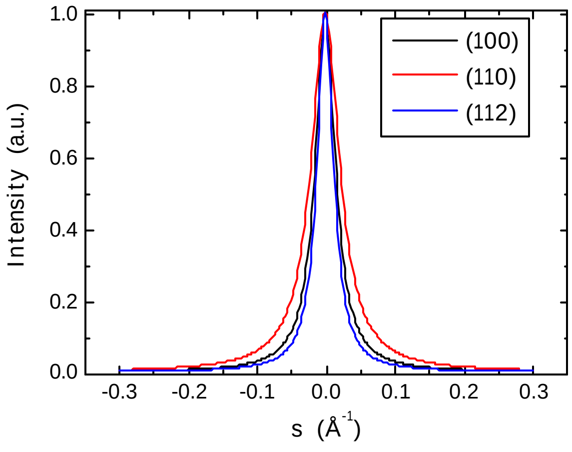

Fig. 1. *Line profile of some superstructure reflections of Cu_3Au with an APB probability of 5%.*

intensity profile ($I^{APD}(s)$) is a Lorentzian.

For the case of Eq.(5) (conservative boundaries along {100} planes) the intensity profile is given by:

$$I^{APD}(s) = k(s)\left[1+\left(\frac{p\, d_{hkl}\left(h^2+k^2+l^2\right)\cdot s}{g\left(|h|+|k|\right)}\right)^2\right]^{-1} \qquad (6)$$

Line profiles according to Eq. (6) are shown in Fig. 1, for the case of an ordered Cu_3Au phase with a 5% of APB probability. The three low-angle superstructure reflections ((100), (110), (112)) are shown, to highlight the specific *hkl* dependence of the line broadening effect of the APDs.

WPPM ANALYSIS OF APDs IN Cu_3Au

The main advantage of using a WPPM approach is the possibility of including the effect of APDs in a more general modelling of the diffraction pattern, considering different APB models and their simultaneous effect [7,11].

To test the proposed procedure we used data from the book of Warren (Fig. 12.9 in [5]), where the interesting case of conservative boundaries along {100} planes in Cu_3Au is considered. A Cu_3Au powder sample was first disordered at 420°C for 2h, then annealed at 360°C for 0.5h, in order to produce a long range order with APDs. A further treatment at 380°C for 50h led to a complete elimination of APDs. Given the long annealing time, the pattern of the latter specimen can be taken as a measure of the instrumental component. The results of the modelling is shown in Fig. 2a (fundamental reflections are not available from the data).

Fig. 2b shows the WPPM result for the sample annealed 0.5 h at 360°C, modelled by using an APB model of conservative boundaries along {100} planes. An APD probability $\gamma_{\{100\}}$=4.2(2)% and average crystallite size 24(5) nm were refined. The dislocation density is below the sensitivity ($<10^{13}$ m^{-2}), and faulting probability is also zero. Other APB models [7,11] do not produce acceptable results.

However, the match between data and model in Fig.2b is not totally satisfactory with this APB model. Similar conclusions were drawn by Warren from integral breadth data extracted from the pattern of Fig. 2b [5] (and also by Wilson on analogous samples [7,11]). The result considerably improves by adding to the modelling a fraction of randomly oriented APBs [7]. In this case, as shown in Fig.2c, APD probabilities are $\gamma_{\{100\}}$=3.5(2)%, γ_{Random}=2.5(2)%, with an average crystallite size 38(5) nm .

A similar agreement can be obtained by considering, in addition to the {100} conservative boundaries, a fraction of non-conservative boundaries along the same planes (i.e., gold atom in contact), as proposed by Wilson and Zsoldos [11]. However, the best result (in terms of modelling) is given by the modelling with conservative APBs along {100} planes plus a fraction of random APBs, as shown in Fig. 2c.

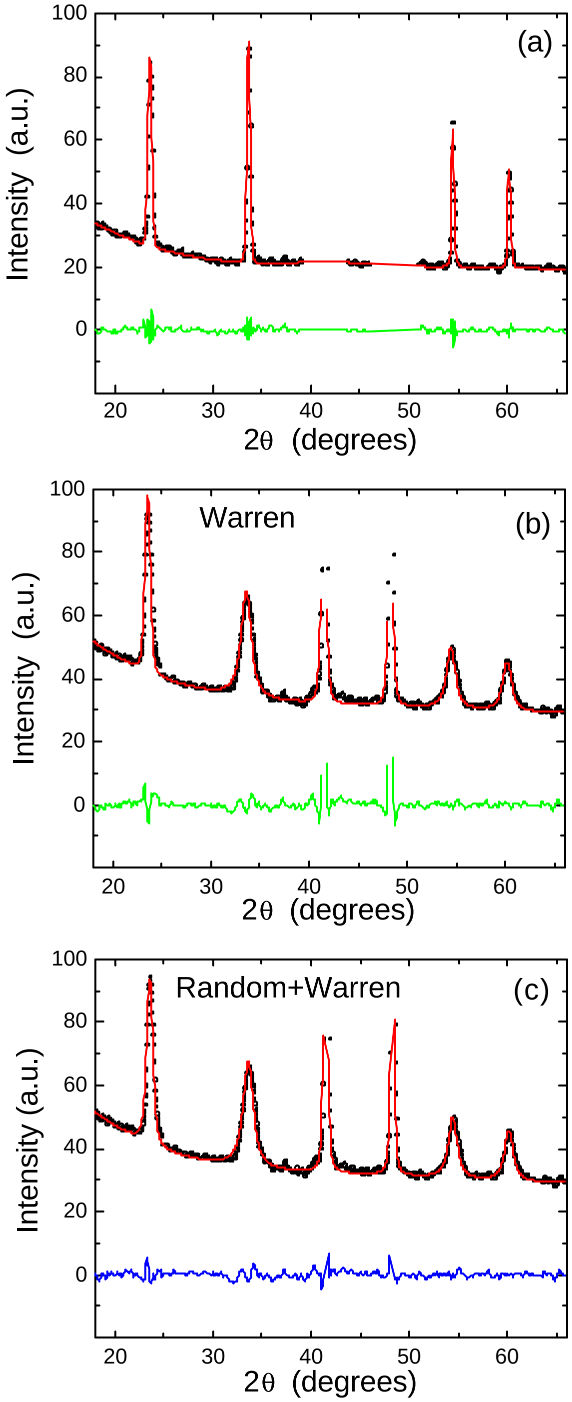

Fig. 2. *Diffraction patterns for a Cu_3Au sample: disordered at 420°C for 2h, then annealed at 360°C for ½h ((b) and (c)) to produce APDs. After a further annealing at 380°C for 50 days to eliminate APDs (a). Data taken from Fig.12.9 in reference [5].*
Courtesy of Dover Publications, Inc., New York.

CONCLUSIONS

The present study supports the early observation of Wilson [7] and Warren[5] that the main fraction of APBs in Cu_3Au is {100}, with a majority of conservative boundaries. However, a proper modelling

can only be obtained by adding an additional (random) APB component, and including a size broadening effect [9]. The two contributions (APD and size broadening) are different owing to the specific selection rules of APD line broadening. The advantage of the WPPM approach is evident: line broadening sources can be compared and/or included in the same data modelling procedure, without using arbitrary assumptions on the profile shapes and extraction of line profile parameters.
Further activity is currently in progress to study APDs in Cu$_3$Au and similar L1$_2$ phases.

REFERENCES

[1] R.M. Fisher & M.J. Marcinkowski, Phil. Mag. 6 (1961) 1385-1405.
[2] Cheary, R.W. & Grimes, N.W. (1978). Acta Cryst. A34, 74-84.
[3] M.K. Hudait & S.B. Krupanidhi, *J. Appl. Phys.* **89** (2001) 5972-5979
[4] M. Heggen, M. Feuerbacher, P. Schall, K. Urban, R.Wang, *Phys. Rev.* **B64** (2001) 014202-1 – 6.
[5] B.E. Warren, "X-ray diffraction", 2nd edition, Dover (New York), 1990 (1st edition, Addison Wesley, Reading, Mass., USA, 1969)
[6] R. Kikuchi. & J.W. Cahn, *Acta Metallurgica* **27** (1979) 1337-1353.
[7] A.J.C. Wilson, *Proc. Roy. Soc. London* **A181** (1943) 360-368.
[8] P. Scardi, Y.H. Dong, M. Leoni, *Mat. Sci. Forum* **378-381** (2001) 132-141.
[9] P. Scardi, M. Leoni, *Acta Cryst.* **A57** (2001) 604.
[10] P. Scardi, M. Leoni, *Acta Cryst.* **A58** (2002) 190.
[11] A.J.C. Wilson & L. Zsoldos, *Proc. Roy. Soc. London* **A290** (1966) 508-514.

Bayesian/Maximum entropy analysis of nanocrystallite-broadened line profiles

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INTRODUCTION

We present the results of a combined *Bayesian/Maximum Entropy* (MaxEnt) method for analyzing size-broadened x-ray line profiles, to be used in the certification of a new NIST nanocrystallite particle-size Standard Reference Material, SRM 1979 (see [1, 2]). Novel features of our method include:

- complete generality in removing instrumental broadening from the observed line-profiles
- ability to determine average crystallite sizes, the distribution of sizes, and the average shape of crystallites
- calculation of uncertainties in all derived quantities.

We have applied the new method to the CPD round-robin CeO$_2$ specimens [10] and compared the Bayesian/MaxEnt results with transmission electron microscopy data.

NEED FOR A NIST NANOCRYSTALLITE SIZE SRM

A NIST size SRM will address a significant shortfall in standards for analyzing the size, shape and distribution of nanocrystallites developed in the nanotechnology industry. This SRM will enable any laboratory to assess its experimental and analytical techniques for quantifying size-broadened x-ray profiles, and will complement electron microscopy techniques for analyzing nanocrystallites.

The NIST size SRM will include two material specimens, with two different morphologies in the 10-60 nm size range. The first will be a cerium oxide (CeO$_2$) specimen with a spherical morphology in the 10-30 nm size range. This specimen will enable traditional and recently developed line broadening methods to be used to analyse size broadening [4-9]. The second size SRM will be a zinc oxide (ZnO) specimen in the 30-80 nm crystallite size range. This specimen will be designed to have a hexagonal morphology [5, 9] and will require more complicated morphology and distribution models to be applied in order to quantify its size broadening.

GENERAL OVERVIEW OF BAYESIAN/ MAXENT ANALYSIS

In the realm of thermodynamics, entropy is a measure of the "randomness" of a system. In data analysis, on the other hand, the MaxEnt method has its origins in *Information Theory*, seeking to extract the "most random" solution under a given set of constraints [3]. When we apply maximum entropy principles to a problem, the aim is to deduce as much information as the noise in the data will allow, while taking into account any limitations of the experiment; this produces the most general solution which assumes the least about information that is *not* available [12, 16]. A consequence of this approach is that it ensures no *structure* (i.e. detail) will appear in the solution unless there is evidence for it in the data.

Having formulated a suitable entropy function, *S*, MaxEnt analysis of the particle size-broadened data uses Bayes' theorem to combine the experimental data with any hypotheses we may have about the solution (see [14]). To this end, we introduce Lagrangian multipliers to establish a compromise between maximizing the *entropy function* while minimizing χ^2, a parameter related to the difference between the model and fit [14, 16].

Our method satisfies the important requirements that it should:

- preserve the positivity and additivity of the distributions
- make the least possible number of assumptions about the solution (e.g. profile shape and specimen broadening distribution)
- incorporate all the available data (e.g. observed profile, instrument kernel, statistical noise and background characteristics)
- test/include all available *a priori* information (e.g. TEM, SEM, AFM data and theoretical models)
- quantify uncertainties in the results (i.e. give error bars).

EXPERIMENTAL DETAILS & ANALYSIS

XRD measurements

Diffraction patterns were collected on a Siemens D500[1] diffractometer equipped with a focusing Ge incident beam monochromator, sample spinner and a scintillation detector. Copper $K_{\alpha 1}$ radiation was used. The divergence slit was 0.67°, while the receiving optics included a slit of 0.05° and 2° Soller slits. The instrument profile function was determined using a split-Pearson VII profile shape function fitted to 22 reflections collected from SRM 660a (LaB_6). The non-overlapping lines for the CPD CeO_2 lines were collected to optimize the signal-to-background ratio. The non-overlapping lines included 111, 200, 220, 400, 422, 511 and 531.

As an example of the CeO_2 data collected, the observed 200 profile and the instrument profile are shown in Fig. 1, while Fig. 2 shows the observed profile before and after background estimation.

TEM measurements

A series of TEM micrographs of crystallites were taken at a fixed magnification of 200kX. The negatives of the micrographs were scanned and analysed by manually approximating some 853 crystallites with an oval.

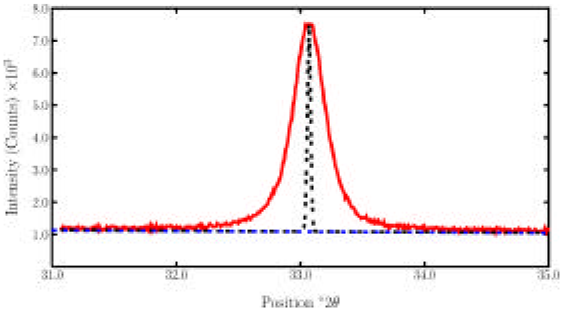

Fig. 1. *Observed CeO_2 200 line (solid curve), instrument profile (dotted peak) and background.*

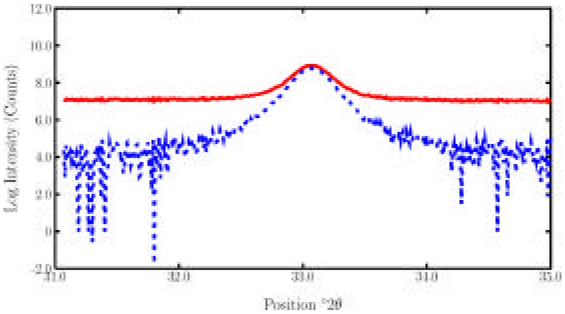

Fig. 2. *Observed CeO_2 200 profile before (upper curve) and after (lower curve) background subtraction.*

Analysis of CPD CeO_2 round-robin data

Preliminary analysis of the line profile data identified size broadening as being the dominant broadening component and determined the area- and volume-weighted diameters, using the approach of Krill & Birringer [4], while similar results were obtained using a Bayesian/Markov Chain Monte Carlo (MCMC) method (see [2]). Table 1 provides a summary of the experimental results from line profile analysis of the CPD CeO_2 specimen. The results from this preliminary analysis became the non-uniform *a priori* information for the full Bayesian/MaxEnt method.

	Method			
	Krill & Birringer	Bayes/ MCMC	Full Bayes/ MaxEnt (uniform)	Full Bayes/ MaxEnt (non-un.)
$<D>_a$ (nm)	24.9(2)	-	-	-
$<D>_V$ (nm)	29.6(3)	-	-	-
D_0 (nm)	16.5(6)	15.1(6)	14(1)	16.0(2)
s_0	1.51(3)	1.55(2)	1.7(2)	1.49(1)
$<D>$ (nm)	17.9(7)	16.6(6)	16(2)	17.3(3)
$<s>^2$ $(nm)^2$	53(7)	58.6(9)	100(70)	52(3)

Table 1 *Summary of size distribution results for the CPD CeO_2 specimen, for the various analysis methods used.*

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[1] Certain commercial materials, equipment and software are identified in order to adequately specify the experimental procedure. Such identification does not imply a recommendation or endorsement by NIST, nor does it imply that the materials or equipment or software are necessarily the best available for the purpose.

The full Bayesian/MaxEnt method was used to determine the morphology and size distribution of the nanocrystallites from the CeO_2 diffraction data. In this analysis, two models for size distributions are compared— a uniform distribution, $D \in [0, 60]$ nm, and a log-normal distribution, using the D_0 and σ_0 from Table 1.

Fig. 3 presents the Bayesian/MaxEnt results for the 200 line of CeO_2. In this figure the log-normal model and final Bayesian/MaxEnt distribution, with error bars, are shown. The error bars take into account the statistical noise and the uncertainty in determining the background level. In this analysis, the non-uniform *a priori* model was set equal to the log-normal model for the size distribution.

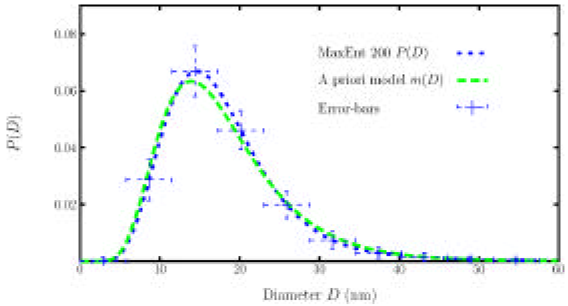

Fig. 3. *Size distribution and a priori model for the CPD round-robin CeO_2 200 line.*

Fig. 4 shows the Bayesian/MaxEnt size distributions for the non-overlapping hkl lines; they are in close agreement with each other, suggesting that the size distribution closely resembles a log-normal distribution.

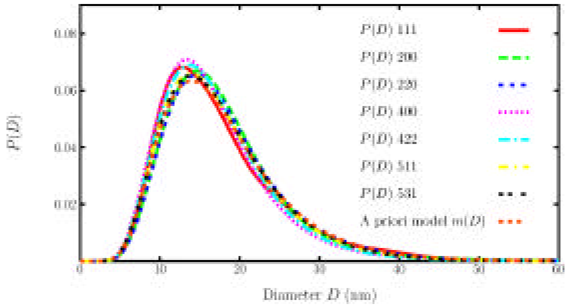

Fig. 4. *CPD round-robin CeO_2 size-distributions for all non-overlapping lines, which including 111, 200, 220, 400, 422,511 and 531.*

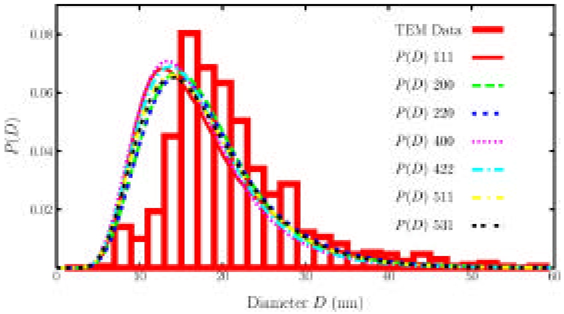

Fig. 5. *Bayesian/MaxEnt and TEM size distributions of the CPD round-robin CeO_2 specimen. The TEM distribution was developed from 853 crystallites, while the Bayesian/MaxEnt distributions were determined from the non-overlapping profiles (see Fig 4).*

The final test for the Bayesian/MaxEnt size analysis comes in comparing the Bayesian/MaxEnt size distribution with a TEM-derived distribution. The techniques are independent of each other, but the x-ray analysis was able to provide more information than did the TEM analysis. This is highlighted by the results in Figs. 5 & 6, from which it can be seen that TEM could not resolve overlapping crystallites in the size range $D \leq 14$ nm. However, for $D > 14$ nm the agreement between the two distributions is very satisfactory. The difference between the x-ray and TEM size distributions, given in Fig 5, is due to difficulties in dispersing the CPD CeO_2 specimen. This comparison between the x-ray and TEM data illustrates the need for a nanocrystallite size SRM. Fig. 6 is a TEM micrograph showing that the CPD CeO_2 crystallites have a near-spherical morphology. It also reveals that there is considerable overlap of crystallites, making it difficult to distinguish between smaller and large crystallites.

The main disadvantage of the (present) Bayesian/MaxEnt method is that it only takes into consideration size broadening contributions, requiring a relatively good understanding of the material specimen. However, the present method has established a basis for a *generalized* Bayesian/MaxEnt method that quantifies the size, stacking/twinning and dislocation broadening contributions, while taking into consideration any suitable *a priori* information. In addition, the present method only analyses non-overlapping line profiles; further improvements can be gained if the method were extended to whole pattern analysis, since this would reduce the likelihood of systematic errors from peak overlapping. A project is currently underway to develop a whole pattern method. It could also be argued that the need and use of *a priori* information is a disadvantage of the method; however, we argue that it is a strength, in that it tests the available *a priori* information in the light of experimental data. This in turn is the basis of scientific reasoning [14].

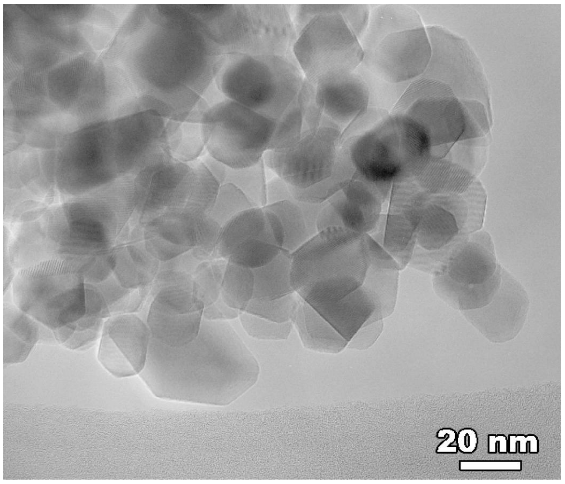

Fig. 6. *TEM micrograph of the CPD round-robin CeO_2 specimen used in this analysis. The crystallites have a near-spherical morphology, while overlapping of crystallites make it difficult to distinguish the boundaries between individual crystallites.*

CONCLUSION

- The development of a NIST nanocrystallite size SRM will address a significant shortfall in the analysis of crystallite size using x-ray diffraction and electron microscopy techniques.
- This SRM will have broad applications in the rapidly developing nanotechnology industry.
- We have demonstrated that a full Bayesian/MaxEnt (quantitative) analysis can be used to determine the crystallite size distribution. This approach incorporates all the available information and quantifies uncertainties in the solution; importantly, it makes no explicit assumptions about the shape of the profile or crystallite distributions.
- The development of a whole pattern Bayesian/MaxEnt method is the next important development.
- We expect this approach to form the basis of a more general method for separating size, strain and stacking fault/twinning effects.
- Unlike existing techniques, our approach has determined the size distribution from a first-principles application of the underlying Physics, and without making any assumptions about the size distribution.
- This study of CeO_2 has found it to be suitable for a size SRM; it can be easily mass-produced in feedstock amounts in the required size range, and the manufacturing process developed results in negligible strain broadening.

REFERENCES

[1] N. Armstrong, W. Kalceff, J. P. Cline, and J. Bonevich. “Bayesian inference of nanoparticle broadened x-ray line profiles”. *Submitted to J. Res. Nat. Inst. Stand. Techn., 2001*. Proceedings of Accuracy in Powder Diffraction III, 22-25 April 2001, NIST, Gaithersburg, USA.

[2] N. Armstrong, W. Kalceff, J. P. Cline, and J. Bonevich. “A Bayesian/Maximum Entropy method for certification of a nanocrystallite-size NIST Standard Reference Material” in *Diffraction analysis of the microstructure of materials*. Springer-Verlag, Berlin, 2003.

[3] E. T. Jaynes. *Phys. Rev*., **106(4)**:620-630, 1957.

[4] C. E. Krill and R. Birringer. *Phil. Mag.*, **A77(3)**:621-640, 1998.

[5] J. I. Langford. NIST Spec. Pub., **846**:110-126, 1992.

[6] J. I. Langford and D. Loüer. *J. Appl. Cryst.*, **15**:20-26, 1982.

[7] J. I. Langford and D. Loüer. *Rep. Prog. Phys.*, **59**:131-234, 1996.

[8] J. I. Langford, D. Loüer, and P. Scardi. *J. Appl. Cryst.*, **33**:964-974, 2000.

[9] J. I. Langford and A. J. C Wilson. *J. Appl. Cryst.*, **11**:102-113, 1978.

[10] D. Loüer and N. Audebrand. University of Rennes. For details follow the links provided at www.iucr.org/iucrtop/comm/cpd/projects/index.html, 2001.

[11] P. Scardi and M. Leoni. *J. Appl. Cryst*., **32**:671-682, 1999.

[12] D. S. Sivia. “Data Analysis: A Bayesian Tutorial”. Oxford Science Pub., Oxford, 1996.

[13] J. Skilling and R. K. Bryan. *Mon. Not. R. astr. Soc*., **211**:111-124, 1984.

Report on the Size-Strain Round Robin

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INTRODUCTION

CPD-sponsored size-strain round robin was recently organized to provide a better insight into effects of crystallite size and lattice strain on diffraction line broadening, which is a vibrant field of modern powder diffraction [1]. The full motivation for the round robin was discussed earlier [2]. As line-broadening analysis is an inherently difficult field of powder diffraction and some previous size-strain round robin attempts had failed, it was decided to begin with a sample with a limited degree of line overlapping, isotropic broadening, and a simple sample microstructure. Measurements were taken at different diffraction facilities ("representative measurements") to study influence of measurement conditions (mainly instrument resolution, type of radiation, and instrument setup). Here, the aim is to give a short overview of specimen preparation, preliminary analysis of the measurements, and the results of the round robin, in which the participants have applied different methods of line-broadening analysis to the representative measurements. The complete results and a comprehensive review of the methods employed will be published elsewhere. A more extensive report on the round-robin results is posted at http://www.du.edu/~balzar.

SAMPLE PREPARATION

Nanocrystalline CeO_2 (ceria) was prepared from thermal treatment of hydrated ceria, according to the method reported in detail elsewhere [3]. Cerium sulfate, $Ce(SO_4)_2 \cdot 4H_2O$, was used as starting material. Hydrated ceria was precipitated at room temperature, under vigorous stirring, from the addition of 250 g of the Ce(IV) salt in 4 L of a 1M ammonia solution. The precursor so obtained consists of ultrafine hydrated cerium oxide $CeO_2 \cdot xH_2O$, which has the crystal structure of ceria, and has been characterized by spherical crystallites of ~20 Å diameter, on average [3]. This yellow colloidal hydrated ceria was washed with distilled water three times, with alcohol, filtrated and then dried at room temperature for three days. In order to have a sample without too large diffraction line broadening, the annealing temperature was selected to be 650 °C. The hydrated ceria was heated in a silica crucible with the heating rate of 120 °C h^{-1} until 650 °C and then kept for 45 hours at this temperature in order to ensure complete annealing. From this procedure 50 g of ceria were obtained (here designated as S1).

Annealed ceria was used to characterize instrumental broadening. Commercially obtained ceria was annealed at different temperatures and times to achieve minimal line broadening without inducing growth of too large grains, which would be detrimental to counting statistics and shape of the diffraction-line profiles. An optimum behaviour was obtained with annealing at 1300 °C for 3 h in air. Powder was slowly cooled overnight in the crucible. This sample is designated here as S2. The comparison between annealed ceria and an NIST SRM660 LaB_6 powder, when used for correction of instrumental broadening, did not show significant changes (within a single standard deviation) in the final parameters of interest, that is, domain size and strain values.

REPRESENTATIVE MEASUREMENTS

Measurements were collected on both ceria samples at seven instruments:

(i) University of Birmingham: a high-resolution x-ray laboratory setup with an incident-beam monochromator;

(ii) University of Le Mans: a "common" x-ray laboratory setup;

(iii) National Synchrotron Light Source (NSLS): 2nd-generation synchrotron, flat-plate geometry;

(iv) European Synchrotron Radiation Facility (ESRF): 3rd-generation synchrotron, capillary geometry;

(v) NIST Center for Neutron Research (NCNR): constant-wavelength (CW) neutron source;

(vi) Institute Laue-Langevin (ILL): CW neutron source;

(vii) ISIS at the Rutherford-Appleton Laboratory: Time-of-flight (TOF) neutron source.

Figure 1 compares instrument resolutions, ? *d*/*d*, calculated from the FWHM of instrumental standard profile (sample S2), as obtained by Rietveld refinement of line-profile parameters.

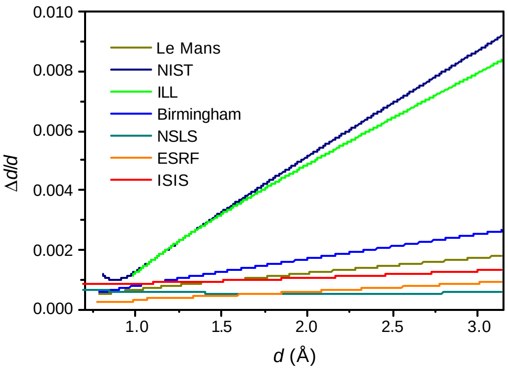

Fig. 1. *Resolution function ? d/d as a function of interplanar spacing d for all instruments, as calculated from the FWHM, for the sample S2.*

In order to ensure the self-consistency of measurements before the round-robin data were made available to the round-robin participants, an analysis of all the measurements was carried out by three methods: Bayesian deconvolution followed by the Warren-

Averbach (WA) analysis of line broadening, an assumed physical model of lognormal size distribution of spherical crystallites (LNSDSC), and Rietveld refinement. Recommendations for refining profile parameters in Rietveld refinement and their interpretation through the physical parameters of interest (domain size and strain) are given elsewhere [4]. Both the WA and Rietveld approaches yielded a relatively small strain, as opposed to the LNSDSC method. On constraining the strain to zero, all three methods gave similar values of domain size (Table 1). The values given for the LNSDSC method correspond to the lognormal distribution with the average diameter (the first distribution moment) of spherical crystallites equal to approximately 183 Å with the distribution standard uncertainty of approximately 78 Å (an average over all data sets).

	LNSDSC (Å)	WA (Å)	Rietveld (Å)
Birmingham	223	228	227
Le Mans	229	226	224
ESRF	229	224	219
NSLS	228	229	224
ILL	225	224	220
NIST	232	230	216
ISIS	231	240	224

Table 1. *Apparent volume-averaged domain size, as calculated by three methods (acronyms explained in text).*

ROUND ROBIN RESULTS

The measurements and instructions were made available to the round-robin participants for download at the NIST Web site. 18 reports with results were received. To be able to compare the results, an attempt was made to scale all the reported quantities into groups of results that are consistently defined. An initial screening of results has eliminated 2 sets with clearly erroneous values of both domain size and strain. The results for the apparent volume-averaged domain size were clustered in two regions: below and above 250 Å. The latter results had a much larger scatter, which can be explained by an oversimplified analytical model used for the size-broadened profile (a single Lorentzian function), although the size-broadened profile had a significant Gaussian component. This is inherent to the Lorentz-Lorentz and Lorentz-Gauss integral-breadth methods, and often a consequence of incomplete refinement of profile parameters in Rietveld refinement. For instance, the participants that did not refine the Gaussian size term (proportional to 1/cos^2?) have obtained a larger value of domain size, as the corresponding line broadening was probably erroneously absorbed into another refined parameter. This has systematically shifted the averages toward the larger domain sizes (Figure 2 gives average results for different analysis methods). Conversely, the participants using double-Voigt methods (VV.1 [5] and VV.2 [6] in Fig. 2) obtained a lower value for domain-size.

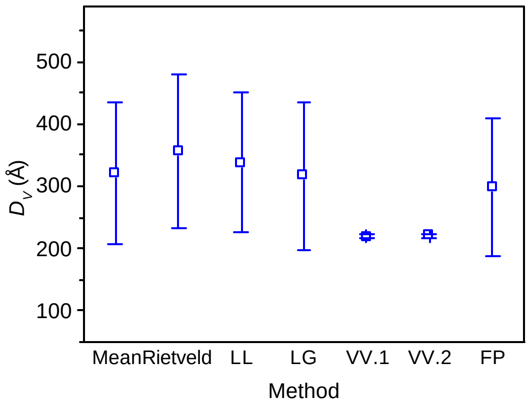

Fig. 2 *Apparent volume-averaged domain size: The mean is an average over all results, LL is the Lorentz-Lorentz and LG is the Lorentz (size)-Gauss (strain) integral-breadth method, VV.1 and VV.2 are double-Voigt methods, FP is "Fundamental parameters" approach.*

CONCLUSIONS

Round-robin results indicate that the ceria powder shows dominant domain-size related isotropic line broadening. The results obtained on instruments with different resolution do not vary significantly. The size-broadened profile is not pure Lorentzian but has a strong Gaussian contribution. If the Gaussian contribution is neglected, erroneous results can be obtained, in particular in Rietveld refinement.

ACKNOWLEDGEMENTS

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REFERENCES

[1] J. I. Langford and D. Louër: *Rep. Prog. Phys.* **59** (1996) 131-234.
[2] D. Balzar: CPD Newsletter 21, p. 3.
[3] N. Audebrand, J.-P. Auffrédic and D. Louër: *Chem. Mater.* **12** (2000) 1791-1799.
[4] D. Balzar, N. Audebrand, M. R. Daymond, A. Fitch, A. Hewat, J. I. Langford, A. Le Bail, D. Louër, O. Masson, C. N. McCowan, N. C. Popa, P. W. Stephens and B. Toby: *J. Appl. Cryst.* (2003) submitted.
[5] J. I. Langford: In *Accuracy in Powder Diffraction,* NBS Special Publication No. 567, pp. 255-269.
[6] D. Balzar and H. Ledbetter: *J. Appl. Cryst.* **26** (1993) 97-103.

Dislocation density tensor for diffraction line analysis

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INTRODUCTION

The present work deals with microstructure analysis of crystalline materials, especially concerning the role of dislocations. At this scale, the effect of dislocations on the crystals properties is associated basically with the local internal strain and stress fields. A dislocation elasticity theory is then a necessary prerequisite for the development of a quantitative analysis of dislocations. Several models based on the notion of a continuous medium and elasticity theory, sometimes called the continuum theory of dislocations [1-4], were developed and applied to many cases, e.g.: single edge or screw dislocation, straight dislocations, interaction between two screw dislocations, dislocation cell, dislocation loops.

Major advances in processing control or service life safety are facilitated by rapid feedback between properties and microstructure measurements. X-ray diffraction (XRD) is a non-destructive technique widely applied for the crystalline materials characterisation. XRD enables one to study dislocations microstructures, their spatial distribution and especially to determine their density. Starting from the scattered intensity, the Fourier coefficients of the diffraction line which characterize its broadening can be obtained. This broadening is due to the size of diffracting coherent domains, and to the lattice distortion heterogeneity (spatial positions of atoms) generated by imperfections, mainly dislocations [5-11].

In this work, dislocation analysis will be done at a scale where effect of dislocation groups prevails, so that it is important to take into account the strong interactions between dislocations. For this purpose, it will be developed a micromechanical approach [1, 12] at an intermediate scale, between random dislocations distributions and exact dislocations space positions. Furthermore, the proposed approach will not describe the setting in configuration of dislocations but it will consider a given configuration to calculate the exact associated fields in a deterministic way [12].

CRYSTALLOGRAPHIC DISLOCATION DENSITY TENSOR

In the following, it is show how the displacement u_i and then the elastic distortion field β_{ij} for a given plastic strain ε^*_{ij} (or distortion β^*_{ij}) due to dislocations are determined. The resolution of this micromechanical problem is based on the knowledge of the three equations: of the equilibrium, behaviour and strain compatibility. It is also considered that the total strain ε_{ij} is equal to the sum of the ε_{ij} elastic and the plastic ε^*_{ij} ones. The equation of equilibrium allows one writing:

$$C_{ijkl}\, u_{k,lj} = C_{ijkl}\, \varepsilon^*_{kl,j} \tag{1}$$

where u_i is the displacement vector, and C_{ijkl} is the elasticity stiffness tensor. The displacement solution is thus related to the plastic strain distribution. Supposing that this strain is periodic and given by a Fourier integral, we obtain [1]:

$$u_i(x) = -\int_{-\infty}^{+\infty} C_{jlmn}\, \varepsilon^*_{mn}(x')\, G_{ij,l}(x-x')\; dx' \tag{2}$$

$G_{ij}(x-x')$ is the Green's function. Elastic distortion is related to total and plastic ones by $\beta_{ji}=u_{i,j}-\beta^*_{ji}$ and the plastic strain to distortion by $\varepsilon^*_{ij}=(\beta^*_{ij}+\beta^*_{ji})/2$.

The plastic distortion is caused by the slip b_i of the plane whose normal vector is n_j [2]:

$$\beta^*_{ij}(x) = -b_i\, n_j\, \delta(S-x) \tag{3}$$

where $\delta(S-x)$ is the one-dimensional Dirac delta function in the normal direction of S, being unbounded when x is on S and zero otherwise. Using Stoke's theorem and introducing the permutation tensor $\in_{jnh}$, equations (2) and (3) allows one to write the elastic distortion in the form:

$$\beta_{ji}(x) = \oint_L \in_{jnh} C_{pqmn}\, b_m\, G_{ip,q}(x-x')\, \chi_h\; dl(x') \tag{4}$$

where χ is the direction of the dislocation line l, and dl is the dislocation line element. The dislocation density tensor α_{hm} is defined by the x_m-component of the total Burgers vector of dislocation threading the unit surface perpendicular to the x_h-direction [1]:

$$\alpha_{hm}(x') = b_m\, \chi_h \frac{dl(x')}{dx'} = b_m\, dl_h(x') \tag{5}$$

The dislocation density tensor $\alpha_{hm}(x)$, which characterizes the incompatibility of deformation at each point of the lattice network, was first introduced by Nye [1]. In the sense of general thermodynamics, the dislocation density is a state quantity, i.e. a quantity that, at least in principle, can be measured without knowing anything about previous times. It is very important to notice that the dislocation density tensor can give information on the nature of dislocations, because the diagonal components represent screw dislocations and the off-diagonal ones characterize the edge dislocations. Finally, introducing (5) into (4) the elastic distortion is given by:

$$\beta_{ij}(x) = \int_V \in_{jnh} C_{pqmn}\, G_{ip,q}(x-x')\, \alpha_{hm}(x')\; dx' \tag{6}$$

$G_{ij}(x-x')$ characterizes the specific spatial position interaction, in comparison with approaches using the principle of superposition of each single dislocation contribution [3, 6, 10, 13].

DIFFRACTION LINE FOURIER COEFFICIENTS

In previous section, we introduced the relation between distortion and dislocation density tensors. Now, we present the relation between distortion tensor and Fourier coefficients of the peak, providing to link between the dislocation density tensor to the Fourier coefficients.

When two atoms ‘p’ and ‘q’ are moved of δR_p and δR_q compared to their initial positions R^0_p and R^0_q, introducing the Bragg centred variable s, the scattered intensity takes the following form:

$$I(s) = f \sum_{(p,q)=1}^{N} A(n) \quad \exp\left(2\pi i s \left\{R_p^0 - R_q^0\right\}\right) \qquad (7)$$

$A(n)=<\exp(2\pi i g\{\delta R_p-\delta R_q\}>$ represents the Fourier coefficients of the diffraction peak, g is the reciprocal space diffraction vector and n, the Fourier parameter. The scattered intensity shows that line broadening results from the distortion fields. The information on these fields is contained in the Fourier coefficients. It is noticed that only the components of displacements perpendicular to the diffracting planes contribute to the line broadening. Moreover, these coefficients result in fact from the average on the atoms pairs characterized by the same projection distance on the diffraction vector n.a ($n.a=R^0_p-R^0_q$ is the periodicity distance in the diffraction vector direction). The displacement related to the initial position $\varepsilon_n=\{\delta R_p-\delta R_q\}/n.a$ is the projected distortion. The Fourier coefficients are now given by the following equation [14, 15]:

$$A(n) = <\exp\left(2\pi\ i\ g a n\varepsilon_n\right)> \qquad (8)$$

The symbol < > denotes the averaging over the crystal volume (summation over all p and q atoms corresponds to each n value). In a first approach, one considers only the symmetrical part of the exponential.

It was show that the Fourier coefficients are closely related to the distortion state of the microstructure. Knowing the latter by the micromechanics theory, one can calculate these coefficients by an averaging operation, in which, one varies the Fourier parameter by taking the corresponding distortion field projected on the diffraction vector:

$$\varepsilon_n = \left\langle \frac{g_i b_{ij} g_j}{g^2} \right\rangle_n \qquad (9)$$

SINGLE EDGE DISLOCATION CASE

To illustrate our approach, consider a crystal of infinite dimension, filled with a single edge dislocation. Let us examine the case of an edge dislocation in the crystalline lattice of iron (body-centred cubic crystal) defined by the Burgers vector b=[-111], the dislocation line l=[-11-2] and the normal of the glide plane n=[110] in the (x_1=b, x_2=n, x_3=l) dislocation reference frame. Referring to the definition of the dislocation density tensor, this tensor takes the form of a Dirac’s delta function $\alpha_{31}(x)=b.\delta(x_1).\delta(x_2)$ (b is the Burgers vector modulus) for the single dislocation considered (positioned at $x_1=x_2=0$). Knowing that, the integration of (6) is performed on the half plane ($x_1<0$, $x_2=0$). Figure 1 shows the distortion fields in the crystal considering isotropic elasticity (ν=0.3). These calculated fields were validated by comparison with analytical solutions given in the literature [1-4].

It can be noticed that: (i) the linear elasticity theory predicts distortions (or stresses) that vary as the inverse first power of the distance from the dislocation line. It converges towards zero at a distance of about 40b.

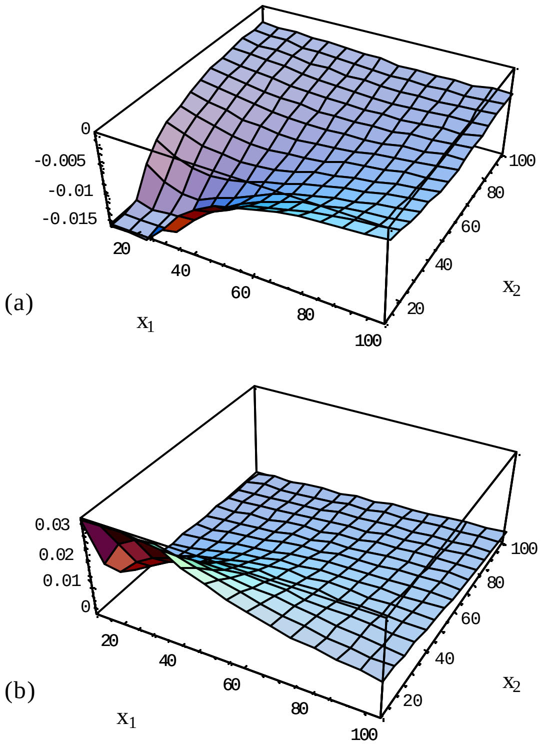

Fig. 1. *Lattice distortion fields b_{11} (a) and b_{12} (b) in the considered edge dislocation reference frame.*

(ii) Close to the singularity (line defect) the strains become very large, and non-linear effects must be taken into account, so that our approach cannot be applied when considering the region of the crystal close to the dislocation line (in our case this distance is taken equal to 4b). (iii) The distortion field of linear defects is of long-range character compared to the point defects (short range) and planar defects [7].

Our program calculates the elastic distortion fields with knowledge of the dislocation density tensor. Knowing the transformation matrix a_{ij} (each column is filled respectively with the components of b, n and l), these fields are determined in the crystal reference frame. The projection of these distortion fields on the diffraction vector makes it possible to calculate the Fourier coefficients of the diffraction peak by an averaging operation. Actually this projection, which is called contrast factors of dislocations, depends on the relative orientations of the diffraction vector, the line and Burgers vectors of the dislocations and the elastic constants of the crystal [7].

UNIFORM DISLOCATION CONFIGURATION

The interaction effect between dislocations is now examined. For that, the introduction of the averaged dislocation density $\overline{a}_{hm}$, which is function of the dislocation density tensor, is a necessary step to determine a continuous analytical relation form of the distortion fields. This is an important point because in (6) we have three-dimensional integrals, which can be calculated only with analytical forms of the two terms

$C_{pqmn}.G_{ip,q}$ and α_{hm}. For isotropic materials, the first term is an analytical relation [1] so that the mathematical solution depends on the form of α_{hm}. The case of an Uniform Dislocation Distribution (UDD), where $\alpha_{hm}(x')$ is kept constant, is now considered.

The considered uniform configuration is based on the single edge dislocation of the previous section. In the dislocation-reference frame, the dislocation density tensor α_{ij} takes the form:

$$\alpha_{ij}=\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ \bar{\alpha}_{31} & 0 & 0 \end{pmatrix} \quad \text{with} \quad \alpha_{ij}=\bar{\alpha}_{31}=\frac{b_1}{H}\delta(x_2)$$

H is the average distance between dislocations (in x_1 direction). b_1 is the Burgers vector component in x_1 direction (in the dislocation reference frame). Distortion field components are deduced from integration of:

$$\beta_{ij}(x) = \bar{\alpha}_{hm} \int_V \varepsilon_{jnh}\, C_{pqmn}\, G_{ip,q}(x - x')\, dx' \qquad (10)$$

We examine in figure 2 the distortion fields of UDD configuration as a function of H. Same data as the single dislocation treatment (e.g. Poisson's ratio ν and Burgers vector modulus) is considered.

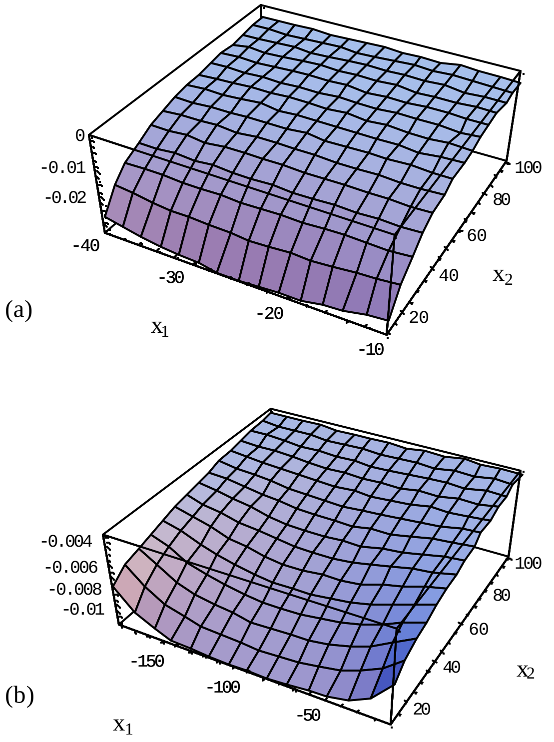

Fig. 2. *Distortion fields* $\beta_{11}(x_1,x_2)$ *for the considered UDD configuration - H=50 Å (a) and 200 Å (b).*

It can observed that when the distance between dislocations increases from H=50 to 200 Å, the $\beta_{11}(x_1,x_2)$ component of the distortion fields decreases. This is a confirmation of the short-range interaction phenomena between dislocations [16, 17]. Therefore, the micromechanical theory predicts the long-range strain and stress for a single dislocation (without interaction). But it is not the case for dislocation configurations (group of dislocations with interaction), where we reduced this effect of long-range to short-range (sometimes mean-range). When H is close to zero (H=0.1 Å), the estimated fields are close to those of the single dislocation case, so that our approach is validated. The results are close but not exactly the same as interaction between dislocations is considered.

CONCLUSION

A micromechanical deterministic approach, which utilizes the crystallographic physics, was developed in order to determine the distortion fields associated with a dislocation configuration. This approach provides one the possibility to relate the estimated elastic distortion with the X-ray scattering intensity. It is worth noting that it is not necessary to separately calculate contrast factors [7, 10, 14]. The need for studying the real dislocations configurations (dislocation dipole, pile-up, dislocation arrays or dislocation cell-walls) forces us to utilize more realistic tools based on the average aspect to describe our configurations.

In prospects, the case of the anisotropic elasticity of cubic crystal must be developed. Then, for a better explanation of the broadening measurement, future work will consider an inverse approach for dislocation microstructures identification by coupling the experiment with the modelling.

REFERENCES

[1] Mura T., 1987. Micromechanics of defects in solids. Mart. Nij. Publishers, Kluwer, Dordrecht, The Netherlands.

[2] Nabarro F. R. N., 1983. Dislocation in solids. North Holland, Amsterdam.

[3] Hirth J.P., Lothe J., 1968. Theory of dislocations. McGraw-Hill, New York.

[4] Teodosiu C., 1982. Elastic models Of crystal deffects. E.A. Bucharest & Spring.-Verlag.

[5] Warren B.E., 1990. X-ray diffraction. Dover Pub, New York.

[6] Wilkens M., 1979. J. Appl. Cryst. 12, 119-125.

[7] Ungar T., 2001. Mat. Sci. & Eng. A309-310, pp. 14-22.

[8] Gaal I., 1994. Internal paper.

[9] Van Berkum J.G.M., Delhez R., Keijser T.H., Mittemeijer E.J., 1996. Mat. Science. Forum, Vol. 228-231, pp. 11-18.

[10] Groma I., 1998. Physical Review B 57, pp. 7535-7542.

[11] Klimanek P., 1991. Mat. Science. Forum Vol. 79-82, pp. 73-84.

[12] Kröner E., 2001. Int. J. of Sol. and Str. 38, pp. 1115-1134.

[13] Raabe D., 1996. Philosop. Mag, A 73, No 5, pp. 1363-1383.

[14] Ghiath M., 1999. Phd Thesis. Ensam Paris.

[15] Ghiath M., Bacroix B., Lebrun J.L., 1999. Proceeding of the 5th ECRS. Delft, Netherlands.

[16] Kocks U.F., Scattergood R.O., 1969. Acta. Met. Vol. 17, pp. 1161-1168.

[17] Kroupa F., 1994. Key Eng. Mat., Vols. 97-98, pp. 377-382.

The Correlation between Line Broadening and the Elastic Properties of Crystals

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STRAIN ANISOTROPY

Strain anisotropy in powder diffraction means that neither the breadths nor the Fourier coefficients of the diffraction profiles in the Williamson-Hall plot [1] or the Warren-Averbach method [2] are monotonous functions of the modulus or the square of the diffraction vector, g or g^2, where $g=2\sin\theta_B/\lambda$, and θ_B and λ are the Bragg angle and the wavelength of radiation, respectively [3-9]. Diffraction peaks broaden either when the crystallites become small or when the crystals contain lattice defects. The two effects usually occur together, however, they can be separated since the size effect is diffraction order independent (at least, as long as shape is more or less isotropic), whereas strain broadening increases with g. In the kinematical theory of diffraction the physical profile of a Bragg reflection (I^F) is given by the convolution of the size (I^S) and the strain (I^D) profiles: $I^F=I^S*I^D$. The Fourier transform of this is the Warren-Averbach equation [2]:

$$\ln A(L) \cong \ln A_L^S - 2\pi^2 L^2 g^2 \langle\varepsilon_{g,L}^2\rangle , \qquad (1)$$

where $A(L)$ and A_L^S are the absolute values of the Fourier coefficients of I^F and I^S, and $\langle\varepsilon_{g,L}^2\rangle$ is the mean square strain in the $\boldsymbol{g}$ direction. L is the Fourier length defined: $L=\mathrm{n}a_3$, $a_3=\lambda/2(\sin\theta_2-\sin\theta_1)$, n are integers and (θ_2,θ_1) is the angular range in which the diffraction profile is measured. Let us define a Cartesian coordinate system with the unit vectors: $\boldsymbol{s}_1$, $\boldsymbol{s}_2$, $\boldsymbol{s}_3$, and its origin in the *hkl* reciprocal lattice node where $\boldsymbol{s}_1$ is parallel to $\boldsymbol{g}$. The reciprocal space vector in the vicinity of $\boldsymbol{g}$ is: $\boldsymbol{K}=\boldsymbol{g}+\xi_1\boldsymbol{s}_1+\xi_2\boldsymbol{s}_2+\xi_3\boldsymbol{s}_3$. The intensity distribution in the *hkl* reciprocal lattice node is a scalar-vector function: $I(x_1,x_2,x_3)$. In powder diffraction experiments carried out in the usual θ-2θ regime the diffraction profiles are automatically integrated over x_2 and x_3: $I^F=\int I dx_2 dx_3$. In a single crystal experiment care has to be taken in order to fulfil this integration. Distortion is defined by the lattice vectors of the *m*th atoms: $\boldsymbol{r}_m=\boldsymbol{R}_m+\boldsymbol{u}_m$, where $\boldsymbol{R}_m$ is the lattice vector of the average or undistorted lattice site and $\boldsymbol{u}_m$ is the displacement vector. We define the vector $\boldsymbol{r}=r_1\boldsymbol{s}_1+r_2\boldsymbol{s}_2+r_3\boldsymbol{s}_3$ in real space over the base $\boldsymbol{s}_1$, $\boldsymbol{s}_2$, $\boldsymbol{s}_3$. With this the longitudinal component of the strain tensor parallel to $\boldsymbol{g}$ is: $\varepsilon_g=\partial/\partial r_1(\boldsymbol{gu})/g$. The spatial average of the square of ε_g is the mean square strain:

$$\langle\varepsilon_g^2\rangle=\langle[\partial/\partial r_1(\boldsymbol{gu})/g]^2\rangle=\langle(\boldsymbol{g}b\,\boldsymbol{g})^2/g^4\rangle,$$

where $b=grad\,\boldsymbol{u}$ is the distortion tensor and *grad* is carried out over r_1, r_2 and r_3. Here we note that the Fourier variable L is also defined in the $\boldsymbol{r}$ space given above. It can be seen that $\langle\varepsilon_g^2\rangle$ is a homogeneous zeroth order function of the diffraction vector which depends only on the direction of $\boldsymbol{g}$ and is independent of its length. Eq. (1) shows that the strength of strain broadening is proportional to $g^2\langle\varepsilon_{g,L}^2\rangle$. The deviation from the monotonous g^2 dependence, incorporated in $\langle\varepsilon_g^2\rangle$ is *strain anisotropy*. $g^4\langle\varepsilon_g^2\rangle$ is a fourth order polynomial of the *hkl* indices: $g^4\langle\varepsilon_g^2\rangle=P_4(h,k,l)$. In a powder specimen $P_4(h,k,l)$ becomes independent of those *hkl* permutations which correspond to the same d values. For this reason, in the fourth order polynomial of $g^4\langle\varepsilon_g^2\rangle$ only the fourth order invariants of the *hkl* indices will appear. These, however, have to satisfy the symmetry of the particular crystal structure. The 4th order invariants of *hkl* can be found in the book of Nye [10] and have been recompiled by Popa [11]. In cubic crystals the only non-trivial 4th order invariant of *hkl* is: $h^2k^2+h^2l^2+k^2l^2$. Especially, in cubic crystals the mean square strain has the *hkl* dependence [12]:

$$\langle\varepsilon_g^2\rangle=A+B[(h^2k^2+h^2l^2+k^2l^2)/(h^2+k^2+l^2)^2], \qquad (2)$$

where A and B are constants. The derivation up to this point has been completely general and no assumption has been made either about the character of strain or the elastic properties of the crystal. Stephens [8] starts from the variance of $1/d^2$, Stokes and Wilson [11] use simple plasticity and both arrive at the same result as presented here. The two constants, A and B, can be determined from experiment. Their physical interpretation needs, however, further discussion of the origin of microstrain.

THE DISLOCATION MODEL OF STRAIN

Experiment shows that the mean square strain is never independent neither of g nor of L, cf. [13]. The L dependence reveals a double singularity, at small L values $\langle\varepsilon_{g,L}^2\rangle$ diverges logarithmically and at large L values it decreases like $1/L$, latter indicating the long range character of the mean square strain. Krivoglaz [14], Wilkens [15], Gaál [16], Groma et al. [17], vanBerkum et al. [18], Levine and Thomson [19] and Groma [20], Kamminga and Delhez [21], all have shown that this particular behaviour of the mean square strain indicates that the major contribution of strain to diffraction peak broadening comes from dislocations. The mean square strain of a dislocated crystal can be given as [15]:

$$\langle\varepsilon_{g,L}^2\rangle=(b/2\pi)^2\pi\rho C f(h) , \qquad (3)$$

where $h=L/R_e$, R_e is the effective outer cut off radius of dislocations. $f(h)$ is the Wilkens function as given in eqs. A.6 to A.8 in [15], it starts logarithmically for small h values and ends hyperbolically for large h values. The constant C depends on the relative orientation between the Burgers- and line vectors of dislocations and the diffraction vector and on the character of dislocations, e.g. edge or screw in cubic, or basal, prismatic or pyramidal in hexagonal crystals [22,23]. Equation (2) allows to factorise the mean square strain into g and L dependent parts: $<\varepsilon_{g,L}^2>=C<\varepsilon_L^2>$, where $<\varepsilon_L^2>= f(h)$. In an untextured cubic polycrystal or powder specimen C can be averaged over the permutations of *hkl*:

$$\overline{C} = A'+B'[(h^2k^2+h^2l^2+k^2l^2)/(h^2+k^2+l^2)^2]. \qquad (4)$$

$\overline{C}$ is called the average *dislocation contrast factor* in analogy with the term used in electron microscopy. It can be given as:

$$\overline{C} = \overline{C}_{h00}(1-qH^2), \qquad (5)$$

where $\overline{C}_{h00}$ is the average *dislocation contrast factor* of the *h00* type reflections, $q=-B'/A'$ and $H^2=(h^2k^2+h^2l^2+k^2l^2)/(h^2+k^2+l^2)^2$. The values of $\overline{C}_{h00}$ and the q parameter can be obtained numerically for different dislocation types as functions of the elastic properties of a crystal [22,23]. A powder diffraction experiment provides experimental values for both, $\overline{C}_{h00}$ and q. From eq. (3) it is clear, however, that the experimental value of $\overline{C}_{h00}$ depends on the absolute value of the dislocation density, ρ. The only parameter in eq. (5) which is *well* defined by strain anisotropy is q. It is a function of: (i) the type of dislocations and (ii) the ratios of the elastic constants of the crystal [12,22,23]. For this reason there are two ways in which the experimental values of q can be used: (*a*) if the elastic constants are known the dislocation structure or character can be deduced or, (*b*) if the elastic constants are unknown than, by making some assumptions about the dislocation structure or character, certain ratios of the elastic constants can be deduced. It is important to note that $q=-B'/A'=-B/A$ which means that the experimental strain anisotropy parameters provided by the analysis of Stephens [8] can also yield the *ratios* of the elastic constants. As a specific example we take the values of $S_{400}=3.43\text{x}10^{-8}$ and $S_{220}=-1.13\text{x}10^{-8}$ for the *fcc* Rb$_3$C$_{60}$ specimen from Table 3. in [8]. Simple algebra provides $q=-3.035$.

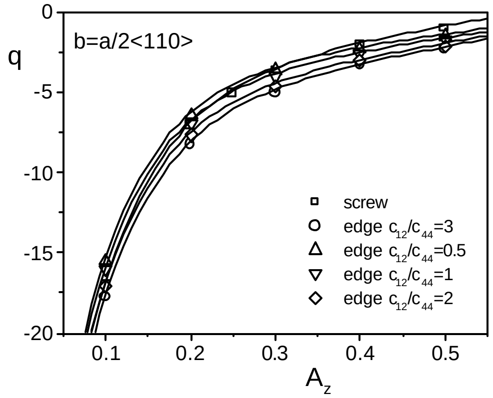

Fig. 1. *q as a function of the anisotropy constant, $A_z=2c_{44}/(c_{11}-c_{12})$, for different dislocations and c_{11}/c_{12} ratios.*

Figure 1 shows the values of q as a function of the anisotropy constant, $A_z=2c_{44}/(c_{11}-c_{12})$, for the simplest dislocation type in *fcc* crystals with Burgers vectors *a*/2<110>, for different c_{11}/c_{12} ratios and for screw and edge character, respectively [23]. From Figure 1 we conclude that the elastic anisotropy of Rb$_3$C$_{60}$ is: $A_z=0.4\pm0.1$.

REFERENCES

[1] Williamson, G. K. & Hall, W. H., 1, 22-31 (1953)

[2] Warren, B. E. and Averbach, B. L., J. Appl. Phys. 21, 595 (1950)

[3] Caglioti, G., Paoletti, A. and Ricci, F. P., Nucl. Instrum. 3, 223-228 (1958)

[4] Ungár, T. and Borbély, A., Appl. Phys. Lett., 69, 3173-3175 (1996)

[5] Le Bail, A. & Jouanneaux, A., J. Appl. Cryst., 30, 265-271 (1997)

[6] Scardi, P. & Leoni, M., J. Appl. Cryst., 32**,** 671-682 (1999)

[7] Dinnebier, R. E., Von Dreele, R., Stephens, P. W., Jelonek, S. & Sieler, J., J. Appl. Cryst., 32, 761-769 (1999)

[8] Stephens, P. W., J. Appl. Cryst, 32, 281-288 (1999)

[9] Cheary, R. W., Dooryhee, E., Lynch, P., Armstrong, N. & Dligatch, S., J. Appl. Cryst., 33,1271 -1283 (2000)

[10] J. F. Nye, Physical Properties of Crystals, their Representation by Tensors and Matrices, Oxford Clarendon Press, 1957.

[11] A.R.Stokes and A.J.C.Wilson, Proc. Phy. Soc. London, 56, 174 -181 (1944)

[12] T. Ungár & G. Tichy, Phys. Stat. Sol. (a) 171, 425 (1999)

[13] J. van Berkum, PhD Thesis, Technical University Delft, Holland, 1994.

[14] M. A. Krivoglaz, in Theory of X-ray and Thermal Neutron Scattering by real Crystals, Plenum Press, N. Y. 1969; and in X-ray and Neutron Diffraction in Nonideal Crystals, Springer-Verlag, Berlin Heidelberg New York, 1996.

[15] Wilkens, M., in Fundamental Aspects of Dislocation Theory, ed. J. A. Simmons, R. de Wit, R. Bullough, Vol. II. Nat. Bur. Stand. (US) Spec. Publ. No. 317, Washington, DC. USA, pp. 1195-1221 (1970)

[16] Gaál, I., in Proc. 5th Riso Int. Symp. on Metallurgy and Material Science, eds. N.H. Andersen, et al., Riso Nat. Lab., Roskilde, Denmark, p. 249-254. (1984)

[17] I. Groma, T. Ungár, and M. Wilkens, J. Appl. Cryst. 21, 47 (1988)

[18] van Berkum, J. G. M., Vermuelen, A. C., Delhez, R., de Keijser, T. H. and Mittemeijer, E. J. J. Appl. Cryst. 27, 345-357 (1994)

[19] Levine, L. E. and Thomson, R., Acta Cryst. A, 53, 590 (1997)

[20] Groma, I., Phys. Rev. B, 57, 7534-7542 (1998)

[21] Kamminga, J. D. & Delhez, R., J. Appl. Cryst. 33, 1122-1127 (2000)

[22] T. Ungár, I. Dragomir, Á. Révész and A. Borbély, J. Appl. Cryst. 32 992 (1999)

[23] I. Dragomir and T. Ungár, Powder Diffraction, 17, 104-111 (2002)

Surface relaxation in nano-sized powders

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Nanocrystalline materials usually exhibit unusual properties when compared to their coarse-grained counterparts. From the X-ray diffraction point of view, frequently observed is the increase (decrease) of the unit cell parameter when decreasing the grain size, often interpreted in terms of oxygen incorporation or stoichiometry variations[2] (cf. [1] and refs. Therein).

Seldom considered, yet alternative, is the presence of Grain Surface Relaxation (GSR). To lower their energy, the atoms next to a surface tend to shift from their regular lattice positions: the variation is followed by the majority of sub-surface atoms, thus mimicking a unit cell parameter change.

Full-pattern structural (Rietveld method [2]) and microstructural (Whole Powder Pattern Modelling, WPPM [3,4]) refinement techniques do not traditionally consider any GSR phenomenon. A Fourier formalism, following the ideas of Warren and Bertaut [5], has been therefore introduced to bridge the gap [1] and is briefly introduced here. This approach permits the diffraction profile to be synthesised from first principles, without recurring to arbitrary bell-shaped profile functions.

A lognormal distribution of spherical crystallites, taken as independent coherent scatterers, is considered. To simplify the mathematics involved, each crystallite is supposed as made of concentric hollow cylinders aligned along the scattering direction, each of them made of columns of blocks (as in Fig. 1).

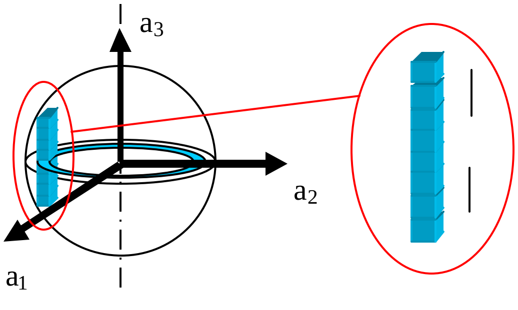

Fig. 1. *Subdivision of a grain into concentric cylinders made of columns of blocks. For clarity only a single column is shown. Because of surface relaxation, the blocks are displaced from their regular lattice positions.*

For symmetry reasons, the total scattering along the cylinders' axis (i.e. parallel to $\mathbf{a}_3$) can be calculated by considering the scattering of just one column of blocks for each cylinder, taken with a proper weight [1].

The problem therefore reduces to calculating the scattering power for a column of blocks arranged on a stretched lattice. The stretching Δz, nil when surface relaxation is absent, is a function of the coordinate z along $\mathbf{a}_3$ as:

$$\Delta z(r,z) = x\frac{z}{|z|}e^{-\frac{z_{\max}(r)-|z|}{k}}$$

where x is the maximum stretch (i.e. maximum cell or atom position shift from the regular lattice), 2 $z_{\max}(r)$ is the length of the column sitting at a distance r from the centre of the grain and k is a relaxation decay constant. An example of the relaxation function is shown in Fig. 2 for grains of 1 and 10 nm in diameter, respectively.

The proposed model is of course suitable to describe a lattice contraction as well (by changing the sign of x).

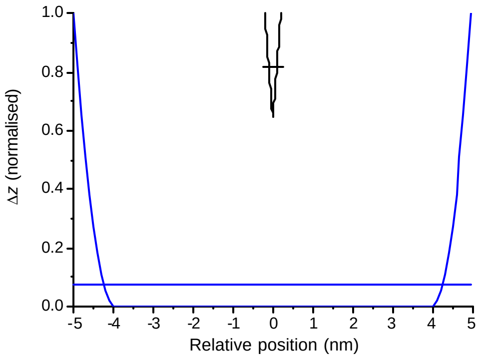

Fig. 2. *Lattice spacing stretching versus position along crystallite radius for grains of 1 and 10 nm in diameter, respectively (x=1.0; k=0.1). Horizontal lines marks the corresponding average shift.*

Taking this stretching into account, the correlation between couples of cells along the column at various (Fourier) distances n must be considered [3,5]:

$$A_n^{SR} = \frac{N_n}{N_3}\langle \cos 2p\,\mathrm{L}Z_n \rangle \qquad B_n^{SR} = -\frac{N_n}{N_3}\langle \sin 2p\,\mathrm{L}Z_n \rangle$$

where Z_n is the distance between the two cells and $\langle\ \rangle$ indicates average over all n-distant couples. In this formulation, both relaxation and size effects are simultaneously taken into account. Besides size and relaxation effects, using the WPPM approach [3] other Fourier components relative to other sources of broadening can be simultaneously considered.

The profile can be finally calculated from the Fourier coefficients A_n^{SR} and B_n^{SR} as:

$$I_{hkl}^{SR}(d^*) \propto \sum_{n=-\infty}^{\infty} \left\{ A_n^{SR}\cos 2p\,nh_3 + B_n^{SR}\sin 2p\,nh_3 \right\}$$

where h_3 is a relative coordinate in the reciprocal space (cf. [1]).

Peak intensities can be left as free parameters (as in WPPM) or bounded to a structural model (as in the Rietveld method) [4]. A nonlinear least squares routine is in both cases used to fit the model to the data.

---

[2] Associated to this is a broadening of line profiles caused by the reducing size of coherent domains.

The calculation is lengthy as it should be carried out for all cylinders of all grains in the powder. Nevertheless, with the aid of fast numerical algorithms, a peak can be synthesized in one second (program compiled with Compaq Visual Fortran Pro ver. 6.6 and running on an AMD Athlon XP 2000+ processor).

The performance of the algorithm has been tested on cerium oxide (CeO_2). Nanocrystalline powder was synthesised using a sol-gel technique [6]: different heat treatments have been studied and the result for a sample calcinated for 1h at 400°C is shown here (Fig. 3). The agreement, witnessed by the small residual, is quite good; it is worth noting that the cell parameter was fixed to a= 0.541134(12) nm, value reported in the JCPDS-PDF card #34-0394 (http://www.icdd.com). The refinement was done in the GSR-Rietveld mode, i.e. constraining peak intensities to a structural model and peak shape to a microstructural model. Conversely, a traditional refinement (Rietveld or WPPM) fails unless a larger, average unit cell parameter is used.

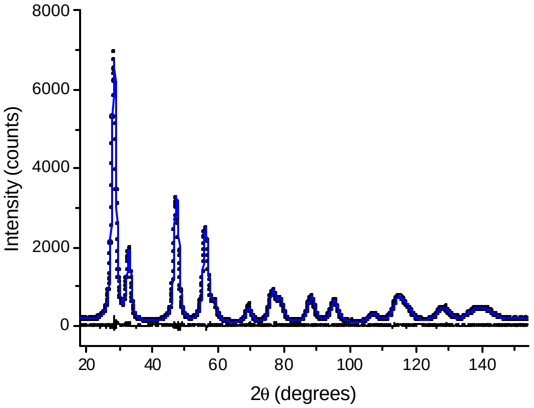

Fig. 3. *Experimental (open dots) and refined pattern using the GSR-Rietveld algorithm (line). The difference between raw data and refinement (residual) is also shown.*

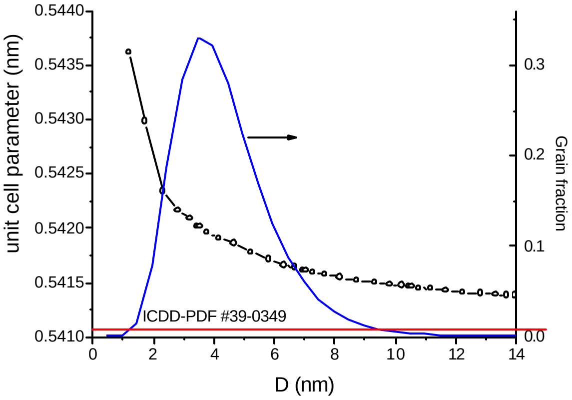

Fig. 4. *Average unit cell parameter versus grain size for the (refined) grain size distribution shown.*

Fig. 4 shows the effect of surface relaxation on grains of different sizes and the corresponding weight given by the grain size distribution: smaller grains are more affected (high surface/volume ratio), thus their average unit cell parameter is intrinsically higher.

The XRD results seems confirmed by other techniques. For example, Fig. 4 shows a Transmission Electron Microscopy (TEM) micrograph of a ceria grain: the interplanar distance increases when running from the middle to the outer surface of the grain.

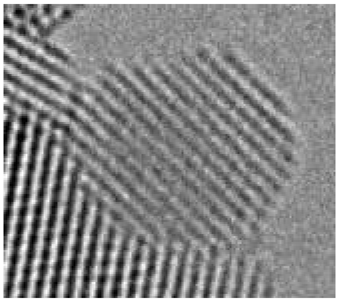

Fig. 4. *TEM micrograph showing surface relaxation in a grain of ceria (outer planes show larger spacing [1])*

A further confirmation can be found in a recent paper of Wu *et al.* [7] where an analogous effect (a core-shell structure for the grains) is introduced to describe the EXAFS patterns of nanocrystalline ceria. Even if not directly comparable, the two results agree both in sign and order of magnitude, possibly validating the present approach.

CONCLUSIONS

Powder diffraction can account for surface relaxation effects in order to explain the anomalous trend of the average cell parameter observed when reducing the grain size to the nanometre range. To this, a Fourier formalism has been developed and implemented in the WPPM and Rietveld frames to synthesise and refine a diffraction pattern constraining the cell parameter to the single-crystal (or coarse grained-powder) value. Diffraction results are supported by TEM observation.

REFERENCES

[1] M. Leoni, P. Scardi in “Diffraction Analysis of the Microstructure of Materials”, Ed. P. Scardi & E.J. Mittemeijer, Springer Verlag (Berlin), 2003.

[2] R.A. Young, “The Rietveld Method”, Oxford University Press (New York), 1993).

[3] P. Scardi, M. Leoni, *Acta Cryst.* **A58** (2002) 190.

[4] P. Scardi, *Z. Kristallogr.* **217** (2002) 420.

[5] B.E. Warren “X-ray diffraction”, 2nd edition, Dover (New York), 1990 (1st edition, Addison Wesley, Reading, Mass., USA, 1969)

[6] R. Di Maggio, P. Scardi, M. Leoni. In preparation

[7] Z. Wu, L. Guo, H. Li, Q. Yang, Q. Li, H. Zhu, *Mat. Sci. Eng.* **A286** (2000) 179.

Powder Diffraction Pattern Of Stacking Faulted Crystal

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INTRODUCTION

Stacking faulted crystals have been extensively studied by X-ray diffraction, the reason for that is the well known fact that planar faulting shift and broadens the diffraction reflections as well as producing asymmetric peak profiles. Early treatment of diffraction in stacking faulted crystals were developed by a number of authors and a review of the early developments can be found in [1]. In a broad sense, the approximations towards diffraction effects of planar faulting can be classified in two types, those which derive a set of observable parameters related to some assumed faulting type probability and those which use simulation techniques to match calculated patterns with experimental ones.

From the first approach the well known treatment of Warren and Wilson based on difference equations [2] (and further development by Jagodzinski and a number of authors, see [1] for references) is still widely used for its simplicity, relating measured parameters of the diffraction pattern with several faulting probabilities. From the second approach different Monte Carlo schemes have been put forward where crystals are "grown" in a computer with a priori faulting probabilities until a match is found with the experimental pattern [3].

Warren´s approach makes a series of strong simplifying assumptions in order to relate peak parameters with simple cases of planar faulting, namely deformation and twinning faults. The resulting relations are limited in applicability and have to be worked out for each particular structure and faulting type. It has been pointed out that even in the case of low faulting probability, it is controversial were the calculated deformation and twin faulting probabilities are correct even predicting the faulting trend [4].

Monte Carlo approaches are useful for investigating more complex faulted structure, yet they still rely on the ingenuity of the researcher to propose a faulting model fit for the investigated sample. Simulation approaches are indirect in nature: they depend on trial and error procedures, making little use of the observed experimental data up to the last stages of analysis were comparison is performed.

Both, difference equation methods and current simulation approaches, are to be considered to be faulting models: an underlying structure is assumed and faulting is seen as a perturbation to the otherwise perfect ordering along the stacking direction. Faulting models are at least dubious in their applicability to phase transformations between polytypes, involving only reordering of the layers sequence order, and in heavy faulted structure. In both cases it is not physically clear which underlying perfect periodic sequence should one consider.

Recently a different approach has been proposed for analysing diffraction patterns of faulted crystal [5]. The approach is based on the determination of the pair of layers probability correlation functions directly from the diffraction pattern through a Fourier series, which in the case of powder diffraction reduces to a cosine series. The Fourier coefficients are related linearly to the correlation probability functions ($P_s(D)$). From the $P_s(D)$ functions other parameters can be defined which can be related to more used faulting parameters if needed.

THE PROBABILITY CORRELATION FUNCTION

The probability correlation function $P_s(D)$ is defined as the probability of finding two layers, Δ-layers apart, and laterally (in the sense of perpendicular to the stacking direction) displaced, one with respect to the other, a integer number ***s*** of times a minimum displacement vector.

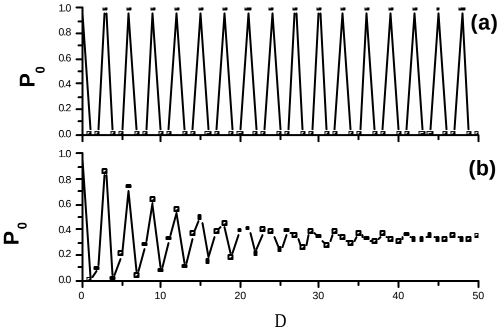


Fig. 1. *The $P_0(D)$ correlation function for a (a) perfect FCC structure and for a (b) 0.05 deformation faulted structure.*

To better understand the probability correlation function *Figure 1a* shows the corresponding $P_0(D)$ of the perfect FCC structure. The correlation function is consistent with the ABCABCAB… ordering, as for every multiple of three layers, the probability of finding layers not displaced one with respect to the other is 1, otherwise being zero.

For faulted crystals the periodic behaviour of the $P_s(D)$ function is absent, and correlation is lost with increasing Δ values. *Figure 1b* shows the $P_0(D)$ function for a 0.05 deformation faulted structure still for the FCC structure.

Figure 1b shows two important characteristics of the correlation function of faulted structure. They consist of two contributing terms: one periodic of oscillatory nature and the other a decaying term. From the decaying term a critical Δ_c length can be defined as the characteristic correlation length of the system (*Figure 2*). It can be shown that Δ_c is related to peak broadening and asymmetry, while the oscillating term is related to the shifting of the diffraction peak due to the faulting.

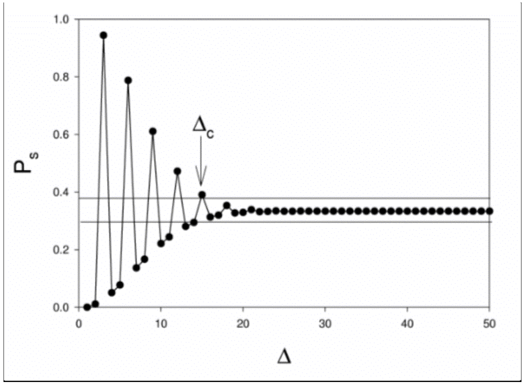


Fig. 2. *The definition of the correlation length as the characteristic length where correlation between layers can be considered lost.*

THE DIRECT SOLUTION APPROACH

The determination of the $P_s(D)$ functions from the diffraction data is direct in nature and full use of the whole information contained in the diffraction data is made through the Fourier series decomposition. The Fourier decomposition obtained is periodic in the reciprocal variable *l* (assuming that the stacking direction is c) and the frequent problem of peak truncation in Fourier analysis is avoided. Constant background influence is also avoided by proper normalization of the probability function under physical constrains.

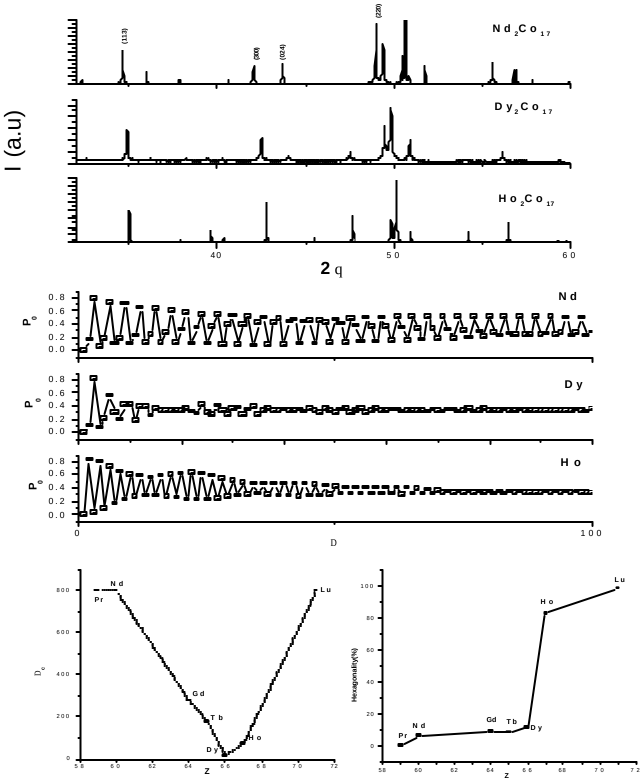
It has to be pointed out that in the determination of the $P_0(D)$ function from the diffraction data no assumption has to be made about the type of stacking disorder occurring in the crystal structure, nor is it limited by the density of faulting.

The introduction of the Δ_c parameter as a measure of disorder allows the comparison of different faulted structures, regardless of the difference of faulting type between them, and gives a structure insensitive parameter for faulting measure.

For the case of compact structures the $P_0(D)$ function also allows the direct determination of the amount of hexagonality in the structure as the $P_0(2)$ value. Extension to non-compact structures can be easily made, being the percent of non compact layer arrangement given by $P_0(1)$.

In the case needed, the relation between the Δ_c and $P_s(D)$ to other more often used parameters can be made. For example Δ_c and peak maximum can be related to the deformation (a_o) and twin (b_o) faulting probability in compact structures. In this case the obtained probabilities are not affected by the approximations usually made in, for example, the Warren approach.

It has been shown that from the $P_0(D)$ values representative stacking sequences of the structure can be reconstructed [6]. The determination of the stacking sequence allows the use of other distance measures for a more complete characterization of faulting and polytype occurrence. Further discussion of this topic is beyond this short comment and will be published in the near future.



TWO EXAMPLES

Fig. 3. *(a) The diffraction pattern of RE$_2$Co$_{17}$ (RE: rare earth) affected by stacking faults disorder. (b) The calculated correlation function of three representative samples. (c) The correlation length for all studied samples together with the hexagonal percent.*

As an example of the use of the above approach to compact structures, the experimental diffraction pattern of a RE$_2$Co$_{17}$ (RE: rare earth) is shown in *Figure 3a*. These binary compounds show a transition from hexagonal packing for the heavy rare earth to rhombohedral stacking for the light ones. The pattern was processed according to the above approach (practical details of pattern decomposition and treatment can be found in [7]) and *Figure 3b* shows the ***P_0(D)*** values for three representative samples. *Figure 3c* plots the evolution of Δ_c with the rare earth species. The heavy nature of faulting in the intermediate rare earths is immediately seen and a comparison of faulting for the whole series is made possible by the use of the Δ_c value.

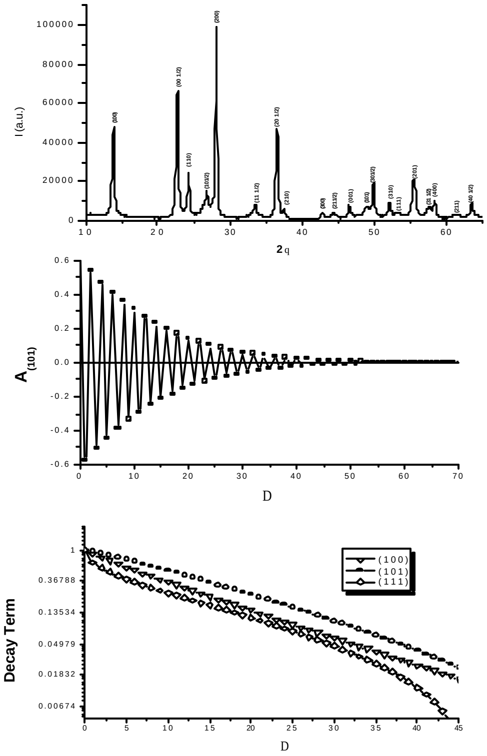


Fig. 4. *(a) Diffraction pattern of WO_3. (b) The Fourier coefficients. (c) The decay term for several diffraction peaks in a semi logarithmic scale, the correlation length will be given by the inverse of the slope of each curve and it was found to be D_c=12 layers.*

The hexagonality percent of the structure can be calculated from the ***P_0(2)*** values for each sample.

As another example of the use of the above approach the WO_3 diffraction pattern obtained form the PowBase database [8] (and said to be affected by stacking faults) is shown in *Figure 4*. This corresponds to a non-compact structure with space group P6/mmm. The Fourier coefficient behaviour is shown in *Figure 4b*. From the slope of the logarithm of the decaying term, the Δc value was obtained (*Figure 4c*) giving a value of 12 layers.

EER wish to acknowledge the AvH Foundation for a Humboldt fellowship where part of this work was completed. This work was carried out partially financed by a TWAS research project and an Alma Mater project from the University of Havana. We also thank the LNLS at Campinas, Brazil where the diffraction experiments for the RE_2Co_{17} samples were made.

REFERENCES

[1] T. R. Welberry, Rep. Prog. Phys., **48** (1985), 1543.

[2] Warren, B. E. X-Ray Diffraction (Addison-Wesley, 1969).

[3] R. Berliner and S. A. Werner, Phys. Rev. B **34** (1986), 3586; R. Berliner, O. Fajen, H. G. Smith, R. L. Hitterman, Phys. Rev. B **40** (1989), 12086; R. Berliner and R. J. Gooding, Acta Cryst. **50** (1994), 98.

[4] L. Velterop, R. Delhez, Th. H. Keijser, E. J. Mittemeijer, D. Reefman, J. Appl. Cryst. **33** (2000), 296

[5] E. Estevez-Rams, J. Martinez, A. Penton-Madrigal, R. Lora Serrano, Phys. Rev. B, **63** (2001), 54109.

[6] E. Estevez-Rams, Private Communication (2002).

[7] E. Estevez-Rams, A. Penton-Madrigal, R. Lora Serrano, J. Martinez, J. Appl. Crys., **34** (2001), 730.

[8] PowBase can be freely accessed at: http://pcb4122.univ-lemans.fr/cgi-bin/powbase.pl

News from the
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2002 Denver X-ray Conference

The 51st Denver X-ray Conference was held in Colorado Springs, Colorado from 29 July to 2 August, attracting nearly 300 registered attendees and over 200 exhibit personnel.

Front: Eileen Jennings, Donna Barry: Middle: Bob Snyder, Sheila Snyder, Terry Maguire, Denise Flaherty, Jim Kaduk, Leah Mooney. Back: Cam Hubbard

The Plenary Session, “Applications of X-ray Analysis to Forensic Materials”, was organized by Dr. David F. Rendle, of The Forensic Science Service, Metropolitan Laboratory, London, UK and the late Dr. Ron Jenkins, Emeritus, International Centre for Diffraction Data, Newtown Square, PA. The Plenary Session presented a series of fascinating criminal investigations where X-ray analysis provided key evidence in the solution of a crime. Invited talks presented during the Plenary Session were: “X-ray Analysis in the U.S. Customs Laboratories”, M.H. Liberman, US Customs Laboratory, San Francisco, CA; “Underkarat Jewelry: The Perfect Crime? Investigations and Analysis of Jewelry Using XRF”, D. Kloos, Industry Consultant, Westminster, CA; “X-ray Diffraction Analysis in the Forensic Science Laboratory of Stuttgart, Germany—The Last Resort in Many Criminal Cases”, W. Kugler, Forensic Science Laboratory, Stuttgart, Germany; “Portable XRF for Forensic Investigations”, D.C. Ward, Federal Bureau of Investigation, Washington, DC; “Use of X-rays in the United Kingdom Forensic Science Service”, D.F. Rendle, The Forensic Science Service, London, UK and “XRD at the FBI: The Three C’s of Forensic Science”, M.C. Bottrell, Federal Bureau of Investigation, Washington, DC.

The following awards were presented during the Plenary Session: 2002 Birks Award to Michael Mantler, Vienna University of Technology, Vienna, Austria; 2002 Jerome B. Cohen Student Award to Jay C. Hanan, The California Institute of Technology, Pasadena, CA and the 2002 McMurdie Award to Camden R. Hubbard, Oak Ridge National Laboratories, Oak Ridge, TN.

Forty-two companies exhibited at the conference, displaying their various products and services for X-ray powder diffraction and X-ray fluorescence spectrometry. The ICDD would like to thank the vendors who participated at the conference and also sponsored evening receptions: Bede Scientific, Bruker AXS, Corporation Scientifique Claisse, Materials Data, Inc., PANalytical (formerly Philips Analytical), Rigaku/MSC and SPEX CertiPrep.

PPXRD-2

The ICDD organized the 2nd Pharmaceutical Powder X-ray Diffraction Symposium, PPXRD-2, which was held in Concordville, Pennsylvania, USA on 9–12 December 2002. Hosting over 70 participants, the Symposium focused on high-throughput crystallization and screening, polymorph characterization, and powder pattern indexing. The attendance was truly international with half the participants coming from 12 different countries. The first three days were dedicated to technical sessions and round table discussions. A companion, hands-on workshop, held on the fourth day at ICDD Headquarters in nearby Newtown Square, concluded the symposium.

The first day was dedicated to acquisition and analysis of XRPD data. Creative approaches in pre-formulation and formulation were discussed. A comparative analysis between brand name drugs and generic drugs was given. Several presentations discussed the advantages of capillary sample holders, especially with single characteristic wavelength monochromators and parallel beam geometries.

Polymorph characterization was the main focus during the second day. Results from challenging problems, including, for example, determining the dynamics of dehydration in indapamide hemihydrate, using “clustering” of low-quality XRPD patterns for phase identification, characterization of four polymorphs of fananserine, and high-throughput crystallization techniques that allowed up to ~300 crystallizations per day for a single lead compound were also clearly explained. The fananserine work showed the opportunity to connect structural results from X-ray powder diffraction with thermodynamic properties. Studies using structure determination techniques were discussed on a wide range of examples including zopiclone, anhydrous caffeine (Z'=5) and a compositionally disordered form of ranitidine HCl form 2. Strong contributions from academia, the pharmaceutical industry, analytical laboratories, equipment manufacturers and database organizations were evident in all sessions.

The third day session on regulatory and patent issues focused on a number of well-known litigation cases including cefadroxil and ranitidine hydrochloride. The discussion centered on distinguishing differences between how courts interpret X-ray diffraction patents and how scientists interpret X-ray powder diffraction patterns. This session ended with several tutorial talks on SAXS and SANS, where contrast matching and other techniques to characterize length scale distributions up to several thousand Angstroms were discussed.

The companion workshop, held on 12 December 2002 included practical guides to powder pattern indexing and a discussion on round robins that can be used to help researchers compare their instrument performance with others in the pharmaceutical industry. The workshop registrants participated in hands-on exercises, focused on the use of in-house XRPD methods and practices. Discussions included the critically important results that can be obtained from synchrotron-based sources.

High-quality data collection and data analysis were common themes in most PPXRD-2 presentations.

New Product Release: PDF-4/Organics 2003...Now Available!

At PPXRD-2, the ICDD announced the availability of its exciting new relational database of organic materials targeted for pharmaceutical analyses, PDF-4/Organics 2003. This database contains over 147,000 entries (24,385 experimental and 122,816 calculated), representing a 500% increase in available organic X-ray diffraction patterns, making it the world's largest X-ray powder diffraction database for organics! Resulting from a four-year collaboration with the Cambridge Crystallographic Database Centre, PDF-4/Organics 2003 is targeted for the pharmaceutical and specialty chemical industries where special attention has been given to new pharmaceuticals and drug active substances with 2D chemical structure representations and subfile classifications. Experimental and calculated data can be quickly converted into fully digitized patterns using ICDD's enhanced "on-the-fly" calculation and display technology. PDF-4/Organics 2003, like other PDF-4 designed products, integrates both display and search software into the database. In addition, ICDD's PDF-4 products offer unparalleled data with unprecedented power to data mine 30+ separate diffraction and physical property data fields

You're Invited!

The ICDD will hold its Annual Spring Meetings for members and nonmembers the week of 17–21 March 2003. In addition to the traditional meetings of our Committees, Subcommittees, and Task Groups, some new and exciting changes are planned, including....

- A Plenary Session focusing on "Advances in Automated Phase Identification"—Leading experts in phase ID will discuss the new possibilities available today along with their expectations for future development.
- A Historical Tour of Philadelphia—Walking tour through the "City of Brotherly Love", retracing the steps of one of the great scientists, Ben Franklin. During the tour, we'll visit some of the sites where U.S. history was made, and even meet Ben himself along the way!

If you'd like to take this opportunity to...

- Learn more about the ICDD organization, its programs, products, and services,
- Network with peers in all fields of materials characterization,
- Benefit from the advice of others working in similar environments,
- Provide input to make the PDF more useful to you in your analyses,

mark your calendar and join us! Members, friends, and colleagues in the scientific community are invited and most welcome. See http://www.icdd.com/profile/march03.htm to register and to receive further details.

Further Information

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

21st EUROPEAN CRYSTALLOGRAPHIC MEETING

DURBAN, SOUTH AFRICA, 24-29 AUGUST 2003

Second Announcement -- Call for papers

Main Conference Information (*website: www.sacrs.org.za/ecm21*)

You are cordially invited to attend ECM-21 in Durban!

ECM-21 will be held at the International Convention Centre (ICC) in Durban located 1 km from the beachfront. Durban is situated in the heart of the Zulu kingdom, Kwazulu-Natal. For the first time an ECM will convene in South Africa -- and indeed Africa. The South African currency (ZAR; South African Rand; 1Euro ca. ZAR9) strongly favours tourism and the conference fees are modest. Participants should at worst not pay more than for a typical ECA meeting at a European destination. Interested participants are encouraged to contact Conference Call (confcall@yebo.ca.za) or Andre' Roodt (Chair: Organising Committee).

Organising Committee

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Dave Billing, WITS, Johannesburg
Demi Levendis, WITS, Johannesburg
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Peet van Rooyen, South Africa
Chick Wilson, United Kingdom
Andrew Venter, South Africa
Svetlana Zheludeva, Russia
Xiaodong Zou, China

Weather & Tourist Attractions

Spring starts in South Africa at the end of August, and temperatures are very mild (min/max: 10 - 25 °C) in Durban (subtropical city). Special visits to game parks are planned, as well as normal pre- and post-conference tours that will be available to experience South Africa's wealth of wild-life (& the big FIVE!), plant diversity and mineralogical phenomena. (Further information, see website & below)

Preliminary Programme

Sunday, 24 Aug:	Registration/Welcome
Mon-Thu (25-28 Aug):	Scientific Programme
Thursday Eve (28 Aug):	Closure & Dinner
Friday, 29 Aug:	Game Park Visits

Important Note

Late winter/early spring is a very good time of the year to view game. ALL participants will be treated to a one day excursion (Friday 29 Aug) *INCLUDED IN CONFERENCE FEE*, to a Game Park, replacing the normal midweek excursion. Scientific programme will thus run non-stop for four days (25-28 Aug).

Important Dates & Deadlines

Applications: Financial Assistance:	28 February 2003
Details: www.sacrs.org.za/ecm21	
Early bird Registration:	31 March 2003
Abstract submission:	31 March 2003
Accommodation:	15 July 2003
Deadline: Registration:	15 July 2003

Scientific Programme

(a) Plenary Lectures: Eight sequential lectures by experts covering a wide selection of topics (confirmed, see below).

(b) Micro-symposia & Posters (See Below): The scientific programme is divided in five parallel sessions addressing Five FOCUS AREAS: i.e., [FC1] Biological and Macromolecular Crystallography, [FC2] Materials and Minerals, [FC3] Experimental and Computational Techniques, [FC4] Chemical Crystallography, [FC5] Special techniques. These Focus Areas will also be covered by ***Poster Sessions***.

Abstracts

One page Abstracts in English are invited covering all aspects of crystallography and closely related fields of interest: (i) For micro-symposia and topics see Programme below. (ii) Online submission via website (www.sacrs.org.za/ecm21) -- submission by 31 March 2003. (iii) With submission please indicate under which micro-symposium / topic the Abstract is submitted, e.g., FC56 indicates topic of 'Polymorphism' with Chair & co-chair Bernstein & Caira. **Please Note**: Small changes in the programme, dependent on the number of Abstracts received for different micro-symposia, may occur.

Exhibitors

Excellent venue to ensure maximum interaction with delegates & reasonable rates -- information & arrangements based on ECA recommendations via website (www.sacrs.org.za/ecm21).
Information: confcall@yebo.co.za

Registration & Accommodation

Electronically – request documents from conference organisers: confcall@yebo.co.za or, download from website (www.sacrs.org.za/ecm21) ***or*** fax Registration Form given below

Travel Arrangements: via Internet

Booking flights using South African Travel agents will result in significant saving on flights from Europe. The official Travel agent of ECM-21 is ASTRA/ SURE Travel. Block bookings by e.g., student groups, can result in even larger savings. Detailed Information: Johan le Roux: Tel. +27-51-4476352: Fax: +27-51-4476665; johanlr.astraho@galileosa.co.za

The Organizing Committee of ECM-21 shall observe the basic policy of nondiscrimination and affirms the rights of scientists throughout the world to adhere or to associate with international scientific activity without restrictions based on nationality, race, color, age, religion, political philosophy, ethnic origin, citizenship, language, or sex, in accordance with the Statues on the International Council of Scientific Unions. At this meeting (or symposium etc) no barriers will exist which would prevent the participation of bona fide scientists.

21st European Crystallographic Meeting
Programme

A. Plenary Lectures

Tom Blundell	Structural biology of multiprotein complexes involved in cell signalling.	Robert McGreevy	Measuring and modelling atomic and magnetic disorder in crystals
Ted Janssen	Quasicrystals	Bill David	Structure determination from powders - crossing the 100-atom threshold.
Emil Makovicky	The wonderful world of crystal structures of sulfosalts	Wim Hol	Drug targets in tropical diseases
Gilberto Artioli	Tools for mineralogical crystallography	Yu. A. Ossipyan	Space materials research. Present status and perspectives

B. Micro-symposia (Chair / co-chair indicated) [NOTE NUMBERING: e.g., FC56 indicates 'Polymorphism' Chair / co-chair Bernstein & Caira]

	[FC1]: Macromolecular and Biological Crystallography	**[]FC2]: Materials and Minerals**	**[FC3]: Experimental and Computational Techniques**	**[FC4]: Chemical Crystallography**	**[FC5]: Special techniques**
1	Crystallisation T. Bergfors/ J. Garcia Ruiz	New developments in the structure determination of quasicrystals G. Chapuis / W. Steurer	Electron crystallography and real structures (with SIG4) S. Hovmöller / I. Dodony	Synergy of experiment and theory in studies of charge, spin and momentum densities P. Becker / C. Gatti	Powder diffraction in applied and industrial mineralogy J. de Villiers / I. Madsen
2	Synchrotron radiation and radiation damage E. Garman/ D. Bourgeois	Electron crystallography on beam sensitive samples U. Kolb / C. Kübel	High photon energy techniques J. Schneider / P. Suorrti	Impact of charge and spin density studies on molecular sciences F.K. Larsen / N. Ghermani	Fast diffraction - high energy and high throughput powder diffraction R. Dinnebier / S. Verryn
3	Structure refinement and analysis A. Jones / G. Murshudov	Electron crystallography on inorganic materials C. Gilmore / M. Gemmi	Grazing angle techniques J. Nilssen / G. Fragneto	Rooted in nature: compounds -chirality, absolute structure, absolute configuration J. Grochowski / T. Auf der Heyde	Materials for energy storage and the environment M. Thackeray / W. Richter
4	Atomic resolution C. Jelsch / V. Lamzin	Mineralogical mrystallography T. Balic-Zunic / S. Krivovichev	Automatic structure determination: Challenges for the future A.L. Spek / D. Billing	Towards the unification of shared-proton interactions G. Gilli / L. Nassimbeni	Structure determination from powder diffraction data L. McCusker / G.J. Kruger
5	Proton and electron transfer processes M.A. Carrondo	Modular aspects of inorganic crystals – in memory of Boris B Zvyagin S. Merlino / M. Nespolo	Can modern programming languages and -- techniques lead to higher reliability and programmer productivity? L. Cranswick / J. Dillen	Molecular interactions at extreme conditions E. Boldyreva / G. Hearne	Joint powder diffraction and non-diffraction techniques K. Shankland / L. Smrcok
6	HIV/ AIDS (Infectious diseases) A. Wlodawer / T. Sewell	From minerals to materials science E. Scandale / J. Kreisel	Diffraction image processing and data quality E. Dodson / S. Parsons	Inclusion compounds and intercalates: Structure and application S. Bourne / S. C. de Sanctis	Polymorphism J. Bernstein / M. Caira
7	Large systems A. Yonath / H. Dirr	Relaxor ferroelectric materials P. Thomas / T. Woike	Algorithms of the future D. Watkin / S. Urzhumtsev	Structure-properties relationship in molecular crystals C. Wilson / D.C. Levendis	Use of synchrotron and neutron powder diffraction A. Hewat / A. Fitch
8	Enzyme catalysis G. Dodson / R. Hilgenfeld	Charge/orbital ordering in strongly correlated electron systems P. Bordet / A. Guehria- Laidoudi	High resolution X-ray diffraction at new European SR sources M.V. Kovalcuk / B. Capelle	Core chemical crystallography F. Lahoz / J. Rutherford	Indexing powder diffraction patterns: Opportunity for new heuristic and global optimisation methods R. Shirley / C. Rademeyer
9	Transcription and translation A. Liljas / V. Oosthuizen	Crystallography in Africa A. Thalal / G. Kamau	Crystallography at extreme conditions: recent results and new developments J.P. Itié / M. Catti	From structural knowledge to chemical reactivity C. Mealli / P.H. van Rooyen	Time resolved spectroscopy M. Wulff / S. Techert
10	Molecular recognition in molecules and macromolecules S. Larsen / C. Kenyon	Perovskites ancient and modern - in memory of Helen D Megaw M. Glazer / P. Boucher	Crystallisation techniques frontier N. Chayen / A. Zagari	Structural applications in coordination complexes A. Roodt / P. Comba	Spectroscopy - an approach to local structure E. Libowitzky / A. Beran

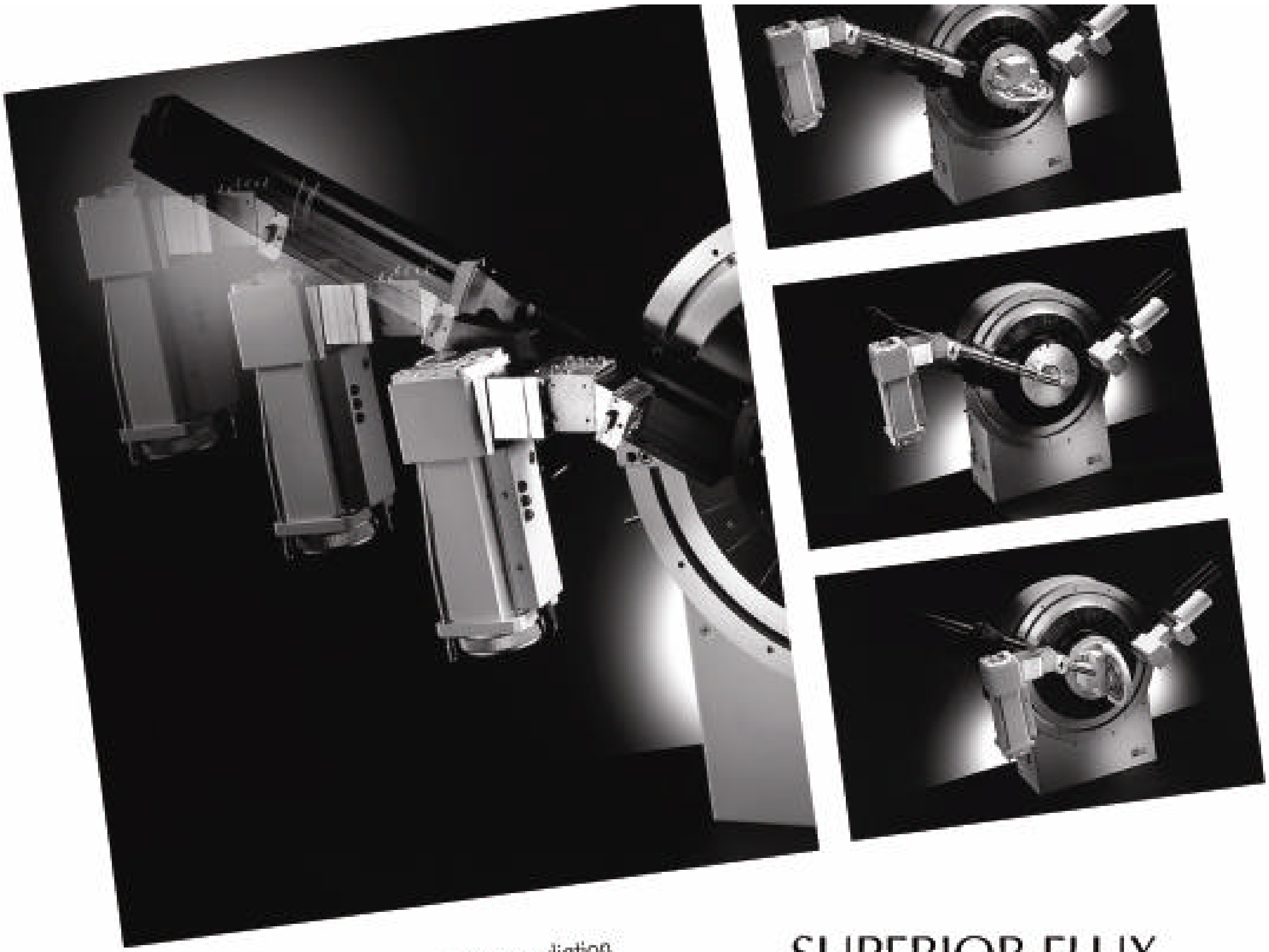
Satellite Meetings: To ensure maximum attendance all aspects of crystallography will be adequately covered by the ECM programme. Only two satellite meetings are scheduled:

(a) ***Neutron Diffraction***: 21-22 August at Centurion/ Pretoria with visits to the Safari-1 research reactor at Pelindaba. Organised by Chick Wilson (C.C.Wilson@rl.ac.uk) & Andrew Venter (amventer@aec.co.za).

(b) ***Indaba4*** The fourth in the multidisciplinary **Indaba series** of the Structural Chemistry Commission of the IUCr. This meeting takes place at Skukuza, in the Kruger National Park, 18-22 August 2003 -- Attendance limited to about 120 delegates. Theme for **Indaba4: '*Patterns in Nature*'**. Enquiries to Peet van Rooyen: pvrooyen@scientia.up.ac.za: www.sacrs.org.za/indaba4

Workshops: Three workshops are scheduled, ***free of charge***, on a first come first serve basis. These will be full-day workshops and will run in parallel on Sunday, 24 Aug 2003. Please reserve place via email to confcall@yebo.co.za -- Further detail on website *(An additional workshop or two, based on substantial delegate interest might be included – consult website on regular basis for updated information)*

Title and Coordinator	Participants
1. Cambridge Structural Database (F Allen: UK; allen@ccdc.cam.ac.uk)	40
2. Single Crystal and Powder Diffraction Software Workshop (L Cranswick: UK; l.m.d.cranswick@ dl.ac.uk)	70
3. Introduction to Protein Crystallography (E Dobson: UK; ccp4@ysbl.york.ac.uk)	40



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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Let the good times roll for Powder Indexing!

Mid to late 2002 has been an exciting time for powder indexing enthusiasts, not only with updated versions of Crysfire, EFLECH/Index, but also in the exposition of new, available indexing algorithms that try to be insensitive to impurity peaks. Known available examples include the new powder indexing option within the Bruker Topas software; a new indexing program by Accelrys; and a third written by Armel Le Bail. This is most timely considering that powder indexing (and also refinement of organic structures) could now be considered bottlenecks in structure solution by powder diffraction data.

New McMaille (GPL'd) whole profile Monte Carlo powder indexing software by Armel Le Bail

The first freely available whole profile powder indexing program has been released by Armel Le Bail called McMaille (Monte Carlo Cell). McMaille allows for a major advance for powder indexing users by the application of Monte Carlo and/or grid search methods on a pseudo-pattern regenerated from peak positions and intensities (with the option of defining separate widths for each peak). This makes McMaille relatively insensitive to trace impurity peaks, even if they are some of the low angle reflections. If you do not have intensities with your peak position data, you can just give every peak 100% intensity; and can also up-weight/down-weight desired reflections by changing its intensity.

While originally released in September 2003, the latest version 3 is 20,000 times faster than version 2, putting in a speed range close to Dicvol. There is an easy to start black-box starting mode that tries to index the cell in a default manner. Running in black box mode also creates a more elaborate starting control file in case further work is required using non-defaults.

Output files include a Fullprof/Winplotr PRF Rietveld plot file of the top solution, plus a Chekcell CKM summary file of found trial cells for use with Chekcell for graphically exploring which solution and spacegroups look the best.

For non-trivial problems, the Monte Carlo method can mean that potential cells could take hours to days to reveal themselves. Thus over lunch and overnight runs can be desirable. The latest December version of McMaille can also attempt the indexing of dual phase mixtures. Though it could be more effective to go back into the laboratory and try and obtain more pure materials.

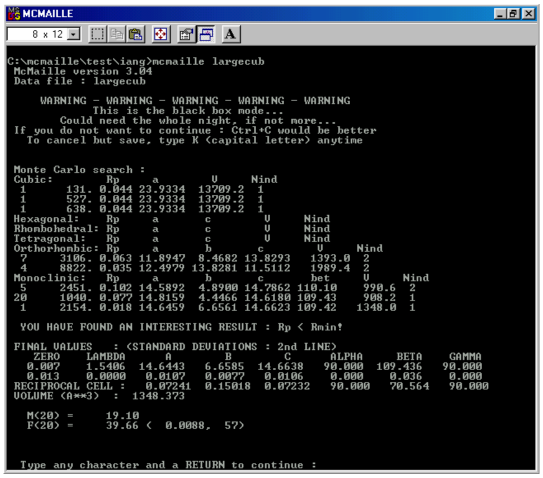
It should also be noted that McMaille, like other indexing programs, requires high quality data. While McMaille could be considered a program of last resort, its failure may indicate either data quality problems or the application of "brain power"™ may be required.

As McMaille is GPL'd, the Fortran source code is included and can be freely modified and redistributed under the terms of the Gnu Public Licence. As it can also be spawned from the command line, it should be relatively easy to link with other powder diffraction programs.

Following is an example "black box" starting file for McMaille on an 800MHz PC Pentium running Windows 98. Within 3 minutes on this example, McMaille has finished, terminating on a monoclinic cell due to a very good solution being found. Examination in Chekcell can show that a cubic solution is the "best". Traditional powder indexing programs running in default mode would be stumped due to the low angle impurity peak (even if "rescaling" of the data a programs such as Crysfire was used). As is the way with Monte Carlo, different runs may produce different results depending on the random number generation. Though in the following example, the cubic solution is always found in every run.

```
large cubic with low angle impurity peak
! Wavelength, zeropoint and NGRID
1.54056 0.0 3
! Couples of 2-theta and intensities
!    2Theta     Area
4.7575     7.7676
6.3866     2474.7675
7.2979     82.4634
10.4412    774.9840
12.2385    171.4875
12.7871    422.2225
14.7257    3.6086
16.0971    34.4029
18.1222    123.0149
19.2677    1087.7178
20.0663    7.7595
20.9921    229.7027
22.2682    7146.9366
23.4698    71.6624
24.3546    5.7305
24.6169    37.6828
25.7650    58.4862
26.5452    750.2571
26.8630    19.9016
27.8433    328.0867
28.5897    205.9600
29.8069    29.1420
30.0920    22.1179
30.6141    46.3798
30.7613    72.7655
31.6693    17751.3605
32.3504    326.8591
```

Fig 1: *An example McMaille "black box" starting file with a very low angle impurity peak (first reflection).*



```
C:\mcmaille\test\iang>mcmaille largecub
 McMaille version 3.04
 Data file : largecub

     WARNING - WARNING - WARNING - WARNING - WARNING
             This is the black box mode...
        Could need the whole night, if not more...
 If you do not want to continue : Ctrl+C would be better
   To cancel but save, type K (capital letter) anytime


 Monte Carlo search :
 Cubic:         Rp      a         V      Nind
  1       131. 0.044 23.9334  13709.2  1
  1       527. 0.044 23.9334  13709.2  1
  1       638. 0.044 23.9334  13709.2  1
 Hexagonal:     Rp      a       c         V      Nind
 Rhombohedral: Rp      a       c         V      Nind
 Tetragonal:   Rp      a       c         V      Nind
 Orthorhombic: Rp      a       b       c         V      Nind
  7      3106. 0.063 11.8947  8.4682 13.8293   1393.0  2
  4      8822. 0.035 12.4979 13.8281 11.5112   1989.4  2
 Monoclinic:   Rp      a       b       c       bet       V      Nind
  5      2451. 0.102 14.5892  4.8900 14.7862 110.10    990.6  2
 20      1040. 0.077 14.8159  4.4466 14.6180 109.43    908.2  1
  1      2154. 0.018 14.6459  6.6561 14.6623 109.42   1348.0  1

  YOU HAVE FOUND AN INTERESTING RESULT : Rp < Rmin!

 FINAL VALUES    : (STANDARD DEVIATIONS : 2nd LINE)
    ZERO     LAMBDA       A         B         C       ALPHA      BETA     GAMMA
   0.007     1.5406   14.6443    6.6585   14.6638    90.000   109.436    90.000
   0.013     0.0000    0.0107    0.0077    0.0106     0.000     0.036     0.000
 RECIPROCAL CELL :    0.07241   0.15018   0.07232    90.000    70.564    90.000
 VOLUME (A**3)   :  1348.373

   M(20) =      19.10
   F(20) =      39.66 (  0.0088,  57)


  Type any character and a RETURN to continue :
```

Fig 2: *Example screen image of McMaille running the above control file.* ***"Nind"*** *is the number of unindexed lines.*

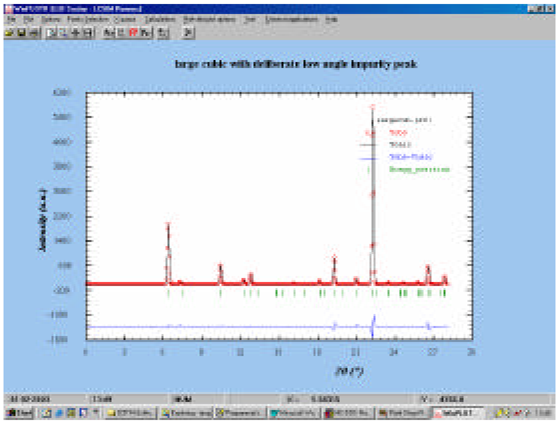


Fig 3: *Profile from top solution displayed in Winplotr using the McMaille generated PRF file.*

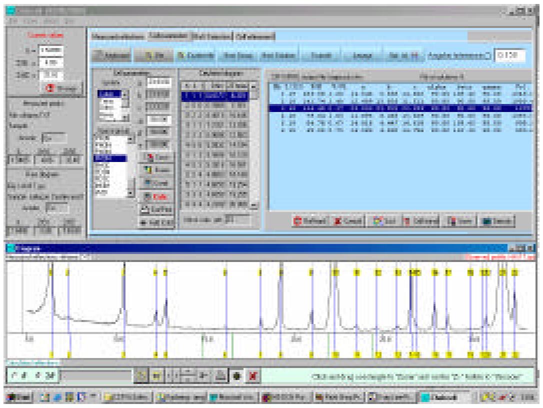


Fig 4: *Comparison of the raw diffraction data and peak list with the resulting solutions displayed in Chekcell using the McMaille generated CKM Chekcell summary file. (one line per solution)*

McMaille, along with examples, hints and advice on its usage, is available via the web at http://www.cristal.org/McMaille/ ; http://sdpd.univ-lemans.fr/McMaille/ and CCP14 Mirrors.

Fityk GPL'd Peak Profiling software by Marcin Wojdyr

A new Open Source GPL'd peak profiling program, Fityk, by Marcin Wojdyr is now available via the web with executables for Windows and Linux (as well as C++ source code). In theory, it is portable to any computer system where the wxWindows library is supported (http://www.wxwindows.org/). The Fityk program can be controlled via a Graphical User Interface (GUI) as well as a Command Line Interface (CLI).

While individual peaks can be profiled on demand, it is also possible to define crystallographic phases using cell constants, and instruct the program which hkl's are present.

Available Peak profile functions within Fityk include: Gaussian; Lorenzian; Pearson VII; pseudo-Voigt; and Fifth-order Polynomial. Three algorithms are available for global optimisation of peak profiling parameters, Levenberg-Marquard, Nelder-Mead and a Genetic Algorithm. Background fitting options include a spline function through fixed points or a refined polynomial background function.

The command line and scripting interface also allows for non-standard scripting and instrumental setups. Parameters can also be defined in terms of other parameters. The following example shows the line defining the handling of alpha-2 and parasitic wavelengths, as well as the option of refining their ratios.

c.w ! , _1.54051 _1 , _1.54433 ~0.5, _1.39217 ~0.03

('~' means the variable is refined, and '_' means the variable is fixed)

As Fityk is released under the GPL licence, this means source code is provided; anyone can make use of the software; as well as modify the source code as required. The software is also under heavy development, so it also pays to submit problems and contributed code to Martin as well as to routinely check for updated versions.

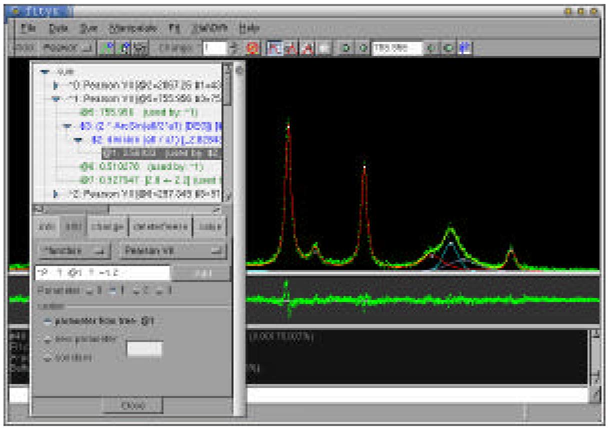
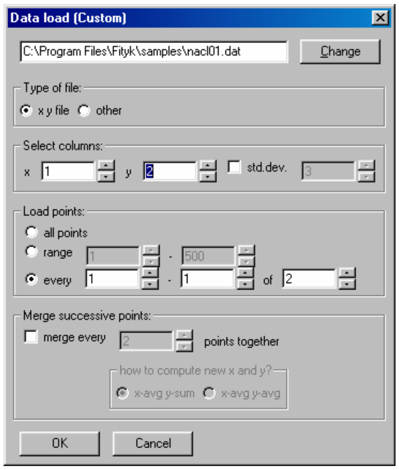


Fig 5: *Screen image of Fityk in action*


Data load (Custom)

C:\Program Files\Fityk\samples\nacl01.dat

Type of file: ● x y file ○ other

Select columns: x 1 y 2 ☐ std.dev. 3

Load points:
○ all points
○ range 1 - 500
● every 1 - 1 of 2

Merge successive points:
☐ merge every 2 points together
how to compute new x and y? ● x-avg y-sum ○ x-avg y-avg

Fig 6: *This screen image shows how Fityk allows you to import other custom data formats by defining them using a Graphical User Screen. Merging of data points can also be performed.*

Latest EXPGUI can now handle GSAS macromolecular structure files

As cited in "*R. B. Von Dreele, P. W. Stephens, G. D. Smith and R. H. Blessing, "The first protein crystal structure determined from high-resolution X-ray powder diffraction data: a variant of T3R3 human insulin-zinc complex produced by grinding", Acta Cryst. (2000). D56, 1549-1553*", GSAS has the capability to refine protein structures from powder diffraction data (and single crystal data).

The latest versions of EXPGUI GSAS interface by Brian Toby can now load GSAS macromolecular files containing a protein structure. This can be convenient for those who prefer to perform Le Bail fitting and control of other refinement variables via EXPGUI. EXPGUI is available via: http://www.ncnr.nist.gov/programs/crystallography/

Advice on importing a PDB file, and other setting up considerations within GSAS for refining proteins is viewable at: http://www.ccp14.ac.uk/solution/gsas/peak_and_proteins.html

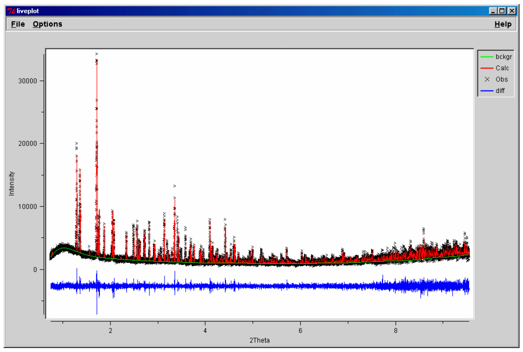


Fig 7: *EXPGUI screens showing the Le Bail fit to protein powder diffraction data (thanks to John Bond of the School of Crystallography, Birkbeck University of London for permission to show this data)*

Possible problems within default GSAS Instrument Parameter files due to X-ray Polarization effects from the monochromators.

It may not be realised by many GSAS users that the default X-ray polarisation values defined by the POLA and IPOLA parameters in the GSAS distribution PRM instrument parameter files may not match users' diffractometers due to the local use of a monochromator. Both incident and diffracted beam monochromators affect polarization of the X-ray beam. But with a suitable standard, this can be refined (or calculated using the CTHM equation as familiar to DBW users). An example of this using cubic Y_2O_3 as a standard to determine POLA and/or IPOLA values is available on the CCP14 webpage at: http://www.ccp14.ac.uk/solution/gsas/graphite_monochromator_and_gsas.html

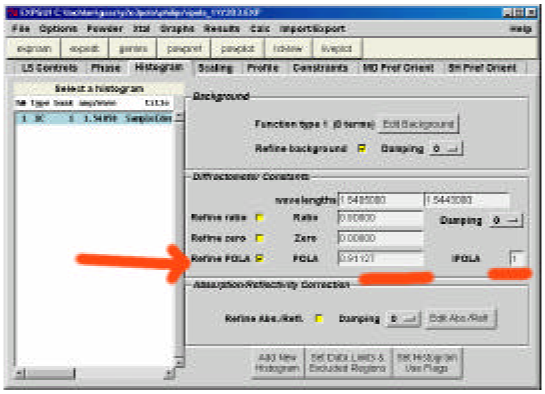


Fig 8: *Screen showing the refinement of IPOLA/POLA on Y_2O_3 data within GSAS using the EXPGUI interface. This is using the CTHM method where IPOLA is fixed to one and POLA now is equivalent to Cos^2(2-theta) of the monochromator.*

Plab perl script for GSAS by Jon Wright

GSAS has spawned a large number of programs and scripts that either enhance its functionality or help make using it easier or quicker. Many of these are listed on the CCP14 website at: http://www.ccp14.ac.uk/solution/gsas/

A new addition to this family of supporting utilities and progarms is the Plab (PerL Angles and Bonds) perl script written by Jon Wright for the creation of GSAS bond length and bond angle macro files for organics structures. Using Plab can save time in the setup of restraints for the refinement of organics in GSAS. This utility script, and a tutorial showing its use, is viewable via:

http://www.ccp14.ac.uk/solution/gsas/jon_wright_restraints_script.html

While Perl normally comes installed by default in UNIX systems, free Perl for Windows binaries are available via http://www.cpan.org/ports/index.html#win32. The Active Perl for Windows is recommended.

Updates to EFLECH/INDEX powder indexing programs by Joerg Bergmann

Due in part to the recent second Structure Determination by Powder Diffractometry Round Robin, there have been significant updates to Joerg Bergmann's EFLECH/INDEX peak profiling/powder indexing software which is available via http://www.bgmn.de/related.html and CCP14 mirrors.

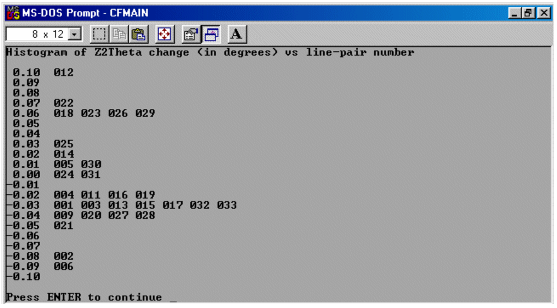
This was this suite of programs that was the only software able to suggest powder indexing solutions to samples 5, 7 and 8 in the recent SDPDRR-2 Structure Determination by Powder Diffractometry Round Robin - 2 (http://sdpd.univ-lemans.fr/sdpdrr2/results/)

EFLECH performs an automatic pattern decomposition by fitting a growing number of (raytraced fundamental parameters) peaks to the measured pattern to give a list of peaks and a covariance matrix. This data is then used by INDEX to try and get a unit cell performing a full search over all possible unit cells.

The new features within EFLECH/INDEX is the ability to cope with synchrotron data, as well as other optimisations to speed and handle more complex ab-initio powder indexing problems.

Updated Crysfire 2002 Powder Indexing suite by Robin Shirley

The Crysfire powder indexing suite by Robin Shirley has gone through a number of minor upgrades since the last newsletter. Updated features include more optimisations to the MMAP program and improved self-calibration facilities to determine possible systematic peak offsets from the internal consistency of the data. Crysfire is available via: http://www.ccp14.ac.uk/tutorial/crys/



```
Histogram of Z2Theta change (in degrees) vs line-pair number

 0.10  012
 0.09
 0.08
 0.07  022
 0.06  018 023 026 029
 0.05
 0.04
 0.03  025
 0.02  014
 0.01  005 030
 0.00  024 031
-0.01
-0.02  004 011 016 019
-0.03  001 003 013 015 017 032 033
-0.04  009 020 027 028
-0.05  021
-0.06
-0.07
-0.08  002
-0.09  006
-0.10

Press ENTER to continue _
```

Fig 9: *The new self-calibration display within Crysfire involving a sample with many multiple line pairs.*

New Sir2002 for Windows and UNIX single crystal structure solution software

While optimised for solving on single crystal data, people who use single crystal solving programs to try and solve on Le Bail or Pawley extracted HKL file may be interested in the availability of the new Sir2002 direct methods software by the Sirware group in Italy. Using single crystal hkl data, Sir2002 can solve on structures with over 2000 atoms in the asymmetric unit. It also has the potential to be useful to smaller structures where only powder diffraction data is available and can be subject to Le Bail or Pawley extraction.

The software can be freely obtained for non-commercial use (after completing and faxing the registration information) via the new Sirware website at http://www.ic.cnr.it

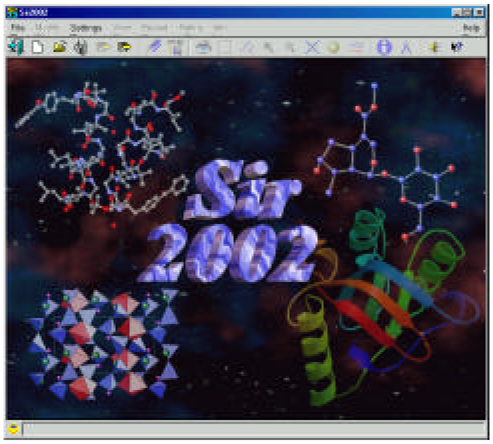
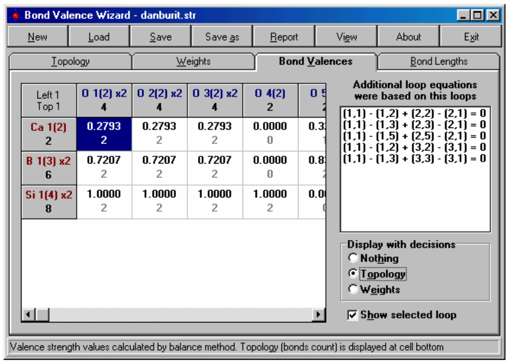


Fig 10: *Starting screen in the new Sir2002 direct methods software for single crystal data. Compared to Sir97, a more elaborate Graphical User Interface is provided.*

Bond Valence Wizard for Microsoft Windows by Ivan Orlov and Konstantin Popov

A new Bond Valence program for MS-Windows is that of Bond Valence Wizard by Ivan Orlov and Konstantin Popov. The software predicts bond lengths in crystals from the topology and chemical composition of the structure using nearest neighbour information. A guide in Adobe Acrobat PDF format is provided with the distribution files showing how to start using the program.



Left 1 Top 1	O 1(2) x2 4	O 2(2) x2 4	O 3(2) x2 4	O 4(2) 2	O 5
Ca 1(2) 2	0.2793 2	0.2793 2	0.2793 2	0.0000 0	0.3
B 1(3) x2 6	0.7207 2	0.7207 2	0.7207 2	0.0000 0	0.8
Si 1(4) x2 8	1.0000 2	1.0000 2	1.0000 2	1.0000 2	0.0

Additional loop equations were based on this loops

(1,1) - (1,2) + (2,2) - (2,1) = 0
(1,1) - (1,3) + (2,3) - (2,1) = 0
(1,1) - (1,5) + (2,5) - (2,1) = 0
(1,1) - (1,2) + (3,2) - (3,1) = 0
(1,1) - (1,3) + (3,3) - (3,1) = 0

Display with decisions
○ Nothing
● Topology
○ Weights

☑ Show selected loop

Valence strength values calculated by balance method. Topology (bonds count) is displayed at cell bottom

Fig 11: *Screen image of Bond Valence Wizard in action.*

Information and download of the program is available via: http://www-sphys.unil.ch/ic/SoftPro/bondval/ and CCP14 mirrors.

SoftBV "Bond softness sensitive" bond valence parameters and software for Java by Stefan Adams

Another bond-valence resource that is available via the internet is that of softBV by Stefan Adams. These suite of programs also make use of “bond softness”. Literature explaining this approach is included on the softBV website. Bond valence calculations using “softBV” data is available for main group cations, transition metal cations as well as the ability to insert a structure in Shelx format and put it through a bond-valence check. Conventional bond-valence data can also be used, if requested.

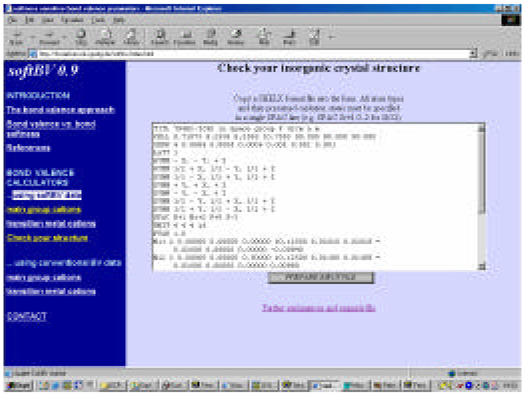


Fig 11: *Screen image showing the input of a Shelx format structure to pass through a softBV check.*

As it uses web based Java, it should run within any Java enabled web browser. It can be downloaded via:
http://kristall.uni-mki.gwdg.de/softbv/index.html

Rietveld Software Updates (as of early January 2003):

Hugo Rietveld website:
  http://home.wxs.nl/~rietv025/
BGMN (20th December 2002)
  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 (2nd January 2003)
  ftp://ftp.lanl.gov/public/gsas/
EXPGUI (27th December 2002)
  http://www.ncnr.nist.gov/programs/crystallography/
Jana (10th October 2002)
  http://www-xray.fzu.cz/jana/jana.html
LHPM-Rietica (27th November 2001)
  ftp://ftp.ansto.gov.au/pub/physics/neutron/rietveld/Rietica_LHPM95/
MAUD for Java (GPL’d) (22nd October 2002)
  http://www.ing.unitn.it/~luttero/maud/
Prodd (7th March 2002)
  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) (29th December 2002)
  http://homepage.mac.com/fujioizumi/rietan/angle_dispersive/angle_dispersive.html
Winplotr/Fullprof (23rd July 2002) (if Fullprof FTP site is unavailable, use the CCP14 Mirrors)
  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 (13th September 2002)
  http://www-cristallo.polycnrs-gre.fr/xnd/xnd.html
  ftp://ftp.polycnrs-gre.fr/pub/xnd/ (if XND FTP site is unavailable, use the CCP14 Mirrors)

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

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

“What do you want to do?“ (lists of software by single crystal and powder methods)
  http://www.ccp14.ac.uk/mirror/want_to_do.html

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/
Rietveld Software
  http://www.ccp14.ac.uk/solution/rietveld_software/
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/

Free one day Single Crystal and Powder Diffraction Crystallographic Software Workshop as part of ECA 2003 in Durban, South Africa

With a main theme of "Crystallographic Software Wizardry in Single Crystal and Powder Diffraction", and thanks to the conference organisers, there will be a free one day single crystal and powder diffraction software workshop on Sunday 24th August 2003 (at the start of the ECA conference). The emphasis will be on practical 20 minute "power user" examples of features within the software that casual users may not appreciate. The workshop will take place in the same facility as the conference, that being the International Conference Centre in Durban, South Africa.

The workshop webpage, with links to the presenters and the software being presented is at:
http://www.ccp14.ac.uk/projects/ecm21-durban2003/

The morning will consist of the powder diffraction session. This will include: use of the ICDD database; powder indexing of large volume cells (including proteins); powder indexing of impure samples using whole profile methods; structure solution using direct methods and EXPO; structure solution using real space methods and the FOX software; Rietveld refinement of complex inorganic materials using Fullprof; Rietveld Structure Refinement of protein powder diffraction data using GSAS

The afternoon will then be on single crystal methods. Topics include: Using CCDs for visually finding tricky cells, supercells and incommensurate cells; Advanced absorption correction options using Platon and Euhedral; Data processing of Bruker and Nonius CCD data using the WinGX Single Crystal suite, incorporating Sortav; SnB (Shake-n-Bake) direct methods software; Dirdif - fragment searching to solve structures that direct methods won't; Crystals to CCDC Mogul geometry validation; and non-trivial applications of Platon, Addsym and intra/inter-molecular validation

Speakers who are presently listed at time of writing include (for Powder Diffraction): Brian O'Connor, Robin Shirley, Armel Le Bail, Radovan Cerny, Mauro Bortolotti, Luca Lutterotti, Juan Rodriguez-Carvajal and Jon Wright. (Single Crystal): Martin Lutz, Louis Farrugia, Charles Weeks, Bob Gould, David Watkin and Ton Spek.

While the workshop is free, places are limited. People attending ECM-21 and who wish to also go to the software workshop are requested to contact Lachlan Cranswick on the information below.

Lachlan M. D. Cranswick
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Powder Diffraction Software: What lies behind the buttons?

Every two years the 'Werkgroep Poederdiffractie' of the Dutch Crystallographic Association (NVK) organizes a day with a special theme. The theme of this year was: “Powder Diffraction Software. What lies behind the buttons?” The chairman of the day, Fokke Tuinstra, mentioned in his opening speech that this years date, Friday the 13th (of December) can be a lucky day, he had met his wife on a Friday the 13th and there was a participant who had his birthday. Five speakers were asked to present a lecture in the new Bruker-Nonius building in Delft.

The first lecture given by **Gerrit Wiegers** (retired) was a historical overview. He gave an admirable inside view of how the first structures were solved from powder diffraction data and which programs were used.

Lachlan Cranswick (Birkbeck College, University of London) gave the next lecture titled ‘What can freely available powder diffraction software via the internet do for you’. Every participant (about 50 persons) got a brand new version of the Xtal Nexus CD. A few of them had never heard from the CCP14 website and were pleasantly surprised with the wealth of software freely available on the Internet.

During the poster session and during lunch, sponsored by PANalytical, lively discussions were held on various diffraction topics including Variable Counting Time procedures.

Leo Woning (Bruker-Nonius) introduced the Fundamental Parameter Approach for powder pattern fitting. He explained the basic concepts, which are built on physical parameters and not on analytical functions. Most persons agreed that the FPA is the way to go, and like someone remarked: ‘we are at the starting point of a new development’

René Peschar (University of Amsterdam) described the attempts that are undertaken in Amsterdam to determine the structure of various ‘larger’ organic molecules (e.g. cocoa butter) from powder data. It was a pity he didn’t bring some chocolates for determining the taste during the tea break.

During the break the participants had a guided tour through the new building of Bruker-Nonius. They saw the production facilities of the single crystal machines and the application laboratory showing single crystal and powder diffraction equipment.

Frans Peerdeman (PANalytical) closed the day with a talk about XRDML, the new data format of PANalytical, and how can it be used. The description of this data format is freely available. He expressed the wish that this new ASCII data format that can be used by the whole diffraction community will be the new standard in the powder diffraction.

The day was a great success and ended with a drink sponsored by Bruker-Nonius.

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WHAT'S ON

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

9th – 11th April 2003
International Workshop on Hard Synchrotron X-rays for Texture and Strain Analysis
DESY, Hamburg, Germany.
Web: http://www-hasylab.desy.de/conferences/workshop/

28 April – 2 May 2003
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.
Web: www.icdd.com/education/clinics/
E-mail: clinics@icdd.com

2 – 6 June 2003
Fundamentals of X-ray Powder Diffraction
ICDD, Newtown Square, Pennsylvania, U.S.A.
Covering instrumentation, specimen preparation, data acquisition, and qualitative phase analysis
Web: www.icdd.com/education/clinics/
E-mail: clinics@icdd.com

9 – 13 June 2003
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
Web: www.icdd.com/education/clinics/
E-mail: clinics@icdd.com

4th – 15th June 2003
International School of Crystallography: High Pressure Crystallography
Erice, Sicily, Italy
Web:http://www.geomin.unibo.it/orgv/erice/highpres.htm and http://www.crystalerice.org
E-mail: paola.spadon@unipd.it and katran@amu.edu.pl

26th – 31st July 2003
American Crystallographic Association Annual Meeting, ACA 2003

Northern Kentucky Convention Center,
Cincinnati, Ohio, USA
Web: http://www.hwi.buffalo.edu/ACA/
E-mail: jeanette.krause@uc.edu

4th – 6th August 2003
Polarised Neutrons and Synchrotrons X-rays for Magnetism - PNSXM
Venice International University, San Servolo, Venice, Italy
Web: http://venice.infm.it
E-mail: massimo.altarelli@elettra.trieste.it

4th – 8th August 2003
52nd Annual Denver X-ray Conference
Denver Marriott Tech Center Hotel, Denver, Colorado, USA
Web: http://www.dxcicdd.com/
E-mail: dxc@icdd.com

10th – 13th August 2003
AsCA'03/Crystal-23 : Asian Crystallographic Association and the Society for Crystallographers in Australia and New Zealand (SCANZ)
Cable Beach Club resort, Broome, Western Australia, Australia
Web: http://www.crystal.uwa.edu.au/CrystalsDownUnder/
E-mail: srh@crystal.uwa.edu.au

24th – 30th August 2003
21st European Crystallographic Meeting
International Conference Center, Durban, South Africa
Web: http://www.sacrs.org.za/ecm21/
E-mail: jboeyens@postino.up.ac.za

8th - 13th September 2003
Aperiodic-2003
Universidade Federal de Minas Gerais (UFMG), Belo Horizonte, Brazil.
Web: http://agora.grude.ufmg.br/aperiodic2003

8th - 18th September 2003

8th Oxford School on Neutron Scattering

Univ. of Oxford, Mansfield College, Oxford, UK
http://www.isis.rl.ac.uk/conferences/osns2003/
E-mail: C.C.Wilson@rl.ac.uk

14th - 19th September 2003

Structure Solution from Powder Diffraction Data - SSPD'03

Congress Center Academia, Stara Lesna, Slovak Republic
Web: http://www.sspd-03.sav.sk
E-mail: Lubomir.Smrcok@savba.sk

13th-15th September 2006

European Congress on Residual Stresses ECRS7, TU Berlin, Germany
E-mail: Walter.Reimers@TU-Berlin.de

9th - 20th June 2004

Diversity amidst Similarity: a Multidisciplinary Approach to Polymorphs, Solvates and Phase Relationships: the 35th crystallographic course at the Ettore Majorana Centre

Ettore Majorana Centre, Erice, Italy
Web: http://www.geomin.unibo.it/orgv/erice/olderice/bernstei.htm and http://www.crystalerice.org
E-mail: Yoel@bgumail.bgu.ac.il

23rd to 31st, August 2005

IUCr XX - XX Congress and General Assembly of the International of Crystallography

Congress Citidal, Florence, Italy
Web: http://www.iucr2005.it

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:

Robert Dinnebier (r.dinnebier@fkf.mpg.de).

The Newsletter can also be downloaded in electronic format, as a .pdf file, from the CPD web-site.

Companies

Call for contributions to the next CPD Newsletter (No 29)

The next issue of the CPD Newsletter will be edited by *Andy Fitch*, to appear in July 2003. Andy 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 29 (addresses are given below)

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