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CPD Chairman’s Message

The two Round Robins currently sponsored by the CPD are producing interesting new results. Both projects received considerable attention, judging by the numerous participation. While the Round Robin on Quantitative Phase Analysis (QPA) organised by *Ian Madsen* is close to a conclusion, the attention is now focussed of the Size-Strain (SS) Round Robin, led by *Davor Balzar*, who will report on this specific project on the next CPD Newsletter (No.25), to be edited by *Bill David*. The SS Round Robin, organised about conventional and new methods of Line Profile Analysis (LPA), is closely related to the main topic of the present issue. From the introduction by *Davor Balzar* and the content of Newsletter 24, it is quite evident that microstructure studies by LPA are gaining an increasing attention, with important advancements and new applications.

Along the same line, an important development of interest to powder diffractionists concerns the certification of two new Standard Reference Materials (SRMs) by NIST: SRM640c (Silicon powder) and SRM660a (LaB_6 powder) (http://www.nist.gov). New materials processing and certification procedures led to remarkable results; both standards will certainly represent a valuable support to LPA and for the testing of instrumentation and methods.

These topics, and the many other applications and methodological developments in Powder Diffraction will be the object of two forthcoming congresses. Details on *Accuracy in Powder Diffraction* III (Gaithersburg, MD, USA, 22-25.4.2001) and on *Size-Strain* III (Trento, Italy, 2-6.12.2001) are reported in the brochures published in the present Newsletter. We really wish and encourage a numerous and qualified participation to these two events.

ICDD is looking for a new Executive Director (see page 39), and this implicitly announces *Ron Jenkins* retirement. We really wish all the best to *Ron* for his future activities, and also to ICDD; it will not be easy to match the quality and quantity of work done by *Ron* during the long ICDD experience.

Paolo Scardi

From the Editor of Newsletter 24

This newsletter focuses on Microstructure of Materials. As implied here, “microstructure” concerns information obtained from diffraction measurement about material imperfections at very different scales: from point defects and short-range (dis)order on the nanometer scale to residual stress and texture effects on the macroscopic (comparable to the specimen size) level. Such diverse information is obtained through the analysis of fine details in a diffraction signature: line shift, line broadening, and changes in intensity, of both Bragg and diffuse-scattering components. Contributions in this newsletter give a snapshot of the current situation: Determination of residual stress in thin layers (Welzel, Leoni, Lamparter, and Mittemeijer) and individual grains (Poulsen and Kvick) are followed by discussions on size (Langford) and size-strain (Ungar) effects in line broadening. A comparison between strain measures, as determined by low-resolution and high-resolution diffraction experiments, is discussed by Fewster. Differences between local and long-range order can reveal very important physical information, as described by Billinge, Petkov, and Proffen. The last two contributions describe modelling of microstructure in Rietveld refinement: the effects of texture, residual macroscopic and microscopic strains are discussed by Popa, and the modelling of line broadening in terms of microscopic strain and structural defects is presented by Scardi, Leoni, and Dong.

An overwhelming impression is that microstructural analysis is becoming very sophisticated; this applies both to more accurate modelling that is necessary to obtain physical parameters of interest, and better experimental tools, to be able to discern fine microstructural details. For some of studies presented here, advanced synchrotron or neutron sources are almost a necessity. This arises particularly for two reasons: (i) high source brightness, to make measurements on individual grains feasible (Poulsen and Kvick); (ii) availability of high x-ray or neutron energies (above 59 keV, W K_α characteristic radiation is not readily available in the laboratory), either because of a need to measure bulk properties (Poulsen and Kvick) or to achieve a good real-space short-range resolution (Billinge *et al.*). High-brightness sources will also make obsolete a (usually necessary) compromise between a need to obtain high resolution in real space as opposed to high resolution in reciprocal space (such as in the reciprocal space mapping of thin films where usually large specimen volumes are irradiated). Accurate modelling of microstructural properties is particularly emphasised in recent developments in Rietveld refinement. This is implicitly present in the contributions of Langford, Ungar, and Billinge *et al.*, and explicitly discussed by Popa and Scardi *et al.*. Nowadays, many Rietveld-refinement programs can handle effects of texture, line shift and broadening at an advanced level, which provides not only for *correction* for these effects, but also allows for *determination* of pole figures, orientation-distribution functions, residual elastic stress/strain tensors, and locally varying lattice strains. Of course, to accurately determine this information, a large set of measurements is required. Again this underscores the interdependence of sophisticated analysis methods, fast computers, and advanced instrumentation; one constantly stimulates others to result in the advancement of our knowledge about materials microstructure beyond current limits.

Davor Balzar

CPD Projects

Information on the current status of the CPD projects is available at http://www.iucr.org/iucr-top/comm/cpd/projects/index.html

Size/Strain Round Robin

The first phase of round robin (methods of line-broadening analysis) was completed on November 15, 2000. The results are being analysed and an extensive report by Daniel Louer, Nathalie Audebrand, and Davor Balzar will be prepared for the next Newsletter (Summer 2001). New developments are available at the http://www.boulder.nist.gov/div853/balzar/s-s_rr.htm and mirrored at the CPD and CCP14 Web sites.

Quantitative Phase Analysis Round Robin

Last CPD Newsletter issue contained an extended report by Ian Madsen on the Quantitative Phase Analysis RR. Recently, a manuscript on the RR results has been submitted for the publication to the Journal of Applied Crystallography by Ian Madsen and co-workers. The CPD will include reprints of this paper with one of the future CPD Newsletters. Information can be retrieved from the CPD web-site: http://www.iucr.org/iucr-top/comm/cpd/QARR/index.html

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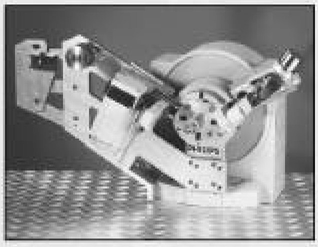

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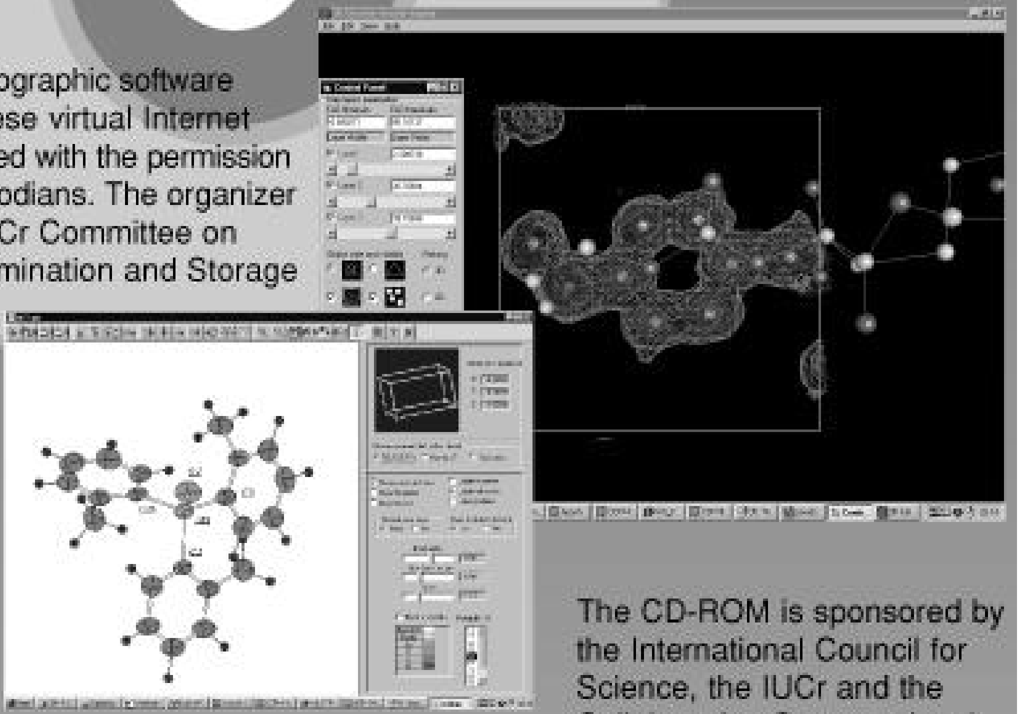

Packed with a host of crystallographic software packages and resources, these virtual Internet CD-ROMs have been produced with the permission of software and website custodians. The organizer of the NeXus project, the IUCr Committee on Electronic Publishing, Dissemination and Storage of Information, invites academics and students in crystallography working in laboratories in developing countries that are isolated from the Internet to register their interest. The CD-ROMs are free of charge and available while stocks last.

The CD-ROM is sponsored by the International Council for Science, the IUCr and the Collaborative Computational Project No. 14 (CCP14) for Single Crystal and Powder Diffraction.

Contents

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Stress in Thin Films; X-ray Diffraction Analysis and Grain Interaction

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INTRODUCTION

The elastic properties of bulk polycrystalline materials have been investigated extensively during the last decades. For a single crystal exhibiting anisotropic elastic behaviour the strain upon any applied stress can be calculated for each direction. However, if the crystal, embedded as a grain in a polycrystalline body, is surrounded by neighbouring grains and connected tightly to them, due to the interaction between the grains, constraints for the strain upon applied stress occur. Up to now, no unique model exists for the exact description of the elastic behaviour. Models for the description of the grain interaction were proposed by Voigt [1] and Reuss [2]. These classical models predict macroscopically isotropic elastic behaviour for non-textured polycrystalline materials. However, thin films are usually not macroscopically isotropic but exhibit at most only transverse isotropy along the plane of the film. The anisotropic elastic behaviour cannot be explained by the classical models.

The present paper presents a summary of recent work [3-5] where it has been demonstrated for the first time by X-ray diffraction (XRD) analysis of stresses in thin films that the elastic grain interaction can lead to macroscopically anisotropic behaviour (shown by non-linear, the so-called $\sin^2 y$ plots, see below). A new model is proposed for the grain interaction that predicts the macroscopically anisotropic behaviour of thin films.

X-RAY ELASTIC CONSTANTS

A plane and rotationally symmetric state of residual stress occurs often in thin films after their production. For a transversely isotropic film the strain-stress state is determined by three parameters, the in plane stress, $s_{||}$, the in plane strain, $e_{||}$, and the perpendicular strain, $e_{\perp}$. The basis for XRD stress analysis is the so-called $\sin^2 y$ method (see, e.g., Ref. [6]). The strain of the $\{hkl\}$ lattice spacing, e_y^{hkl}, is measured in dependence of the tilt angle y of the sample surface with respect to the diffraction vector. In case of a rotationally symmetric state of plane stress this dependence can be written as:

$$e_y^{hkl} = 2\ S_1^{hkl}\ s_{||} + \frac{1}{2}\ S_2^{hkl} s_{||} \sin^2 y\ . \qquad (1)$$

S_1^{hkl} and $\frac{1}{2}\ S_2^{hkl}$ are the so called X-ray elastic constants (XECs). The stress $s_{||}$ is obtained from the slope in the $e_y^{hkl} - \sin^2 y$ plot. For the simple case of a material consisting of elastically isotropic crystallites the XECs are equal to the corresponding mechanical elastic constants $S_1 = -v/E$ and $S_2/2=(1+n)/E$, where E is the elastic modulus and n is the Poisson ratio. In general, the XECs differ from the mechanical constants because the macroscopic strain e_y is the mean value over all crystallites in the sample, whereas the diffraction strain e_y^{hkl} presents an average over a population of selected crystallites whose $\{hkl\}$ planes are perpendicular to the diffraction vector. The application of the diffraction $\sin^2 y$ method for a polycrystalline body requires a (separate) establishment of the XECs e.g. by a model calculation.

The strain of a single crystal can be calculated for each direction $<hkl>$ by means of the so-called single crystal elastic constants. However, the knowledge of these constants is not sufficient to calculate the diffraction strain e_y^{hkl} of a polycrystalline sample subjected to an external stress. The reason for that is the occurring grain interaction. Each crystallite contributing to the measured average e_y^{hkl} is surrounded by other (randomly oriented, in the absence of texture) crystallites and tightly connected to them. The strain of each crystallite, and thus its contribution to e_y^{hkl}, depends on the non-uniform interaction with the neighbouring crystallites.

In the specimen frame of reference S, where one axis is perpendicular to the surface, Hooke's law (Einstein notation), written as

$$e_{ij}^{\mathrm{S}} = S_{ijkl}^{\mathrm{S}} s_{kl}^{\mathrm{S}} \qquad (2)$$

presents, for each crystallite, a system of six relations between six components e_{ij} of the strain tensor and six components of the stress tensor s_{ij} (the single crystal compliances S_{ijkl} in the S system can be calculated from the corresponding single crystal compliances, as given in the crystal frame of reference, see e.g. [5]). Thus for the determination of the 12 unknowns six additional conditions are needed. These are provided by a suitable grain interaction model, that is, by assigning to six of the unknowns, values independent of the orientation of the crystallite in the specimen frame of reference. Then (in principle), the mechanical strain as well as the XRD strain and the corresponding elastic constants can be calculated by proper averaging over the crystallites (all crystallites for the mechanical constants; selected crystallites for the XECs).

Different grain interaction models have been proposed; all of them are based on certain simplifications.

GRAIN INTERACTION; CLASSICAL MODELS FOR MACROSCOPICALLY ISOTROPIC SAMPLES

Two classical models are based on different extreme cases. In the Voigt model it is assumed that the strains in the specimen frame of reference S are equal for all crystallites in the sample, i.e. they are given by the macroscopic values $e_{||}$ and $e_{\perp}$. As a consequence, it follows that the XECs do not depend on *hkl* and thus are equal to the mechanical elastic constants S_1 and $S_2/2$. The Reuss model assumes that the stresses in the S system are equal for all crystallites, i.e. they are given by $s_{||}$ and $s_{\perp} = 0$. In this case the XECs depend on *hkl* and differ from the mechanical elastic constants.

Calculated $e_y^{hkl} - \sin^2 y$ diagrams are shown in Fig. 1 according to the Voigt and Reuss models of grain interaction for a copper film subjected to a rotationally symmetric state of stress with $s_{||}$ = 200 MPa. The Voigt and Reuss models for grain interaction imply that a textureless polycrystalline sample is elastically isotropic; as a consequence these models yield straight lines in the $e_y^{hkl} - \sin^2 y$ plots (Fig. 1). Clearly, the slope in the e_y^{hkl} - $\sin^2 y$ diagram depends strongly on the assumed type of grain interaction.

It should be noted that the Voigt and Reuss models (involving two extreme assumptions for the grain interaction) cannot describe reality because, at the grain boundaries, they imply non-physical discontinuities of stresses and strains.

GRAIN INTERACTION IN THIN FILMS; MACROSCOPICALLY ANISOTROPIC SAMPLES

Thin metallic layers produced by vapour deposition or by sputtering are generally anisotropic. They often exhibit columnar growth of grains, as shown in Fig. 2 for a sputtered copper film. The interaction between the grains parallel to the layer is strong, whereas in the direction perpendicular to the layer the grains can deform more independently from each other.

An approach to grain interaction in thin layers has been proposed by Vook and Witt [7]. It is assumed that under a rotationally symmetric plane state of stress the strain parallel to the surface, $e_{||}$, is the same for all crystallites and that all stress components perpendicular to the surface are zero. On the basis of the Vook-Witt approach, e_y^{hkl} - $\sin^2 y$ diagrams have been calculated theoretically for the first time in the current work [3-5]. An example is presented in Fig. 1 for a textureless copper layer.

A striking result of this study is the non-linearity of the e_y^{hkl} - $\sin^2 y$ diagrams. As a consequence, the application of Eq.(1) is not possible straightforwardly.

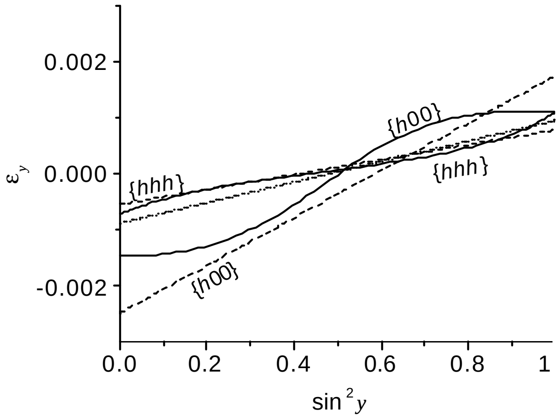

Fig. 1. *$e_y^{hkl} - \sin^2 y$ diagrams for a copper film with 200 MPa stress calculated with different grain interaction models: ...... Voigt model; - - - Reuss model for the {hhh} und {h00} reflections (results for other {hkl} reflections are within the two dashed lines); ¾ new model of grain interaction on the basis of the Vook-Witt approach yields curved lines for the {h00} and the {hhh} reflections.*

Fig. 2. *Columnar microstructure of a 1 mm thick copper film produced by sputtering onto an oxidised silicon wafer (TEM image). Due to the free volume between the grains the interaction between them perpendicular to the film is weak and they can deform rather independently from each other in this direction.*

Keeping Eq.(1) in a formal way means that the XECs depend on the orientation y of the crystallites in the sample which is a consequence of the anisotropic grain interaction. Furthermore, the XECs depend on the crystallographic direction <*hkl*>.

TEXTURED FILMS

The results presented so far refer to polycrystalline layers without texture. The calculation of e_y^{hkl} involves an average over a selection of grains, which are detected in an X-ray diffraction measurement, i.e. all those grains whose {*hkl*} planes are perpendicular to the diffraction vector. Only in case of a non-textured sample, a random distribution occurs for the rotation angle l of the grains around the diffraction vector. In a textured layer, the diffracting grains corresponding to a specific {*hkl*} reflection are oriented more or less preferentially with respect to the specimen coordinate system S. In case of fibre texture, the preferred orientation is described fully by the tilt angle y of the grains with respect to the sample surface; the in plane rotation of the crystals is random. A {*hkl*} fibre texture denotes a sample with preferentially {*hkl*} planes parallel to the surface.

For the theoretical calculation of the elastic response of a textured film using one of the grain interaction models, the statistics of the orientations of the crystallites, which can be described by the orientation distribution function (ODF), has to be known.

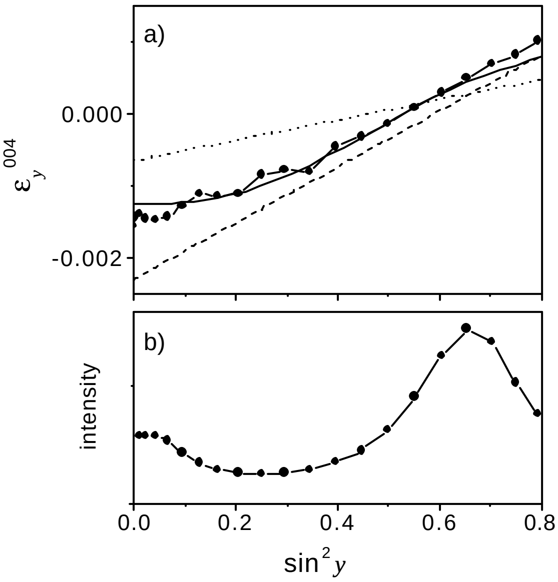

Fig. 3. *a)* $e_y^{004} - \sin^2 y$ *diagram for the {004} reflection from a 1 mm thick sputtered copper film with a {111} fibre texture: measured data by XRD (·) and calculated data (lines) for* $s_{||}$ *= 180 MPa using various grain interaction models (...... Voigt model; - - - Reuss model; ¾ ¾ new model).*
b) Intensity of the {004} reflection at different tilt angles y.

The presence of a texture implies that the crystallites of an ensemble detected during a measurement of the strain e_y^{hkl} do not occur with a random rotation around the diffraction vector, but that a dependence of the crystallite frequency on the angle l exists. Because of the dependence of the strain of the individual crystallites on their orientation with respect to the specimen frame of reference, and thus also on the angle l, for the averaging in the model calculation this frequency has to be known. This frequency can be determined from the ODF.

An example of the application of the new model for the grain interaction in textured films is given in Fig. 3 which shows the $e_y^{004} - \sin^2 y$ diagram as measured by X-ray diffraction for a 1μm thick sputtered copper film and the corresponding calculated diagrams [4]. Since the film has a {111} fibre texture, the {004} planes occur preferentially at a tilt angle ψ of about 55° ($\sin^2 y$ = 0.67) with respect to the surface. The measured intensity of the {004} reflection in Fig. 3b indicates the frequency of crystallites with their {004} planes at a certain tilt angle y. The dotted and dashed lines in Fig. 3a indicate the calculated results for the Voigt and Reuss model, respectively. The full line shows the calculated result for the new model of grain interaction. Evidently, this study on a textured Cu film reveals that only the new model for grain interaction describes satisfactorily the measured $e_y^{004} - \sin^2 y$ diagram.

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3D Characterization of Grains in Powders or Polycrystals

H.F. Poulsen, Materials Research Department, Risø National Laboratory, and Å. Kvick, European Synchrotron Radiation Facility

At Risø we have developed several methods for fast and non-destructive characterisation of the individual grains inside bulk materials (powders or polycrystals) [1-5]. The methods are based on diffraction with hard x rays ($E > 50$ keV), enabling 3D studies of millimetre – centimetre thick specimens. The position, volume, orientation and elastic strain can be determined in up to 100 grains simultaneously. Likewise, for coarse-grained materials the topography of the grain boundaries can be mapped.

In collaboration with ESRF, the methods have been implemented at the 3-Dimensional X-Ray Diffraction (3DXRD) microscope [6] ; a dedicated instrument situated at the Materials Science Beamline ID11. The instrument operates in the 50-100 keV range with a typical resolution of 5x5x50 μm^3. It was commissioned during summer 1999, and is now available through the normal ESRF application procedure. We here outline the methods for 3D reconstruction, the instrumentation available at the 3DXRD microscope and give some examples of use. For details we refer to the references and our web sites: http://www.risoe.dk/afm/synch,and http://www.esrf.fr/exp_facilities/ID11/handbook.

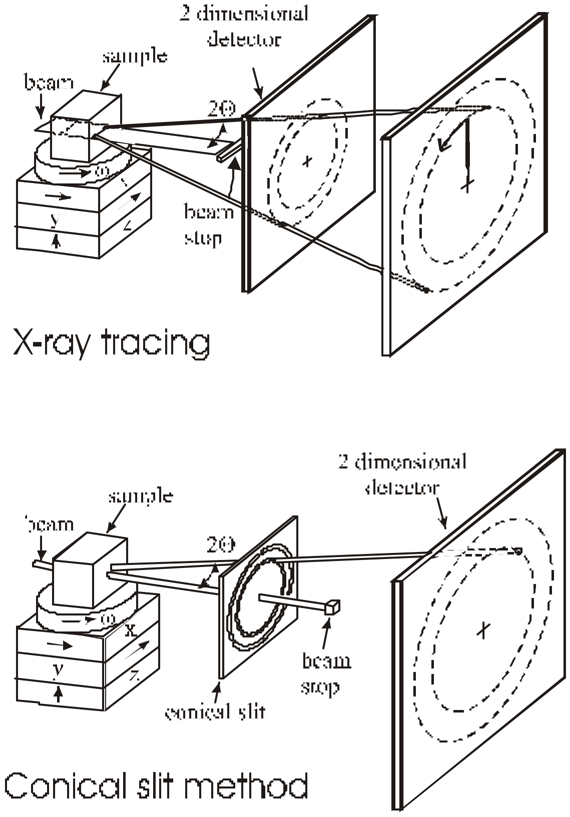

***Fig 1**. Diffraction principles used (see the text).*

SCIENTIFIC CASE

The agglomerate of grains in powders and polycrystals is often highly heterogeneous, especially with respect to their dynamics during processing. As such it is remarkable that state-of-the-art models in metal and ceramic science in general only deals with average properties. A major cause for this calamity is the almost exclusive use of surface probes for structural characterisation. Due to effects such as strain relaxation, pinning and atypical diffusion, samples must be sectioned before investigation to get results representative of bulk behaviour. The destructive procedure prohibits studies of the dynamics of the individual grains. Hence, only static and statistical information is obtained.

The aim of the 3DXRD initiative is firstly to provide three-dimensional mappings of grain characteristics: size, shape, crystallographic orientation, stress-state, stoichiometry as well as neighbouring relationships., and secondly to provide the dynamics of a number of grains simultaneously during processing. In the end statistics over an ensemble of 10-1000 grains is needed.

DIFFRACTION PRINCIPLES

The two main principles are sketched in Fig 1. Both are monochromatic techniques in transmission mode. In the x-ray tracing technique, a line-focus beam is used to define a layer of interest in the sample [2-4]. Images are acquired while scanning a two-dimensional detector parallel to the incoming beam. This procedure is repeated for a number of settings of the ω round table (rotation method). With hard x-rays essentially all reflections are recorded in this way. From the back-projection of the outline of the spots the circumference of the grains and their position is inferred. So is angles 2θ and η. The orientation of the grains are obtained through combining the information from the spots. Strain- and stress tensors can be derived from the variations in angles 2θ and η by adding an extra detector far away from the sample.

For non-deformed grains the method gives a fast and complete characterisation, with one layer characterised in a few minutes. It has been validated with respect to spatial mapping - accuracy of 20 μm - orientations and strain-tensors - accuracy of 10^{-4} [2]. Its limitation is mainly spot-overlap (number of grains in the layer, and especially the mosaic spread of the spots).

The second method is slower, but better suited for deformed specimens [6]. A spot-focus beam is used in combination with a conical slit, which has opening along the Debye-Scherrer rings. In this way an effective intrinsic gauge volume is defined. Again the sample is scanned in ω to obtain orientations. The grain dimensions are determined by scanning the sample in front of the slit.

3DXRD INSTRUMENTATION

The 3DXRD microscope is placed in a new hutch at the beamline. The beam is monochromatized and focused by a combination of bent Laue crystals and laterally graded multilayer mirrors [6]. The energy band is variable from 0.05% – 0.6%. The typical flux in the focal spot is 10^{11} ph/sec. With a focal length of 2 meters there is ample space for auxiliaries, including a 25 kN stress rig and two furnaces, of which one reaches 1500 °C. A range of CCDs with resolutions from 5 µm to 200 µm is available as well as two conical slits with slit gaps of 20 µm and 25 µm - both for FCC materials.

For the tracing method, a program GRAINDEX has been written that sorts reflections according to grain, index them and produce grain maps and information on grain properties. Plans are to introduce on-line data analysis within a year.

EXAMPLES OF USE

The initial work has mainly focused on nucleation, grain growth and deformation of pure metals, where grains are large [4]. As an example we summarise results for recrystallisation of aluminium. Here, a 70 µm broad spot-focus was used to allow a uniform illumination of grains. Grain volume kinetics for ≈ 100 emerging grains were inferred simultaneously from the integrated intensity of individual reflections [7]. X-ray tracing was used to identify valid grains: those fully illuminated by the beam and positioned truly in the bulk. Results for six grains are shown in Fig 2. The limitations of standard models are clearly demonstrated - these typically assume all grains to nucleate at the same time and to grow with the same growth velocity according to a universal curve.

As a second example we mention a combined x-ray tracing and absorption contrast tomography study on the wetting of Ga in an Al polycrystal [8]. Here tomography provided a high resolution map of the boundaries actually wetted. The diffraction technique reproduced this map with a substantially lower resolution. However, it provided all the boundaries (wetted or non-wetted) as well as the grain orientations. As a result the relationship between wetting kinetics and misorientation angle could be studied.

Further work is in progress within the fields of martensitic phase transitions, crack propagation and processing of ceramics. Sub-micron sized grains can be observed, but not resolved. This still allow grains to be classified and grain dynamics to be studies as function of class. Moreover, under favourable conditions dislocation structures can be observed [4].

The hard x-ray rotation technique is also ideal for many engineering studies of the local strain [9] or texture [10]. For layered materials penetration from the side of the specimen is an attractive solution, enabling depth-gradients to be profiled with a spatial resolution down to 1 µm. For mapping of 3D strain distributions, a methodology has been developed based on the conical slit set-up [10].

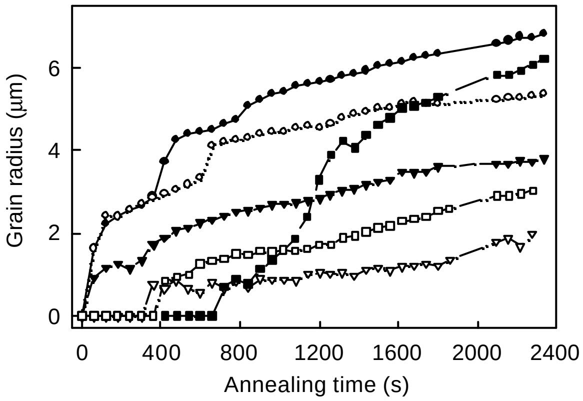

Fig 2. *The nucleation and growth of 6 new grains during annealing of deformed Al at 270 °C.*

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Crystallite Size from Diffraction Data

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INTRODUCTION

Powder diffraction line profiles usually contain a measurable contribution from small crystallites, which depends on the shape of diffracting domains and the distribution of their size. ‘Traditional’ methods for extracting information on sample microstructure from X-ray diffraction (XRD) data are based on the integral breadths of line profiles or on their Fourier representation, but increasing use has been made in recent years of a comparison between an experimental powder pattern and simulated data. The latter are derived from an appropriate physical model and the contribution from crystallite-size effects has been considered by Langford, Louër and Scardi (2000), on which much of the following review of size determination is based. The case of dislocations and other lattice distortions has been discussed by various authors, *e.g.* Ungár *et al.* (1984), van Berkum *et al.* (1992), Gubicza *et al.* (2000), but only ‘size’ effects are discussed here. Even if a study of crystallite size is not the main purpose of a particular application of powder diffraction, its contribution usually needs to be taken into account in any physical approach to pattern simulation or modelling, such as structure refinement by the Rietveld method.

CRYSTALLITE SIZE

The quantity obtained from diffraction data is some measure of the average thickness, in the direction of the diffraction vector, of domains over which diffraction is coherent. This is usually denoted as the crystallite size, but it does not necessarily correspond to the size of individual particles in a powder or grains in a polycrystalline sample. These can be single crystals, but equally each particle or grain may contain several diffracting domains. As is indicated below, the integral breadth and Fourier coefficients of a line profile due to size effects do not give the same measure of crystallite size, nor do they give the arithmetic mean directly, the quantity normally required in practice. However, if the distribution of size is known, the mean value can be determined. Also, the values obtained are not necessarily equivalent to those determined by other techniques, such as TEM or surface adsorption (*e.g.* the BET method). Matyi, Schwartz and Butt (1987) give a useful comparison of the measures of size obtained by various experimental techniques and discuss the concept of particle and crystallite size generally.

DIFFRACTION LINE PROFILE DUE TO CRYSTALLITE SIZE

The line profile for small crystallites can be expressed as

$$I(2\theta) = (\cos\theta/\lambda)I(s), \qquad (1)$$

where $I(s)$ is the intensity in reciprocal space at a distance s from the point hkl. $I(s)$ can be calculated from geometrical considerations for crystallites having the same size and a regular shape (*e.g.* Wilson, 1962) and it can usually be expressed as a polynomial with oscillatory coefficients. For a spherical crystallite with diameter D, for example,

$$I(s) = (\pi D^4/8)\{\psi^{-2} - \psi^{-3}\sin(2\psi) + \psi^{-4}[1 - \cos(2\psi)]\}, \quad (2)$$

where $\psi = \pi sD$.

In practice, crystallites are unlikely to have the same shape and may well be irregular. However, in all methods for determining size parameters from diffraction data, an appropriate regular shape is assumed. The ‘average’ morphology can often be deduced from TEM or from the variation of line breadth with s and hkl (the Williamson-Hall plot). Crystallites are often observed to be approximately equiaxial, when they can be regarded as having spherical morphology. A cylindrical form (Langford & Louër, 1982) can be a suitable approximation when the crystallites are prismatic, acicular or have the form of platelets. Grébille and Bérar (1985) considered the more general case of convex polyhedra.

The distribution of crystallite size in a powder sample or polycrystalline solid depends on a number of factors, including the nature of the material and the method and conditions of preparation. However, by far the commonest distribution reported in the literature is the lognormal, which is asymmetric (Fig. 1). If each particle in a powder sample is a single crystal, the distribution of size frequently has this form and it has also been observed, to a reasonable degree of approximation, for subgrains and dislocation subcells (Valiev *et al*., 1994; Ungar *et al*., 2000). On the other hand, for thin films which exhibit a high degree of orientation, the variation in thickness often tends to be symmetric (*e.g.* Scardi, Matacotta *et al*., 1997; Scardi, Migliori *et al*., 1997), for which the normal (Gaussian) distribution may be a better approximation; it cannot be precisely so, since this would imply crystallites with negative sizes. Further information on the lognormal and Gaussian distributions, in the context of crystallite size, is given by Langford, Louër and Scardi (2000). Multi-modal distributions have also been detected (see, for example, Le Bail & Louër, 1978, 1980; Young & Sakthivel, 1988).

The line profiles for individual domains in a powder sample are additive and the maxima of $I(s)$ for different sizes occur at different values of s. Since there are usually 10^5 or more crystallites contributing to a line profile, there is thus a smooth decrease of intensity in the tails. The effect of a unimodal distribution of size is to reduce the breadth of a line profile, relative to that for a single crystallite, and to lengthen its tails, *i.e.* the intensity falls to zero more slowly. The shape of the line profile for a single crystallite tends to be intermediate between Lorentzian and Gaussian functions and it becomes slightly more Lorentzian in character with increasing dispersion (Langford, Louër and Scardi, 2000). In general, therefore, it is not reasonable to assume that the line profile is Lorentzian, other than as a crude approximation, unless the fitting of an analytical function indicates that it has this form. If line profiles resulting from crystallite size effects are in fact observed to be Lorentzian, or 'super-Lorentzian', then the distribution of size is unlikely to be unimodal. The use hitherto of a Lorentzian approximation for 'size' line profiles arises from the dominant inverse-square term in the expression for $I(s)$ (*e.g.* equation (2) for spherical crystallites); the behaviour of the Lorentzian function is similar for large values of s. An analysis based on this function can in fact lead to an appreciable error in the estimated crystallite size. The Voigt or pseudo-Voigt functions usually model 'size' line profiles satisfactorily, at least in the case of a unimodal distribution of size.

CRYSTALLITE SIZE FROM THE INTEGRAL BREADTH

The reciprocal of the integral breadth $\beta^S{*}$ of the 'size' line profile is usually denoted as the integral-breadth apparent size, ε_β, given by the Scherrer equation:

$$\varepsilon_\beta = 1/\beta^S{*}. \qquad (3)$$

This is a volume-weighted average and only in the case of reflections from planes parallel to the surface of crystallites is it the actual thickness. Otherwise, in order to make allowance for the variation of thickness within a crystallite in the direction *hkl*, some regular morphology must be assumed. For example, in the case of spherical crystallites, the equivalent volume-weighted mean diameter, $<D_V>$, is given by

$$<D_V> = 4\varepsilon_\beta/3. \qquad (4)$$

Jones (1938), in his discussion of the effects of a crystallite-size distribution on line-profile breadths, deduced that the average size, determined from the integral breadth, is simply the ratio of the fourth and third moments of the distribution. Thus, for spherical crystallites,

$$<D_V> = <D^4>/<D^3>. \qquad (5)$$

This can be considerably greater than the arithmetic mean

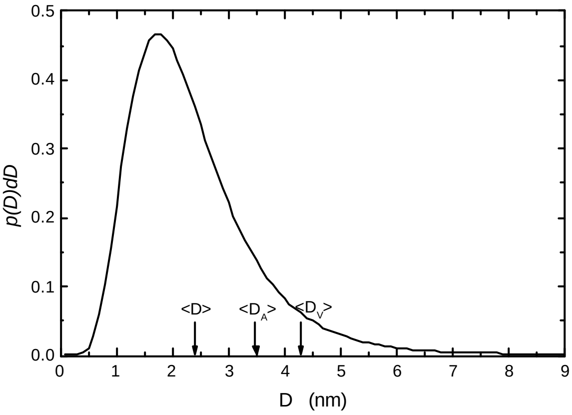

Fig. 1. *Lognormal distribution of crystallite size, obtained by least-squares fitting of XRD data for a nanocrystalline* CeO_2 *powder sample (Guillou, Auffrédic & Louër (1995).*

$<D>$, the quantity normally required in practice (see, for example, Fig. 1).

It should be noted that the value of size obtained from the reciprocal of the full width at half maximum intensity of a line profile has no simple physical interpretation, except for the case of an infinite flat crystallite.

CRYSTALLITE SIZE FROM THE FOURIER METHOD

Methods based on the Fourier coefficients of the line profile due to sample microstructure (*e.g.* the Warren-Averbach approach) give an area-weighted size. The Fourier apparent size, ε_F, is given by the reciprocal of the initial slope of the $A^S{;}_n$ *versus* n curve, where $A^S{;}_n$ are the Fourier cosine coefficients of the line profile arising from crystallite-size effects. For spheres, the corresponding area-weighted mean diameter, $<D_A>$, is then

$$<D_A> = 3\varepsilon_F/2. \qquad (6)$$

This is the ratio of third and second moments of the distribution (Wilson, 1968,1971):

$$<D_A> = <D^3>/<D^2> \qquad (7)$$

Again, this is greater than $<D>$ and in general, at least for a unimodal distribution, $<D_V> > <D_A> > <D>$ and all three quantities are greater than the most probable size (Fig. 1).

If a line profile is approximated by some analytical function, it should be remembered that the Fourier coefficients are those of the function used. The 'size' coefficients derived therefrom will differ from $A^S{;}_n$ unless the function models the experimental data precisely; even a small discrepancy, particularly in the line profile tails, can result in an error in ε_F. ε_β, which depends on the area of the line profile, is less sensitive to imprecise modelling (Langford, Louër and Scardi, 2000).

DETERMINATION OF SIZE DISTRIBUTION

It is often necessary to determine the distribution of crystallite size from diffraction data and this is in fact essential, if the arithmetic mean thickness is required. The pioneering work of Bertaut (1949, 1950) led to procedures for extracting size distributions. He realised that the second derivative of $A^S;_n$ was proportional to the lengths of columns of unit cells in the direction of the diffraction vector. The curve of $A^S;_n{}''$ *versus* n thus gives $P(n)dn$, the fraction of columns having lengths between n and $n + dn$ cells. However, only for the case of reflections from planes parallel to the surface of crystallites does this give the distribution of crystallite size, the quantity normally required in practice. Otherwise, this curve also includes the variation of thickness within crystallites, averaged by the symmetry-related multiplicity of reflections, where applicable. However, the influence of crystallite shape diminishes as the breadth of the size distribution increases (e.g. Rao and Houska, 1986, Figs 1*a* and 2*a* therein) and the Bertaut method has been widely used to estimate crystallite size distributions.

The problem of separating the variation of thickness within crystallites from the distribution of some measure of the overall size is avoided in the method devised by Krill and Birringer (1998). A lognormal distribution of size is assumed and parameters defining the distribution, the lognormal mean (γ) and variance (ω^2), are obtained from ε_β and ε_F. The arithmetic mean, dispersion, etc., can then be obtained from γ and ω^2. However, the method requires a precise determination of ε_β and ε_F and this is not easy to achieve for the latter if there is measurable truncation due to overlap of line profile tails (Young, Gerdes & Wilson, 1967). An approach based solely on ε_β and line-profile shape is given by Langford, Louër and Scardi (2000), but this again requires very precise data.

The best method for determining crystallite size is probably that based on whole-powder-pattern fitting and a physical model. The 'size' line profile can be obtained by summing $I(s)$, weighted by an appropriate distribution function, for a particular morphology. This is convoluted with instrumental line profiles to simulate a powder pattern, which is then compared with the experimental data. For spherical crystallites and a unimodal distribution, there are then only two microstructural parameters to refine, the mean of the distribution and its variance. An application of this procedure to data from a nanocrystalline powder sample (Guillou, Auffrédic & Louër 1995) is presented by Langford, Louër and Scardi (2000). The only assumptions are that the crystallites have a particular shape, on average, and that the distribution of size can be expressed analytically. Justification for both assumptions can usually be obtained from X-ray diffraction data, combined with information from TEM or other techniques.

The above procedure is equally applicable to crystallites having a uniaxial or biaxial morphology, but in such cases there may well be different distributions of thickness along the axial directions. Microstrain can be taken into account if an appropriate model for lattice distortion can be devised and its line profile calculated. This is then convoluted with the 'size' and instrumental line profiles when generating the powder pattern.

INTERPRETATION OF CRYSTALLITE SIZE

'Traditional' methods for determining crystallite size from diffraction data give a weighted average size, whereas the arithmetic mean of the size distribution, or perhaps the most probable value (the mode), together with the standard deviation, usually has more physical relevance. The distribution of size must be ascertained if a full characterisation of crystallite size is required and this can be obtained by refinement of a suitable physical model. Only if the distribution is known can the results be compared with those from other techniques. Indeed, it is always desirable to obtain micrographs of the sample whenever possible. TEM data can give an indication of the nature of the size distribution, whether or not the particles are single crystals, and the form of the crystallites, in support of any information on their morphology deduced from a Williamson-Hall plot. However, mean sizes obtained from XRD data and TEM will not necessarily be identical. When comparing the results from the two techniques, the same quantities must be considered and an appropriate method to obtain particle sizes from TEM must be used (see Matyi, Schwartz & Butt, 1987). If particles contain subgrains that are not revealed in the micrographs, then clearly the mean size obtained by XRD will be smaller. Also, there is the possibility that TEM measurements may be biased towards larger particles. An advantage of methods based on diffraction data is that the number of crystallites contributing to the analysis is likely to be larger by several orders of magnitude, greatly reducing the sampling error. Also, it is a more general procedure involving an average over all crystallographic directions.

Integral breadths or Fourier coefficients are often used to study changes in crystallite size due to varying experimental conditions or different methods of sample preparation. All that can then be reported with certainty about any variation in the volume-weighted or area-weighted size is that the size distribution has been modified. It should not be assumed that the arithmetic mean has the same trend. This can only be established if the full distribution has been obtained.

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Dislocation Structure and Crystallite-Size Distribution from Peak Profile Analysis

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Size and strain are two fundamental aspects of the microstructure in crystalline materials. They interplay since coherence can be interrupted by tilted regions where tilt is caused by strain or in conglomerates of nano-particles adhering grain boundaries cause strains. The first can occur even in large single crystals whereas the second is typical of nanocrystals. It happens very seldom that they are present without the counterpart. In plastically deformed metallic single crystals large dislocation densities exist concomitantly with macroscopic coherence lengths [1]. Whereas, in carefully prepared nanocrystalline oxide particles strain can be absent [2]. However, usually they go together. The separation of size and strain effects is one of the major issues in peak profile analysis. All procedures are based on the different diffraction order dependence. The matter is further complicated by strain- and shape anisotropy. First can be solved either phenomenologically [3] or assuming that strain is caused by specific lattice defects, in particular by dislocations [4] or dislocations and stacking faults [5]. Shape anisotropy has been solved in strain free nanocrystalline materials, e.g. in ZnO [6]. Why do dislocations play an overwhelming role in the strain part of peak broadening? The strain fields of specific lattice defects are well known and have been categorised in terms of diffraction effects by Krivoglaz [7]. The strain fields of: (i) point defects decay as $1/r^2$, where r is the distance from the defect, (ii) of dislocations decay as $1/r$, and (iii) of planar defects they are space independent, or homogeneous. This hierarchy has strong consequences on the shape of diffraction profiles. The three different types of spatial dependence are of *short-* and *long* range order or *homogeneous*, respectively. Due to the reciprocity between crystal and reciprocal space, the scattering related to point defects is extended far from the fundamental Bragg reflections. This is often called Huang scattering. The strain fields of dislocations is of *long-range* character, therefore their diffraction effects cluster around the fundamental Bragg reflections. This is the diffraction effect called: diffraction peak broadening or line broadening and the topic related to it is peak- or line profile analysis. Since the strain fields of planar defects are space independent or homogeneous they cause lattice parameter changes or shifts of Bragg reflections. If such defects, especially stacking faults, extend to finite volumes they can also cause peak broadening or asymmetries in peak shape.

The classical methods of Williamson-Hall and Warren-Averbach are often limited to the harmonic series of *hkl* due to strain anisotropy. Classical Warren-Averbach procedure has further conceptual difficulty in that it assumes that the mean square strain $\langle\varepsilon_{g,L}^2\rangle$ is a constant.

This would be true if atoms were displaced randomly from their ideal positions in the crystal. Here g is the absolute value of the diffraction vector, it indicates the mean square strain in the $\boldsymbol{g}$ direction, L is the Fourier length, $L=na_3$, where $a_3=\lambda/2(sin\theta_2-sin\theta_1)$, n are integers starting from zero, λ is the wavelength of X-rays and $(\theta_2-\theta_1)$ is the angular range of the measured diffraction profile [8]. Experiment shows that $<\varepsilon_{g,L}{}^2>$ is never a constant but it strongly decays with L. Strain or microstrain is often given as a number: the value of $<\varepsilon_{g,L}{}^2>$ corresponding to a particularly selected L value. In dislocated crystals, for small L values, Krivoglaz [7] and Wilkens [9] have given:

$$<\varepsilon_{g,L}{}^2> \cong (r\,\overline{C}\,b^2/4p)ln(R_e/L) \qquad (1)$$

where r, b and R_e are the density, the modulus of Burger's vector and the effective outer cut-off radius of dislocations, respectively. Peak broadening caused by dislocations depends on the relative orientations between the Burgers and line vectors of dislocations and the diffraction vector, $\boldsymbol{b}$, $\boldsymbol{l}$ and $\boldsymbol{g}$, respectively. This effect is taken into account by the dislocation contrast factors C [4,7,9,10]. In a texture free polycrystal or if the Burgers vector population on the different slip systems is random the C factors can be averaged over the permutations of the hkl indices and for cubic crystals they are [11]:

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

where $\overline{C}_{h00}$ are the average dislocation contrast factors for the $h00$ reflections, $H^2=(h^2k^2+h^2l^2+k^2l^2)/(h^2+k^2+l^2)^2$ and q is a parameter depending on the elastic constants of the crystal and on the edge or screw character of dislocations [12]. For other Bravais lattices the appropriate fourth order invariants of hkl are relevant.

Using the above equations the classical Williamson-Hall and Warren-Averbach methods have been *modified* [4]:

$$DK = 0.9/D + \alpha(K\overline{C}^{1/2})^2 + O(K\overline{C}^{1/2})^4 \qquad (3)$$

$$\ln A(L) \cong \ln A^S(L) - r\,BL^2\ln(R_e/L)(K^2\,\overline{C}) + O(K^4\,\overline{C}^2) \qquad (4)$$

where $K=2sin(\theta)/\lambda$, $DK=2cos(\theta)(\Delta\theta)/\lambda$, D is the apparent size parameter corresponding to the FWHM. It is obtained by extrapolation to $K=0$ in the usual manner. O stands for higher order terms not interpreted here. A similar equation can be given for the integral breadths and the corresponding apparent size parameter is denoted by d. $B=\pi b^2/2$ and O stands again for higher order terms. The size parameter corresponding to the Fourier coefficients, denoted by L_0, is obtained from the size Fourier coefficients A^S as described by Warren [8]. d and L_0 give the volume- and area-weighted mean column length, respectively [2]. The classical and the *modified* Williamson-Hall plots of the FWHM are shown for bulk nanocrystalline and plastically deformed copper specimens in Figs. 1 and 2, respectively. Strain anisotropy can be seen in Fig. 1, which has been rationalised by the dislocation model of the mean square strain as shown in Fig. 2.

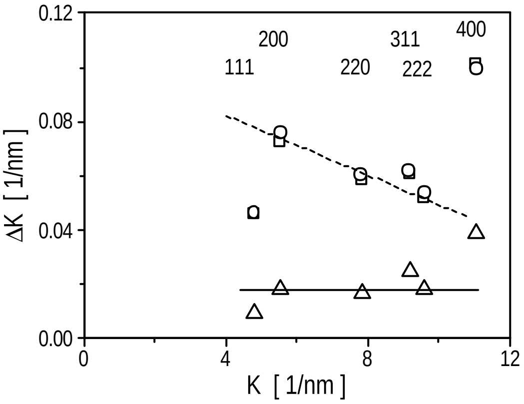

Fig. 1. *Conventional Williamson-Hall plot of the FWHM of a bulk nanocrystalline [14] (open circles after polishing, open squares after additional chemical etching) and a plastically deformed [4] (open triangle) copper specimen. The horizontal solid- and slanted dashed lines go through the FWHM of the 200, 220 and 222 reflections, respectively.*

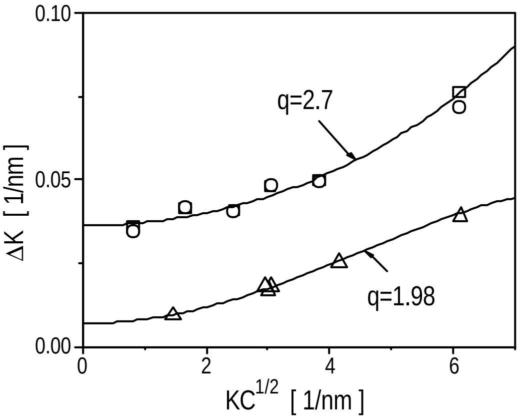

Fig 2. *The same data as in Fig. 1. plotted in the modified Williamson-Hall plot. The best fitted q values are also indicated. The solid lines are the best fitted curves according to the equation above. The q=1.98 and q=2.7 values correspond to equal screw and edge dislocation populations and an abundance of Lomer-Cottrell locks, respectively [14].*

The median and the variance , m and s, of a log-normal size distribution of crystallites in the presence of strain can be obtained by a simple and pragmatic method from the three apparent size parameters: D, d and L_0 [13]. The intensity distribution corresponding to size broadening is obtained as:

$$I^S(s) = \int_0^\infty M \cdot \frac{\sin^2(\pi M s)}{2(\pi s)^2} \cdot erfc\left[\frac{\ln(M/m)}{\sqrt{2}\,\sigma}\right] dM \tag{5}$$

where *erfc* is the complementary error function. This function is mathematically equivalent to the one given by Langford *et al*. in [2]. The theoretical function $I^S(s)$ provides numerically calculated apparent size parameters corresponding to its FWHM, integral breadth and Fourier coefficients denoted by $D_{s,\mathrm{m}}$, $d_{s,\mathrm{m}}$ and $L_0^{s,\mathrm{m}}$, respectively. The median and the variance of the size distribution function are obtained by the method of least squares fitting:

$$(D_{s,\mathrm{m}} - D)^2 + (d_{s,\mathrm{m}} - d)^2 + (L_0^{s,\mathrm{m}} - L_0)^2 = minimum \tag{6}$$

in which the fitting is carried out by varying σ and m. The *modified* Warren-Averbach equation can be evaluated for the density and the effective outer cut off radius of dislocations. The values of q have been evaluated numerically as functions of the elastic constants for cubic and hexagonal crystals and can be discussed in terms of edge or screw character of dislocations or, to a limited extent, in terms of the elastic constants of crystals [12]. The *modified* Williamson-Hall and Warren-Averbach equations can be considered as the rehabilitation of the classical procedures for the case of strain anisotropy, based on the dislocation model of the mean square strain.

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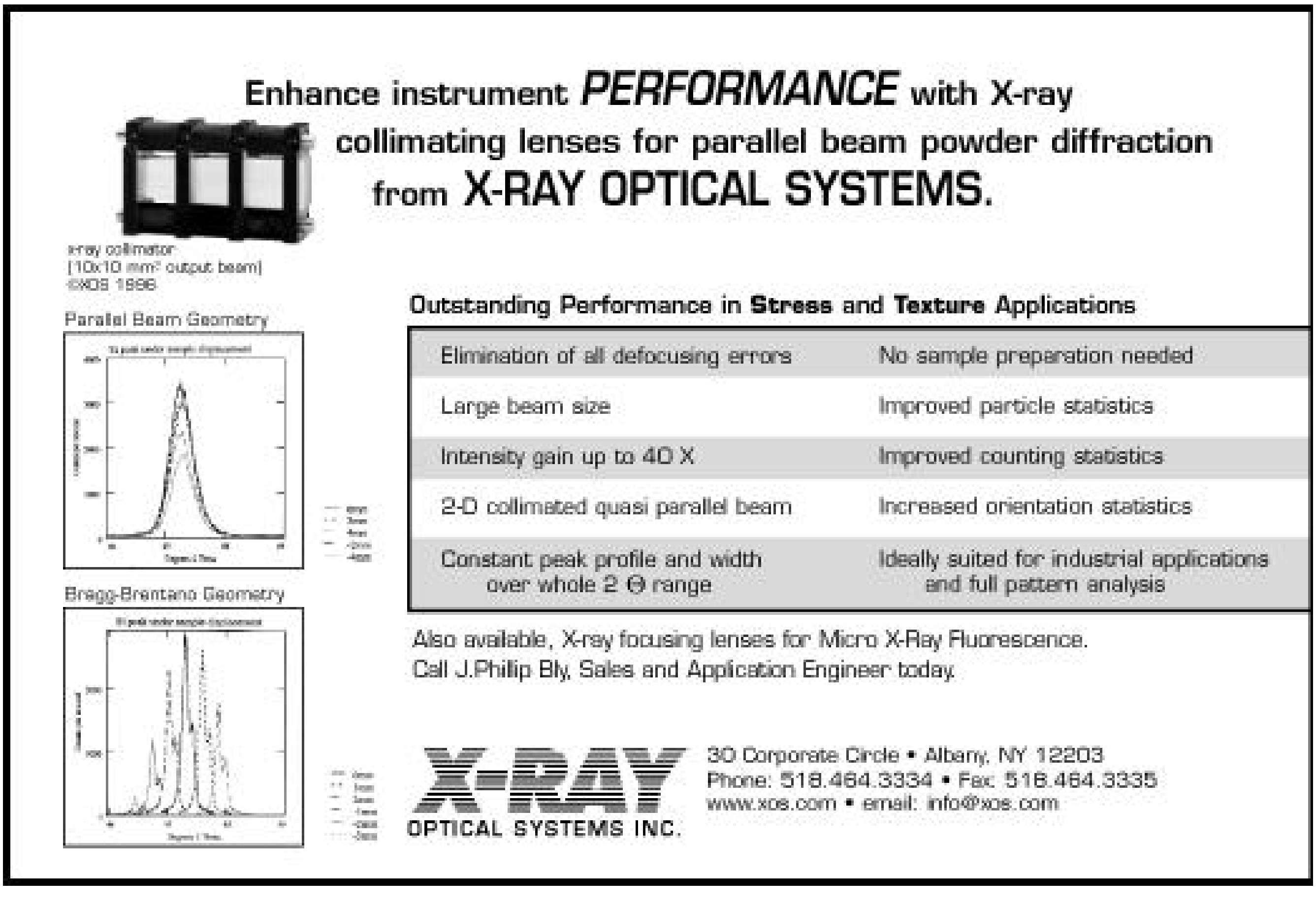
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Insight into Polycrystalline Materials with Ultrahigh Resolution and Reciprocal Space Mapping

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ABSTRACT

The microstructure of bulk and thin-layer polycrystalline materials can strongly influence the physical properties from hardness to piezo-electricity. However, the measurement of the crystallite size and strain is fraught with complexities due to the scattering of many crystallites. The crystallites in general have a distribution of orientations that may not be random. In general, the scattering is weak and thus requires a large divergent incident beam to maintain reasonable intensity. This large "instrument function" introduces many complexities to the extraction of good data. These complications are discussed and how further insight can be achieved with an instrument with very high angular resolution. Generally, all the problems above are the result of projections of the captured scattering and the assignment to a specific set of diffractometer angles. Reciprocal space mapping can resolve these projection effects and can prove a very powerful tool in interpreting strain and as an aid to obtaining data from very weak scattering.

INTRODUCTION

Suppose we have a diffractometer with a divergent incident beam on the sample, then the traditional approach is to express the diffraction profile, *p*, as a correlation of the sample intrinsic scattering width, *f*, (including micro-structural effects) and the "instrument function", *g*,

$$p = f * g$$

To obtain the micro-structural information, we can deconvolve the instrumental broadening effects by making certain assumptions[1]. The mathematics of this approach can be fairly rigorous however it is important to be sure that this very first step is valid for the sample that we may be analysing.

The analysis of any sample based on this approach assumes that there is an orientation distribution that makes full use of the "instrument function." We therefore have to consider what we mean by the "instrument function." The scattering profile is in fact a very complex function and simplifying its contributions into instrumental and intrinsic sample responses is not at all straightforward. We can quite easily determine the distribution of photon trajectories onto the sample and similarly determine the range of trajectories accepted from the sample into the detector. However, what happens at the sample can be very complex and is of course unknown. Immediately we can see a problem, we do not know what the sample scattered trajectories are that will be accepted by the detector, therefore the sample cannot be considered in isolation of the whole experiment[2].

Suppose we now make the "instrument function" far smaller than the scattering effects of the sample, then we are left with a profile dominated by the sample scattering. If we reverse the situation, such that the "instrument function" is large and the sample is a single small crystallite, then the divergence of the incident beam as far as the crystallite is concerned will be defined by the sample's view of the X-ray focus. The sample acceptance will depend on the relative orientation of this crystallite and its intrinsic scattering width. The probability of this crystallite having its scattering vector in the diffractometer plane is very small. If we extend these arguments to an aggregate of crystallites then the chances are that most of the intensity originates from an oblique interaction of the instrument function with a slightly misoriented crystallite.[*] This becomes clear when we study samples with texture, such that at certain orientations the intensity is dominated by crystallites with their scattering vector in the plane of the diffractometer and the peak narrows[3]. We then have a difficulty in describing an instrument function because it is sample dependent. To overcome this we could create a "perfectly random" orientation of crystallites, such that the majority of the scattering comes from misaligned crystallites, in this case we need to include a very exacting model including the axial and scattering plane divergence throughout the diffractometer[4,5]. Only when we have a sample that will accept the full instrument function can we be sure of the modelling.

Attempts to improve the orientation distribution in Bragg-Brentano geometry of crystallites by spinning are limited since this is based on scattering from planes parallel to the surface. However there are some small benefits because the crystallites away from the centre of the sample are from planes inclined to the surface. Alternatively rocking the crystal can bring many more crystallites into the beam. Improving the experimental method, sample preparation, etc., all helps but there is still some remaining uncertainty. It is the purpose here to examine these difficulties by taking a different approach to validate these methods.

---

[*] Suppose we have a sample 1cm x 1cm with an X-ray penetration depth of 20μm that is composed of perfectly randomly orientated 3μm spherical crystallites. Then there are 7.4×10^{7} crystallites each with a full-width-at-half-maximum (FWHM) of 3.4×10^{-3} degs. Hence, the number of crystallites with their orientation aligned within their FWHM of the incident beam is 0.016. From this argument we can see that the results become more reliable as the intrinsic FWHM increases, i.e. the average crystallite size is small or considerable "micro-strain" exists.

METHOD

The simplest form of reciprocal space mapping (RSM) is obtained photographically (e.g. with a Debye-Scherrer camera), however the dynamic range and resolution is inadequate for many problems. Two approaches have been used for the examples presented; low resolution RSM using conventional Bragg-Brentano geometry[6] and high resolution three-dimensional RSM using multi-crystal optics[7,8,2].

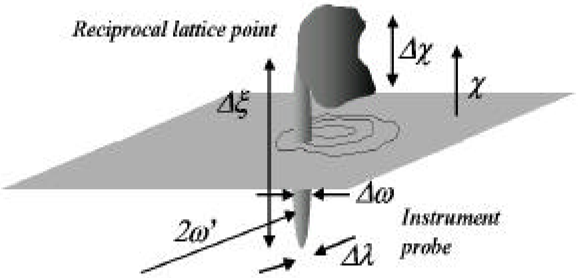

Figure 1: The 3D reciprocal space probe.

Consider the schematic of the reciprocal space probe given in figure 1. This can be considered as the region of intersection of the incident beam divergence and the analyser / detector acceptance for the distribution of wavelengths passed by the monochromator. There will also be a “real space” variation in these parameters, but this is difficult to represent in the same diagram. If the probe is moved around, it will register intensity when the reciprocal lattice point broadened by the influence of the microstructure, etc., is touched. If the probe is small and the reciprocal lattice point is small, then an individual crystallite can be isolated and studied. This is achieved with three-dimensional reciprocal space mapping, with very high angular resolution in the scattering plane and a restricted axial divergence. This differs from micro-diffraction since the beam area on the sample can be large, i.e. the crystallite isolation occurs in reciprocal space and not “real space.”

Collecting a reciprocal space map with a larger probe can also be exceedingly useful for measuring very weak scattering. In this case the axial divergence can be contained with Soller slits and therefore can be achieved with a standard slit-based diffractometer. The basic principle is that observing weak scattering above the level of the background scatter is easier in a two-dimensional map than from a single profile scan. The RSM, because it can capture a larger region of reciprocal space, will also work well with textured materials. Of course a pole-figure is a reciprocal map through a different section in reciprocal space.

EXAMPLES

Strain variation in a grain or each grain with a different strain?

When we measure micro-strain, what are we determining? One significant advantage of multiple-crystal optics is that the scattering angle gives a precise *d*-spacing, the zero error is at the arc second level and there is no displacement error[9]. Of course, the scattering plane must be in the plane of the diffractometer to remove 2θ projection errors, this is naturally removed in a three-dimensional RSM. A textured Al bulk sample was analysed in this way using the strong 002 reflection[3]. The resulting map is given in figure 2, where we can observe distinct branches of scattering and the suggestion of the scattering from individual crystallites. The 2θ values are clearly different for different crystallites and therefore in this case the micro-strain measured by conventional approaches is the result of different crystallites having different lattice parameters.

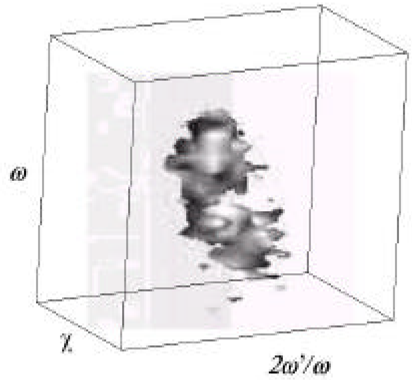

Figure 2: The 3D RSM of the 002 reflections from Al.

In another example[10] a thin diamond film has been studied and an individual crystallite has been isolated. The shape of this reciprocal space feature should now give the strain distribution within this individual crystallite, figure 3.

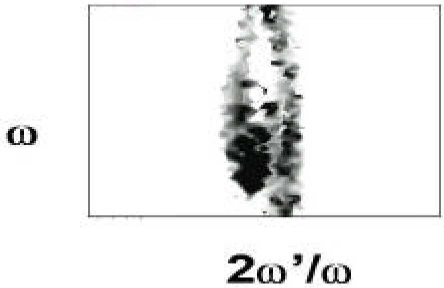

Figure 3: The 3D RSM of the 004 reflections from two diamond crystallites.

Analysing very weak scattering:

Observing the presence or absence of a minor phase in a mixture can prove very demanding, especially when the sample cannot be ground to powder because this could induce phase changes. This example is of a TiAl alloy multilayer, used as a light hard material[8,2]. The presence of Ti (FCC) was observed by electron microscopy, but was not observable with conventional X-ray methods. However, a low resolution RSM, figure 4, yields the reason why. Any single scan indicates no significant intensity above the background level, whereas the map shows a weak line with evidence of texture. The proportion of this phase is ~2%.

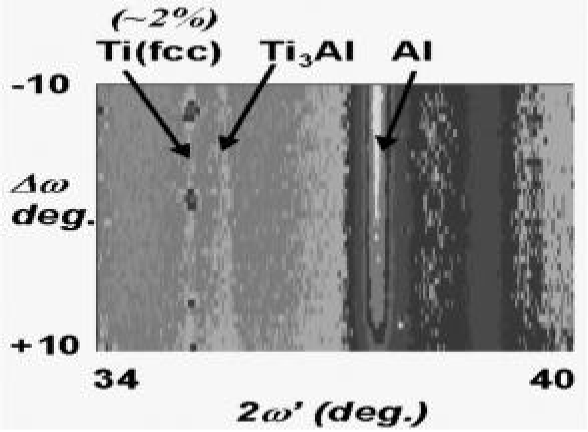

Figure 4: Scattering from a Ti phase in an Al-Ti alloy.

Measuring the crystallite size parallel to the interface of a thin layer is a challenge when the size is small. Again, a single scan gives no real indication of intensity above the background level. A limited area RSM map reveals a band of intensity that was projected onto a line normal to band and yielded a lattice parameter and crystallite size[2], figure 5.

Discussion and conclusions:

These few examples indicate the power of low-resolution RSM for extracting data from very weak scattering. These approaches clearly supplement conventional methodology.

In the case of very-high resolution RSM, this really extracts new data with the scattering placed on an absolute scale. A further advantage of high resolution is that placing an X-ray film after the analyser[11,2] will produce an image of the object under investigation. Such a topograph will aid the interpretation of complex images and provide a useful check on whether an individual or a group of crystallites is contributing to the measured intensity. For RSMs such as that in figure 2, it is instructive to see that the intensity at any one position is usually composed of a strong contribution from a single crystallite with very weak contributions from others not in the Bragg condition. This in a way confirms the complexity of the scattering contributions to a profile discussed in the introduction.

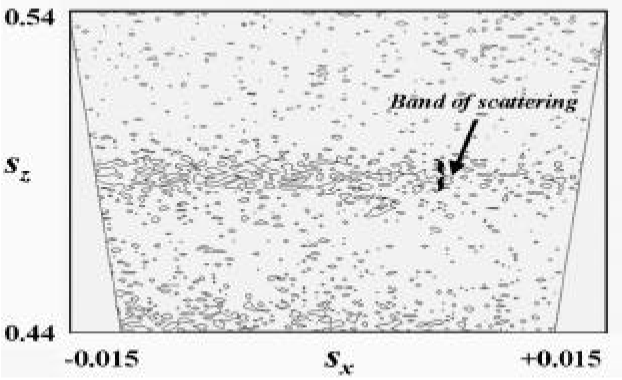

Figure 5: In-plane scatter from a 30nm Cr layer.

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Microstructure Modeling in Rietveld Refinement

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The profile analysis proposed by Rietveld in 1969 has been proved to be a powerful method for the structure investigation of polycrystalline samples. The improvement of the diffraction instrumentation, on one side, and of the models describing different contributions to the measured diffraction pattern, on the other side, have played a major role in the significant increase of the Rietveld method performances. Concerning the second point, important steps have been done by the derivation and use of more accurate analytical models to describe the effects of the microstructure on the integrated intensity [1], broadening [2], and position [3] of the diffraction peaks in the Rietveld method.

The paper [1] by Popa was among the first attempts to introduce the texture analysis by symmetrized spherical harmonics in the Rietveld method. The spherical harmonics representation of the pole distribution replaces the March model, making possible the Rietveld refinement for complicated cases of texture and/or multiple patterns measured in complex diffraction geometries. Von Dreele [4] introduced this model in the Rietveld program GSAS. As Von Dreele proved, by using spherical harmonics in the Rietveld method, it is possible not only to obtain an accurate fit of complex diffraction patterns for complicated texture, but also to determine the orientation distribution function.

Models describing the anisotropic broadening of the diffraction peaks produced by the elastic strain and crystallite size have been also reported by Popa [2]. This is the first model fulfilling the invariance condition to the transformation of the set of Miller indices hkl into an equivalent one. These models are different for different Laue classes.

The strain model has been derived by calculating the dispersion of the strain in a direction normal to the diffraction plane. From this reason the model parameters have a physical meaning, being linear combinations of the elements of correlation matrix of the strain tensor in the crystallite coordinate system. The model has been already introduced in the Rietveld program MRIA of Zlokazov and Cernyshev [5] and applied to many specimens, including pharmaceuticals, based on X-ray laboratory, synchrotron, and neutron data (see Chernyshev *et. al.* [6], Yatsenko *et. al.* [7]). The model has been also included in the Rietveld program MAUD by Lutterotti [8]. The results of the refinement of the Y_2O_3 CPD Round Robin sample were presented in [8] and [9]. In GSAS, the model was included based on an equivalent (with minor differences for some space groups) phenomenological approach by Stephens [10].

In the reciprocal space, the diffraction peak broadening caused by the crystallite size is inverse proportional with the crystallite dimension along the diffraction vector. If the crystallites have a non-spherical shape, this dimension is not unique. In fact, what is "seen" by diffraction is an average dimension in the diffraction direction of all identical crystallites related by the Laue group operations. This aggregate of crystallites related by symmetry we have called in [2] "the composite crystallite". Because the shape of the composite crystallite is invariant to the Laue group operations, its radius can be developed in a series of symmetrized spherical harmonics. For the Laue class $4/m$, for example, we have:

$$\begin{aligned} R_{\mathbf{h}} &= R_0 + R_1 P_2^0(\cos\Phi) + R_2 P_4^0(\cos\Phi) \\ &+ \left(R_3 \cos 4b + R_4 \sin 4b\right) P_4^4(\cos\Phi) + \dots \end{aligned}, \qquad (1)$$

where (Φ, b) are the polar and azimuthal angles of the unit vector $\mathbf{h}$ along the reciprocal lattice vector, in the crystallite orthogonal coordinate system, P_l^m are the Legendre functions of indices l, m and R_i are refinable parameters. The formulae like (1) are not empirical approximations as can be thought at the first sight, but are the rigurous representations of the quantity measured by diffraction: the radius of the composite crystallite. This representation applies to any kind of crystallite shape and size distribution. Because for the Rietveld method it is only essential to have a unique formula (for a given Laue class) to model the crystallite-size broadening, the set of $R_{\mathbf{h}}$ values obtained by Rietveld refinement with (1) generally may correspond to different crystallite shape and size distributions [11].

In our last paper [3], we derived the line shift of the diffracted peak caused by the residual or applied stress in isotropic polycrystals, for all Laue classes, in the Reuss and Voigt approximation. The obtained formulae are compatible with the Rietveld refinement method. In comparison to other papers treating the same problem, in which the so-called diffraction elastic constant are calculated, our approach models directly the strain measured by diffraction. Furthermore, our approach is mathematically much simpler and the correctness of the results are easy to check. Moreover, it is simpler to extend the resolution of the problem to the case of the textured polycrystals, without making Voigt or Reuss approximations.

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Structure on Different Length Scales from Powder Diffraction: the Real-Space Pair-Distribution Function (PDF) Technique

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Modern functional materials often contain defects and are quite disordered. In fact, it is often the defects that give them their interesting properties [1]. It is obviously of the greatest importance to have techniques that can characterise crystalline materials that are significantly disordered at the atomic scale. Powder diffraction data contains a great deal of information, in the form of diffuse scattering, about defects and disorder. When the (properly normalised) powder diffraction data are Fourier transformed into real-space co-ordinates we obtain the atomic pair distribution function (PDF). This is simply another representation of the powder diffraction data; however, it can often be revealing and helpful to study the data in real-space. The PDF has peaks at characteristic distances separating pairs of atoms and by calculating the PDF from model structures and comparing them to the measured PDF we can extract information about the local structure [2].

By studying the same PDF on different length-scales we can get information about microstructured materials. For example, consider the PDF from a sample that has some kind of domain structure with a characteristic domain size of ξ. If you look in the PDF on a length-scale $<< \xi$ the pairs of atoms that you probe will predominantly lie within the same domain as each other and the resulting structure will be the intra-domain structure. If you look in the same PDF at a distance $r > \xi/2$ then most of the pairs of atoms giving rise to features in the PDF lie in different domains and the result is a coherent average of the different local structures. This is nowhere better illustrated than if we think of solid C_{60} as a microstructured material where each bucky ball is a single domain. The bucky ball, its scattering and PDF, are shown in Fig. 1. The diameter of the ball is 7.1 Å. Sharp peaks are observed in the PDF coming from the characteristic C-C pairs on the ball up to 7.1 Å. Thereafter only broad featureless structure exists. The sharp peaks are the intra-molecular structure and the broad features in the data are the inter-molecular structure, or ball-ball correlation. This separation of the intra- and inter-domain structure occurs as a natural consequence of the Fourier transform.

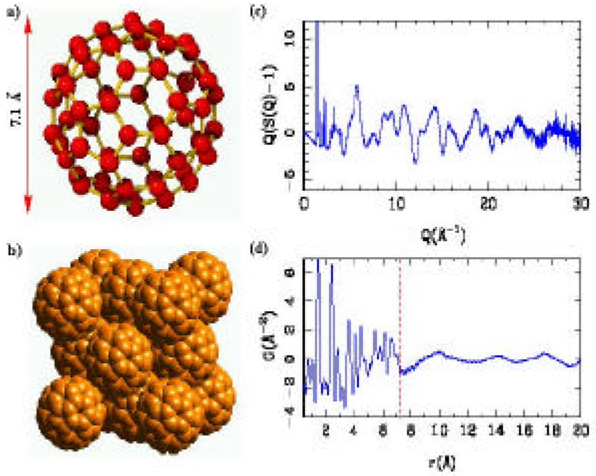

Figure 1. C_{60}(a and b), its normalised neutron diffraction pattern (c) and the corresponding PDF (d). The vertical dotted line in (d) is at 7.1 Å, the diameter of the ball.

Inhomogeneous and microcrystalline materials can have very well defined local structures. An excellent example of this is the metastable structure of exfoliated-restacked WS_2 [3]. The material is made up of covalently bonded S-W-S layers which stack into a three dimensionally ordered crystal structure. The diffraction pattern is shown in Fig. 2(a). After intercalating Li between the layers, they can be stripped apart and form a colloidal suspension of single layers, the exfoliated state. On further changing the chemistry in the beaker the layers can be restacked and the Li removed. We are back to the starting state of a precipitate of pure WS_2; however, the exfoliated-restacked compound has undergone a dramatic structural modification as evidenced by the diffraction pattern in

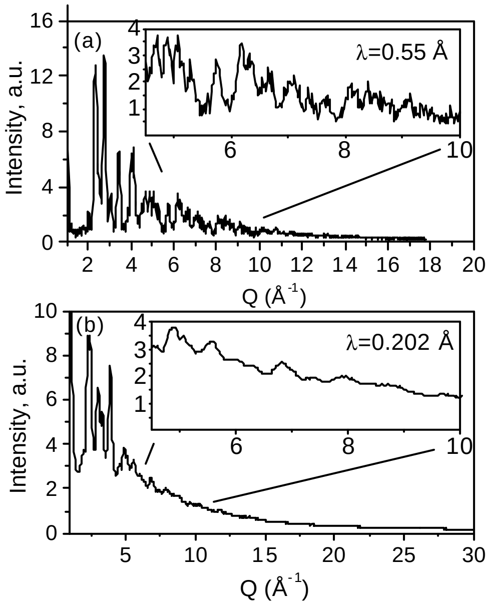

Figure 2. Powder diffraction patterns of pure (a) and restacked (b) WS_2.

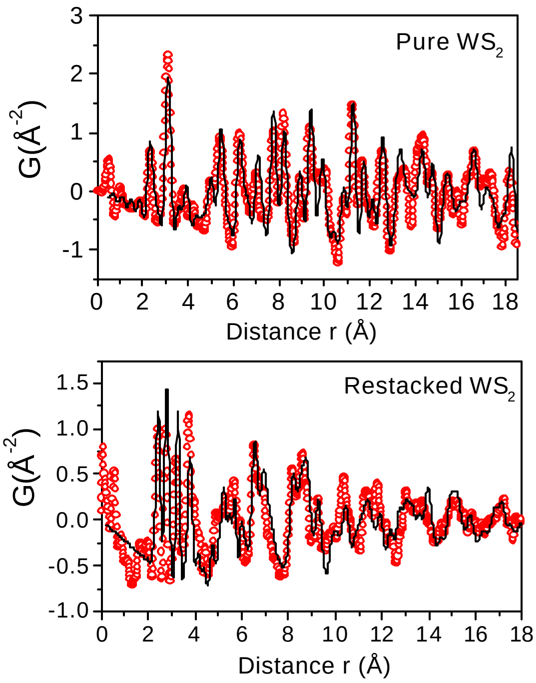

Figure 3. Experimental (symbols in red) and fitted (solid line) PDF's of pure and restacked WS_2.

Fig. 2(b). Bragg peaks are broad and sparse and traditional structure solution methods are powerless. The broad Bragg/diffuse scattering peaks indicate that the sample has become microcrystalline with very limited structural coherence. However, when the data are Fourier transformed to obtain the PDF we see two remarkable things. First, the peaks in the PDF are just as sharp in both the pure and restacked samples (Fig. 3). Both have a very well defined local structure. Second, we see that the first two peaks in the PDF of pure WS_2 have split into 4 peaks. This shows clearly that the symmetry of the local environment of W has fallen. Modelling, shown by the solid lines in Fig. 3, indicates that the environment has changed from octahedral to prismatic and short W-W distances have appeared in a chain-like fashion. The microcrystalline nature of the metastable product is evident by the fall-off in amplitude of the features in its PDF and from this we can estimate the range of the structural coherence to be ~20Å.

By way of illustration we have presented here just a few examples of our recent applications of the PDF technique to study inhomogeneous and microcrystalline materials. Other examples we are studying where the microstructure has a profound bearing on the material properties are high temperature superconductors [4,5], colossal magneto-resistant manganites [6,7], semi-conductor alloys [8] and nanophase carbons [9].

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Whole Powder Pattern Modelling

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Traditional Line Profile Analysis (LPA) methods are based on approximate equations to relate line broadening to lattice distortions and diffraction domain size [1]. Simple expressions like the *Scherrer* formula, the *Williamson-Hall* (WH) plot and derived expressions [2] (frequently referred to as simplified methods) have long been used, and are still employed for a rapid estimation of the so called size-strain effects. The *Warren-Averbach* (WA), which is intrinsically more reliable than simplified methods in the separation of line broadening contributions from domain size and lattice distortion, also involves simplifying assumptions [3,4].

If we consider that the above methods were developed well before the diffusion of fast and cheap computers, it is reasonable to think that approximations and simplifications in traditional LPA were mostly introduced to limit the complexity of data processing.

In the more recent past, a considerable advancement has been the introduction of analytical functions to fit diffraction profiles, leading to the development of the *Rietveld* method [5], pattern decomposition techniques [6] and to the general concept of Whole Powder Pattern Fitting (WPPF) [5-8]. Despite the popularity gained by analytical profile fitting, the arbitrariness in the choice of the profile function is a serious limitation.

Whole Powder Pattern Modelling (WPPM) is a promising development [9,10]. WPPM allows a simultaneous processing of the entire XRD pattern based on suitable models of domain size/shape and lattice defects, without using arbitrary analytical profile functions.

In the following we will review some basic concepts of WPPM for cubic materials.

The intensity diffracted by a polycrystalline material (in absence of texture and applied load) can be written as the sum of the contributions of the *hkl* profile sub-components, $I_{hkl}(s_{hkl})$, composing a {*hkl*} reflection:

$$I_{\{hkl\}}\left(d^{*},d^{*}_{\{hkl\}}\right)=k\left(d^{*}\right)\cdot\sum_{hkl}w_{hkl}\,I_{hkl}\left(s_{hkl}\right) \qquad (1)$$

$$I_{hkl}\left(s_{hkl}\right)=\int_{-\infty}^{\infty}C_{hkl}(L)\exp\left(2p\,iL\cdot s_{hkl}\right)dL \qquad (2)$$

where $d^{*}=2sinq/l$ and $s_{hkl}=d^{*}-(d^{*}_{\{hkl\}}+d_{hkl})$ is the distance from the peak centroid ($d^{*}_{\{hkl\}}$) in the reciprocal space; w_{hkl} is the weight of each *hkl* sub-component and d_{hkl} is a shift, due to lattice defects (e.g., faulting). Constants and trigonometric terms are grouped in $k(d^{*})$ (e.g., Lorentz-polarisation (LP), $|F|^{2}$, etc.).

The Fourier coefficients, ($C_{hkl}(L)$), result from the various line broadening effects. In a rather general form, we can separate contributions from instrumental profile (IP), finite size of diffracting domains (S), faulting (F) and lattice distortions (D) as follows[1]:

$$I_{hkl}\left(s_{hkl}\right)=\int_{-\infty}^{\infty}T^{IP}A^{S}\left\{\left[A^{D}A^{F}-B^{D}B^{F}\right]\cos\left(2p\,Ls_{hkl}\right)+\right. \qquad (3)$$
$$\left.-\left[A^{D}B^{F}-B^{D}A^{F}\right]\sin\left(2p\,Ls_{hkl}\right)\right\}dL$$

Eq.(1) and (3) can be used to model experimental profiles, provided that appropriate expressions for the Fourier coefficients ($A^{S,D,F}$, $B^{S,D,F}$) are available [8,9]. In other words, the XRD pattern can be modelled on the basis of a suitable description of microstructure and lattice defects.

As an example, we can consider the case of lattice distortions due to dislocations, with spherical crystalline domains. In this, as in many other cases of practical interest, $B^{D}=0$ [3,4,8,9]. We assume equally populated {111}<110> slip systems and a lognormal distribution of domain diameters [8,9], whereas faulting is given by *Warren*'s theory [3] (as revised by *Velterop et al*. [12]), and the IP is modelled by a pseudo-*Voigt* [7-9]:

$$I_{hkl}\left(s_{hkl}\right)=\int_{-\infty}^{\infty}T^{IP}_{pV}A^{S}A^{D}_{\{hkl\}}\left[A^{F}_{hkl}\cos\left(2p\,Ls_{hkl}\right)-B^{F}_{hkl}\sin\left(2p\,Ls_{hkl}\right)\right]dL \qquad (4)$$

The split of {*hkl*} reflections in *hkl* profile sub-components is due to the presence of faulting, whereas dislocation line broadening depends on {*hkl*}, and size broadening (in this specific case) is independent of *hkl*.

Explicit expressions for ${T_{pV}}^{IP}$ (Fourier Coefficients of the IP), $A^{S}, A^{D}_{\{hkl\}}, A^{F}_{hkl}, B^{F}_{hkl}, d_{hkl}, w_{hkl}$ have already been presented elsewhere [8,9]; it is worth noting that WPPM allows a direct refinement of microstructure and lattice distortion parameters, namely:

(a) *w* and *g*, respectively, lognormal mean and variance of the grain diameter distribution;
(b) *r*, *Re* and $\overline{C}_{hkl}$, respectively, dislocation density, outer cut-off radius and contrast factor[2];
(c) *a* and *b*, respectively, stacking (deformation) and twin fault probabilities;
(d) a_{o}, lattice parameter (and *Burger* vector, ($|b|=a_{o}/Ö2$,);

Additional parameters in WPPM are background and integrated peak intensities. The latter can be easily used for within a *Rietveld* refinement algorithm.

---

[1] The functional dependence of the Fourier coefficients was omitted for briefness. The instrumental profile has been assumed symmetrical; however, this condition can be changed, if necessary. A general expression for the IP can be given by a fundamental parameter approach [11].

[2] The contrast factor can be written as $\overline{C}_{hkl}=\overline{C}_{h00}(1+q\cdot H)$, where H is a combination of Miller indices; usually, *q*, the factor controlling the dislocation character (screw/edge) can be refined during WPPM. For details see [7] and papers by *Ungar* (e.g., [13]) (see also p.14 in this issue).

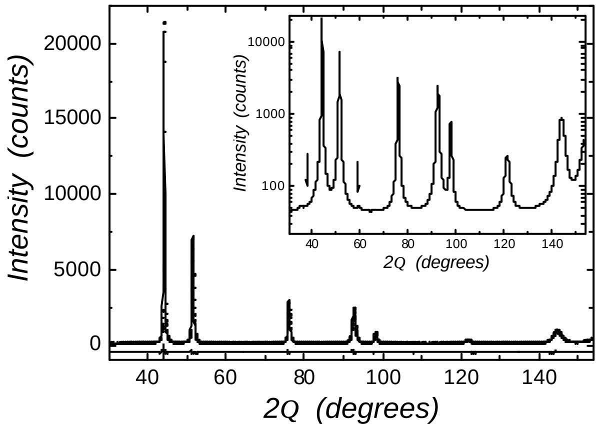

Figure 1. XRD pattern of a ball-milled Ni sample [9,14]. Arrows mark the position of minoritary NiO phase. Results: a_o=0.35240(1) nm; w =3.46(1), g=0.336(7) (Average diameter: 33.8(5) nm); r=7.8(1)x10^{15}m^{-2}, Re=18(1) nm, q=-1.76(2); a=0.5(1)%, b≈0. (R_{wp}= 7.388%; R_{exp}=6.261%; GoF=1.18)

To illustrate the application of WPPM we consider the case of ball-milled Ni. Figure 1 shows the results of the WPPM; the main effect is given by dislocations, whereas faulting is limited (as a consequence of the high faulting energy in pure Ni). Domain size is considerably reduced with respect to the original value (60 nm), and the size distribution is markedly broader, as shown in Figure 2. Several details in the ball milling process can be appreciated, and provide a useful description of the process [14].

It is worth noting that the above results are obtained directly from the measured pattern, without any additional assumption other than microstructure and lattice defects models. In addition, the entire analysis is consistent; this is not always the case with conventional methods. As an example, we can consider the case of a highly dispersed ceria powder (a case similar to that of the Size-Strain Round Robin organised by the CPD; see: http://www.iucr.org/iucr-top/comm/cpd/).

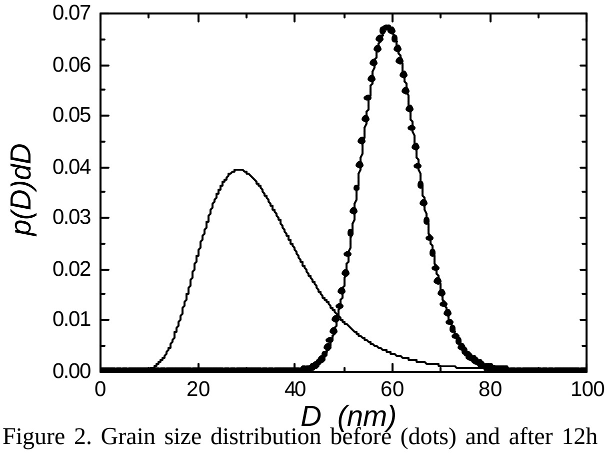

Figure 2. Grain size distribution before (dots) and after 12h of ball milling (line) for a Ni powder.

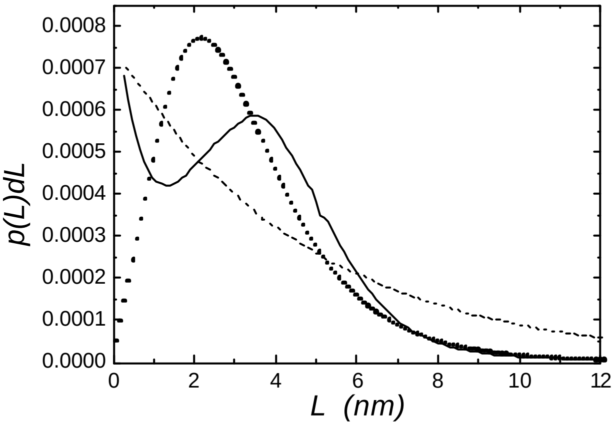

Figure 3. Column length distribution for a ceria sample: WPPM (dots), WPPF with Voigtian profiles (line) and exponential *p(L)* (Lorentzian profile) (dash).

Preliminary TEM micrographs clearly indicate nearly spherical grains, with a lognormal diameter distribution [14]. Figure 3 shows the column length distribution (*p(L)*) obtained by WPPM, as compared with the one given by a WPPF using a *Voigt* profile [8]. It is quite evident that a *Voigt* profile cannot reproduce such a distribution [10]. This is even more so if one assumes an exponential *p(L)* (which corresponds to a Lorentzian profile component, as assumed for example in the WH plot) which is clearly very far from the expected distribution.

Preliminary WPPM results and comparison with WPPF were recently presented [8,9]; further work is to be published in the next future [14].

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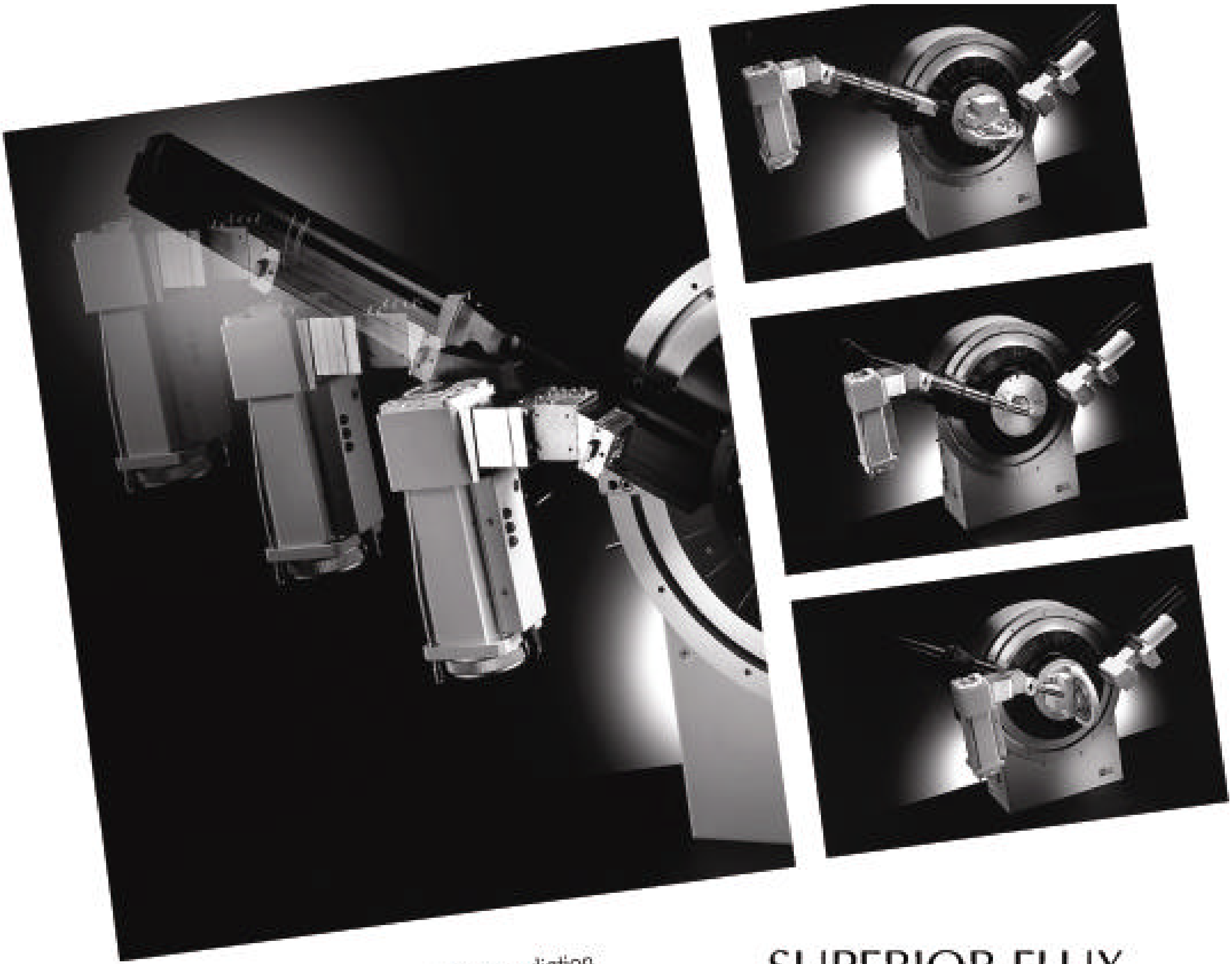

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News from the International Centre for Diffraction Data (ICDD)

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Another Successful Denver X-ray Conference™!

Summertime at the ICDD headquarters was buzzing with activity as we prepared for the 49th Annual Denver X-ray Conference™. The conference was held 31 July–4 August 2000 at the Denver Marriott Tech Center Hotel, Denver, Colorado, U.S.A. Three hundred fifty conference attendees, as well as 210 exhibit staff, filled the conference rooms at the Marriott Tech Center. There were 35 exhibiting companies that occupied 49 exhibit booths. The vendors displayed products and services relating to X-ray powder diffraction and X-ray fluorescence spectrometry for the attendees to visit throughout the week.

Next year marks the 50th anniversary of the conference. Anniversary celebrations will dominate as the theme of the conference with special historical presentations planned throughout the week. The conference will be held 30 July–3 August 2001, in Steamboat Springs, Colorado, U.S.A.

Awards Presented at the Conference

As the most recent recipient of the **Birks Award,** Horst Ebel presented the 2000 Birks Award to Yohichi Gohshi of the National Institute for Environmental Studies, Tsukuba, Japan. The Birks Award was established to recognize outstanding contributions to the field of X-ray spectrometry.

Paul Predecki presented an award to the **ICDD** acknowledging its many years of service to the X-ray analysis community. Contributions from the community were solicited by Vic Buhrke for this award. Cam Hubbard accepted the award on behalf of the ICDD.

Robert L. Snyder presented the 2000 **McMurdie Award,** new this year, to Gregory J. McCarthy of North Dakota State University, Fargo, ND. The purpose of the McMurdie Award is to recognize distinguished work which improves the Powder Diffraction File™ in its purpose of identifying and characterizing inorganic solids.

The **Jerome B. Cohen Student Award** was created this year by the Denver X-ray Conference™ Organizing Committee in honor of Dr. Cohen, a leader in the field of X-ray analysis and in the training of students in this art. Paul Predecki presented the award to Sven Vogel, a student from Kiel University, Kiel, Germany. Sven Vogel received the award for his paper entitled, "Non-destructive In-situ Real Time Measurements of Structural Phase Transitions Using Neutron Transmission".

Recent Schools and Workshops

In addition to the Denver X-ray Conference™ and the annual ICDD® clinics, the ICDD participated in several international schools and workshops.

- ❑ Universidad de Los Andes, Merida, Venezuela was the site for the school, *Characterization of Polycrystalline Materials by X-ray Methods*, held 24–28 January 2000. Ron Jenkins, Bob Snyder and Terry Maguire represented the ICDD and presented lectures at the workshop.
- ❑ A Grant-in-Aid Workshop was held in St. Petersburg, Russia, 22–24 June 2000. The workshop, which took place in Mendeleev's Center of St. Petersburg University, hosted 55 participants from Russia and the surrounding region, including Finland, Sweden, Estonia, France, Poland and Germany. Cam Hubbard, Chairman of the ICDD, lectured about the history of the ICDD, its structure, membership, products and programs, with special emphasis on the Grant-in-Aid Program.
- ❑ The ICDD supported the Workshop on Structure Determination and Refinement from Powder Diffraction Data, held 4–8 October 2000, at the University of Bayreuth, Laboratory of Crystallography, Germany. This workshop was organized by the Powder Diffraction Group of the German Crystallographic Society DGK. John Faber represented the ICDD as a workshop speaker.
- ❑ John Faber and Earle Ryba conducted an ICDD® workshop at SARX 2000, VII Latin-American Seminary of Analysis by X-ray Techniques, held 19–24 November 2000 in São Pedro, São Paulo, Brazil. The workshop hosted over 50 participants and focused on the structure and programs of the ICDD, as well as the use of X-ray diffraction as an analytical tool.

Membership Status

We are proud to announce that the ICDD's membership now approaches 300. We have members residing in nearly every country in the world! The expertise of the ICDD members, shared through volunteer efforts, is instrumental in shaping the structure, culture, and products of the ICDD. We are grateful for their dedication and contributions.

The ICDD Introduces Its Metals & Alloys Relational Database (RDB)

Over the last few years, the ICDD has been making a transition from databases that are organized as "flat files" to relational databases. An RDB is a collection of data items organized as a set of formally described tables from which data can be accessed. This new flexible database construction provides extensive data mining capability.

The first ICDD® RDB product is the Metals & Alloys RDB. We have developed a powerful user interface that integrates all the functionality of PCPDFWIN™, including Boolean search capability. Furthermore, the RDB provides enhanced searching and display functionality. Fully digitized powder patterns, calculated "on-the-fly", are available for all calculated patterns derived from the ICSD. As development of the RDB progresses, full patterns will be extended to include experimental entries in the PDF®.

2001: The ICDD to Celebrate Two Anniversaries

As the year 2001 approaches, the ICDD anticipates the commemoration of two major milestones. The first event is the 60th anniversary of the production of the first set of our PDF-2 database. It is incredible to consider that from the humble beginnings of the 1,000 patterns in the first release, the database has grown to more than 130,000 entries. We are forever grateful for the careful planning and creative insight of the initial small group of scientists who first put the database in place and established data storage and retrieval rules which still persist today.

The second milestone that we will reach in 2001 is the 50th anniversary of the Denver X-ray Conference™. While the ICDD has only had responsibility for the running of this meeting for a few years, the ICDD members have been active on the organizing committee for about 25 years. The Denver X-ray Conference has also grown from very humble beginnings, initially attracting a rather small group of X-ray workers. Last year, nearly 600 participants enjoyed the conference, which is now firmly established as *the major event* for the X-ray analytical community in the United States.

Accuracy in Powder Diffraction III
April 22-25, 2001

National Institute of Standards and Technology
Gaithersburg, MD USA

This will be the third in a series of meetings concerning Accuracy in Powder Diffraction which have been held at NIST approximately every 10 years. These meetings offer a unique perspective on powder diffraction in that the issues under discussion are fundamental to accuracy and how it affects the application of the technique(s) to materials problems.

Advancements in instrumentation continue to increase the breadth of applications which can be considered with powder diffraction methods. Concurrently, the advances in computer hardware have allowed for the implementation of algorithms and concepts developed decades ago, but whose virtues could not be realised until recently. The meeting is structured to cover both instrument / technique specific subjects as well as issues concerning materials characterisation.

The meeting will consist of a single sequence of sessions and all oral presentations will be invited. An afternoon will be dedicated to a poster session of contributed works which will be followed by a round table discussion. This discussion will cover important topics which time constraints prevented from being included in the oral sessions. Contributions concerning topics related to accuracy in powder diffraction are welcome.

Technical Programme

Instrumentation, Optics Characterisation and Powder Diffraction Techniques Topics:

A critical examination of both current and anticipated powder diffraction instrumentation.

Invited Lecturers

K. Bowen (UK/USA), A. Fitch (F), P.G. Radaelli (UK), A. Hewat (F), P. Barnes (UK), M. Leoni (I), R. Cheary (Aus)

Structure Solution and Refinement

New methodology for the determination of structural information from powder diffraction data.

Invited Lecturers

Altomare (I), K. Shankland (UK), B. David (UK), T. Wessels (CH), R. Dinnebier (D), R. Von Dreele (USA), J.P. Attfield (UK), S. Billinge USA)

Microstructure, Lattice Defects & Residual Stress

Use of diffraction line shape and position for engineered materials characterisation

Invited Lecturers

R. Kuzel (CZ), J.-D. Kamminga (NL), N. Armstrong (USA/Aus), T. Gnaeupel-Herold (USA)

Phase Identification and Quantification

Reliability and limits of QPA and search-match methods, databases and software

Invited Lecturers

I. Madsen (Aus), J. Kaduk (USA)

Metrology

Issues concerning accurate determination of lattice parameters

Invited Lecturers

M. Deutsh (ISR),J. Cline (USA), H. Toraya (JPN)

Non-ambient Powder Diffraction

Novel techniques for analyses in high temperature, high pressure and other unusual environments

Invited Lecturers

J. Parise (USA)

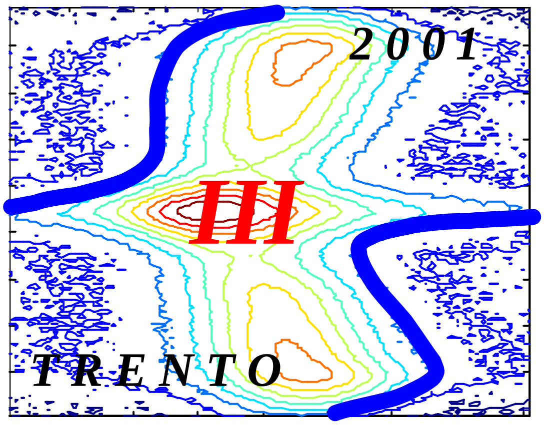
Details concerning the conference are currently being finalised. For information on registration, abstract submission and hotel registration, visit: www.ceramics.nist.gov/events/apd/apd.htm

alternatively contact
Jim Cline at: cline@credit.nist.gov

SIZE - STRAIN III

ANALYSIS OF MICROSTRUCTURE AND RESIDUAL STRESS BY DIFFRACTION METHODS

2-6 DECEMBER 2001, TRENTO (ITALY)



The 3rd Size-Strain conference “*Analysis of microstructure and residual stress by diffraction methods*” (SS-III) is intended as a continuation of the successful series initiated in 1995 (Liptoski Mikulas, Slovakia) and continued in 1998 (Freiberg, Germany). The organisation of the SS-III conference is divided in two committees (Local and Technical programme), and an International Advisory Board composed of representatives of other organisations as well as delegates of main sponsors.

Information is available through the SS-III web-site:

http://bragg.ing.unitn.it/sizestrain

Local Organising Committee	**Technical Programme Committee**	**Conference Chairs**	***IAB Representatives***
G. Carlà	*R. Cheary (AUS)*	*E. Mittemeijer, co-Chair*	*C. Hubbard (ICDD)*
G. Dettori	*J. Cline (USA)*	*P. Scardi, Chair*	*A. Kern (Bruker)*
Y.H. Dong	*R. Delhez (NL)*		*E. Mittemeijer (EPDIC)*
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S. Setti	*D. Louer (F)*		*P. Scardi (CPD)*
C. Tosi	*E. Mittemeijer (D)*		*R. Snyder (IXAS)*
	P. Scardi (I), Chair		
	B. Scholtes (D)		
	V. Valvoda (CZ)		

Main Topics of the conference

Besides the general interest in application of diffraction techniques to polycrystalline and amorphous materials, the main conference topics concern materials microstructure and properties, as they can be studied by diffraction methods. Among the main themes, in close relation with the previous *Size-Strain* conferences, the present conference will focus on methodologies for the study of lattice defects, residual stress and texture in thin films and surfaces, line profile fitting/modelling based on fundamental parameters for applications in materials science problems (including e.g., phase analysis with amorphous fraction, application of structure refinement methods, highly defective materials), simulation of materials microstructure and defects related to diffraction profiles.

Programme

The conference is organised around the topics of *13* invited talks, including the honour lecture by *Ian Langford*, plus *16* contributed talks and two main sessions dedicated to posters, which collect most of the work presented. The programme and the conference venue, where a large part of participants will be hosted, are organised in such a way to favourite a free exchange of information and discussion among attendees, who will have a unique opportunity of meeting most of the experts in the main areas of interest of the conference. Main topics of the conference and list of invited speakers will be reported on the *Preliminary Programme*, available soon on the web-site.

The conference will be held in **December 2-6, 2001** at the **Grand Hotel Trento (Trento (I))**. A block of rooms at a special fare has been reserved at the *Grand Hotel Trento* for conference attendees; details on additional, low cost accommodation will be made available soon. Reservation is guaranteed only within the terms indicated on the *Registration and Hotel Reservation* page. Conference services will be provided by ***Medicina Viva*** (Parma), especially concerning hotel reservation and fee payment. Advanced registration entitles participants to pay a reduced fee. Late registration (after term or at the conference desk) will be more expensive. Refer to *Deadlines* for more information.

Participation

Participants are invited to submit an extended abstract of their contribution no later than ***30.6.2001*** using the format described in the *Instruction for Authors* section of the web-site. All the extended abstracts will be collected in a volume available at the conference and on the *IXAS* web-site.

Submitted works will be presented as posters, to be discussed during two dedicated sessions. Selected contributions, on the basis of the TPC scrutiny, will be presented as contributed oral. Additional information will be included in the *Preliminary Programme.*

Early registration is an important requisite for consideration as possible contributed oral presentation; in any case abstract submitted after the term will only be considered for the poster presentation.

After the conference, manuscripts based on invited talks will be collected in a book; in addition, the most significant contributions presented at the conference will be considered for inclusion; selection criteria will be scientific quality and degree of innovation, especially considering new methodologies, and pertinence to the main themes of the conference (see *Preliminary Programme*). Final publishing is due in one year after the conference.

Consult the URL from time to time to see the *News*. A limited number of *Grants* for young scientists and colleagues from less-favourite countries will be available. To be eligible, candidates should provide a brief curriculum vitae and an extended abstract of their intended contribution. Support can be partial or total, depending on fund availability and unquestionable decision of the TPC.

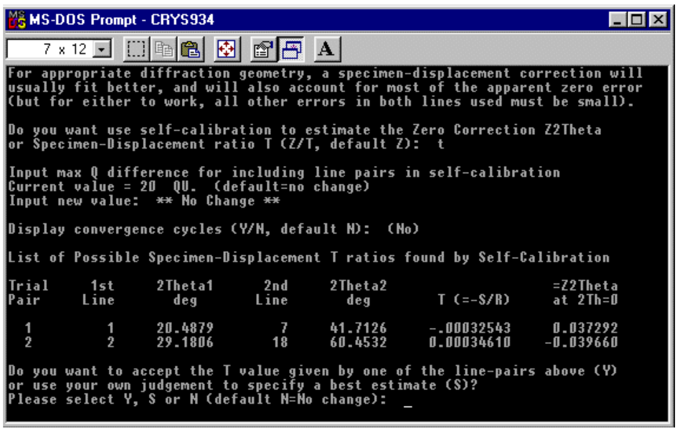
COMPUTER CORNER

Updates on Freely Available Crystallographic and Powder Diffraction Software [•]

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

Updated CRYSFIRE for DOS/Windows Powder Indexing Suite *by Robin Shirley*

As has been mentioned in previous articles, Crysfire is an indexing suite that links to 8 different indexing programs: ito, treor, dicvol, taup, kohl, lzon, fjzn and losh. A new feature in Crysfire is the ability to calibration peak positions using a "sample offset" correction (as well as keeping the two-theta offset of the previous version). Download information as well as tutorials on installing and running Crysfire are available at:
http://www.ccp14.ac.uk/tutorial/crys/ with Internet download areas existing in the UK, Canada and Australia.



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For appropriate diffraction geometry, a specimen-displacement correction will
usually fit better, and will also account for most of the apparent zero error
(but for either to work, all other errors in both lines used must be small).

Do you want use self-calibration to estimate the Zero Correction Z2Theta
or Specimen-Displacement ratio T (Z/T, default Z):  t

Input max Q difference for including line pairs in self-calibration
Current value = 20  QU.  (default=no change)
Input new value:  ** No Change **

Display convergence cycles (Y/N, default N):  (No)

List of Possible Specimen-Displacement T ratios found by Self-Calibration

Trial     1st     2Theta1      2nd     2Theta2                    =Z2Theta
Pair     Line       deg       Line       deg       T (=-S/R)     at 2Th=0

  1         1     20.4879        7     41.7126     -.00032543     0.037292
  2         2     29.1806       18     60.4532     0.00034610    -0.039660

Do you want to accept the T value given by one of the line-pairs above (Y)
or use your own judgement to specify a best estimate (S)?
Please select Y, S or N (default N=No change): _
```

Fig 1: Running through the Crysfire powder indexing suite sample offset procedure

Updated CHEKCELL for Windows powder indexing helper tool *by Jean Laugier and Bernard Bochu*

As discussed in the previous CPD-Newsletter, Chekcell is a graphical indexing helper tool that links into Robin Shirley's Crysfire suite to aid in identification of good cell/space group combinations. This can be done manually or automatically using a Best Solution mode based on "parsimony of extra reflections" for selecting interesting cells. Besides bug fixes and minor feature enhancements, a new addition to the Chekcell for Windows program is the addition of a Truecell function to search for higher volume – higher symmetry cells from the Crysfire summary list. This can be helpful where present indexing programs can favour small volume, low symmetry solutions. The user can run Truecell on trial cells and check for higher volume higher symmetry cells that could be the "true" solution. This has been found to be quite effective in finding "true" cells that were not found by any of the indexing programs in the Crysfire suite. Another new feature is the ability to sort the Crysfire summary ordered in terms of cells that give the best ratio observed to calculated peaks for that cell type. Information and tutorials on using Chekcell are available at:
http://www.ccp14.ac.uk/tutorial/lmgp/#chekcell
with internet download areas existing in the UK, Canada and Australia.

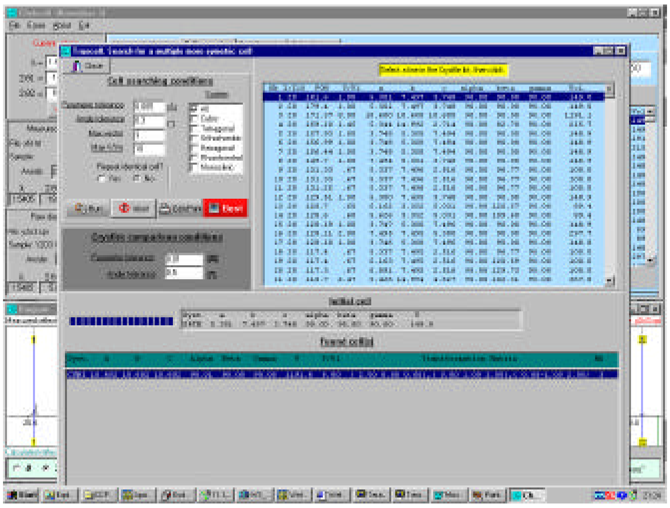
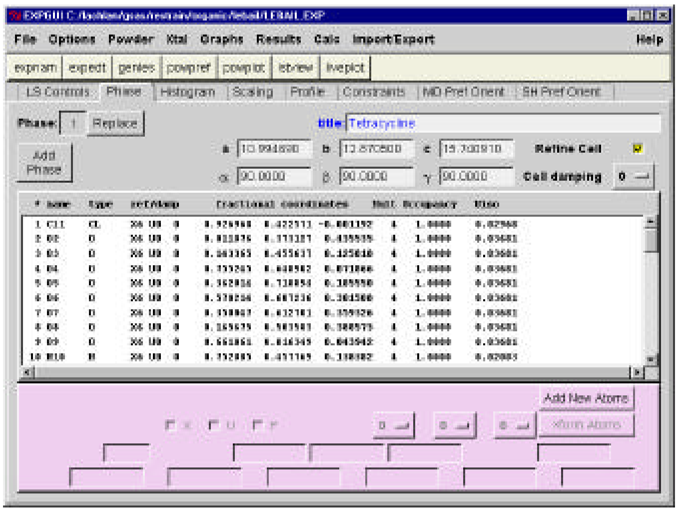


Fig 2: Chekcell powder indexing helper tool running through the Truecell procedure.

Updated EXPGUI for Windows and Linux Graphical User Interface to GSAS *by Brian Toby*

The latest version of EXPGUI can now import Powder Cell and CIF files, as well as being able to perform user-friendly manipulation of the atomic parameters and refinement flags. There is also a new graphical user interface into the Spherical Harmonics corrections. The latest version can be downloaded from:
http://www.ncnr.nist.gov/programs/crystallography/software/expgui/expgui_intro.html (CCP14 Mirror:
http://www.ccp14.ac.uk/ccp/web-mirrors/briantoby/programs/crystallography/software/expgui/expgui_intro.html)

[•] Suggestions, corrections, comments appreciated; especially if you know of program updates and announcements that should be mentioned here



Phase: 1

title: Tetracycline

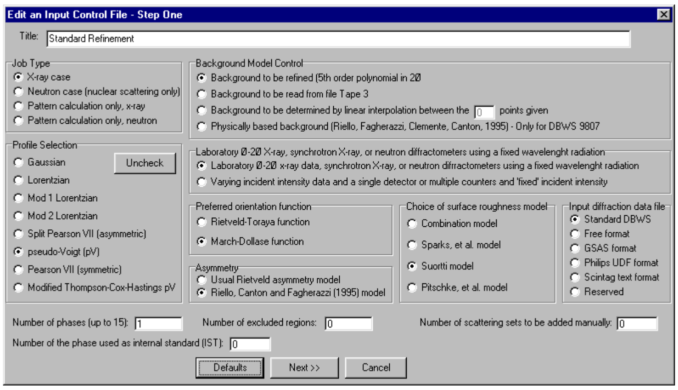
Fig 3: EXPGUI Graphical User Interface for the GSAS Rietveld program.

New DBWSTOOL – graphical user interface for windows over DBWS *by : Bleicher, Sasaki. and Santos*

A graphical user interface over DBWS is freely downloadable off the internet via
http://www.fisica.ufc.br/raiosx/DBWS.htm
and CCP14 mirror at :
(CCP14 Mirror: http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/dbwsgui/pub/) This allows access to many DBWS features via obvious point and click options as shown by the following screen image.

GUFI for DOS Shareware for Powder Diffraction Measurement and Evaluation *by Robert Dinnebier*

A shareware version of GUFI for DOS is available from http://www.uni-bayreuth.de/departments/crystal/gufi/ (CCP14 Mirror: http://www.ccp14.ac.uk/ccp/web-mirrors /robert-dinnebier/ Education/GUFI_5.0/gufi_5.0.html).
It allows the conversion of many different file formats, peak finding, smoothing, data evaluation as well as a range of other relevant functionality.



Title: Standard Refinement

Job Type
● X-ray case
○ Neutron case (nuclear scattering only)
○ Pattern calculation only, x-ray
○ Pattern calculation only, neutron

Background Model Control
● Background to be refined (5th order polynomial in 2Ø
○ Background to be read from file Tape 3
○ Background to be determined by linear interpolation between the 0 points given
○ Physically based background (Riello, Fagherazzi, Clemente, Canton, 1995) - Only for DBWS 9807

Profile Selection
○ Gaussian
○ Lorentzian
○ Mod 1 Lorentzian
○ Mod 2 Lorentzian
○ Split Pearson VII (asymmetric)
● pseudo-Voigt (pV)
○ Pearson VII (symmetric)
○ Modified Thompson-Cox-Hastings pV

Laboratory Ø-2Ø X-ray, synchrotron X-ray, or neutron diffractometers using a fixed wavelenght radiation
● Laboratory Ø-2Ø x-ray data, synchrotron X-ray, or neutron difrractometers using a fixed wavelenght radiation
○ Varying incident intensity data and a single detector or multiple counters and 'fixed' incident intensity

Preferred orientation function
○ Rietveld-Toraya function
● March-Dollase function

Asymmetry
○ Usual Rietveld asymmetry model
● Riello, Canton and Fagherazzi (1995) model

Choice of surface roughness model
○ Combination model
○ Sparks, et al. model
● Suortti model
○ Pitschke, et al. model

Input diffraction data file
● Standard DBWS
○ Free format
○ GSAS format
○ Philips UDF format
○ Scintag text format
○ Reserved

Number of phases (up to 15): 1
Number of excluded regions: 0
Number of scattering sets to be added manually: 0
Number of the phase used as internal standard (IST): 0

Fig 4: DBWSTool setting up a new DBWS Control file.

Updated GSAS Manual and Linux, Windows and Macintosh versions of GSAS.

A new year 2000 version of the GSAS manual by Allen Larson and Bob von Dreele is available for download off the internet at ftp://ftp.lanl.gov/public/gsas/ (and at CCP14 based mirrors in the UK:
http://www.ccp14.ac.uk/ccp/ccp14/ftp-mirror/gsas/public/gsas/manual/; Australia: ftp://ftp.minerals.csiro.au/pub/xtallography/ccp14/ccp/ccp14/ftp-mirror/gsas/public/gsas/manual/ and Canada: http://ccp14.sims.nrc.ca/ccp/ccp14/ftp-mirror/gsas/public/gsas/manual/).

This describes many of the latest features within the GSAS package. At the time of writing, a 16th October 2000 version of GSAS for DOS was available, as well as 17th August 2000 GSAS for Linux; and a shareware Macintosh version being prepared by Allen Larson is also available (refer: http://www.ccp14.ac.uk/solution/gsas/gsas_for_mac.html). A list of GSAS friendly resources and tutorials is also available on the CCP14 website at http://www.ccp14.ac.uk/solution/gsas/.

New RIETAN2000 Rietveld refinement program *by Fujio Izumi*

The new Rietcan has been released under the Gnu Public Licence for Windows/Mac and UNIX and is available for download from http://www.nirim.go.jp/~izumi/rietan/angle_dispersive/angle_dispersive.html (CCP14 Mirror: http://www.ccp14.ac.uk/ccp/web-mirrors/rietan/~izumi/rietan/angle_dispersive/angle_dispersive.html). Maximum entropy based Fourier maps can then be generated and visualised from the Rietan2000 output MEED, Fousyn and Mevius (http://www.bk.tsukuba.ac.jp/~kumazawa/Software/Software.html).

New GRETEP (Grenoble Thermal Ellipsoids Plot Program) for Windows *by Jean Laugier and Bernard Bochu*

A new structure viewing program by Jean Laugier and Bernard Bochu is available for download off the internet via: http://www.ccp14.ac.uk/tutorial/lmgp/#gretep.
GRETEP has a number of features not readily available in other programs. As well as being very friendly to perform "click and drag" rotate, translate and zoom structures, it also allows: point and click enabling/disabling of symmetry operators to examine effects of spacegroup symmetry; complex atom labelling which can then be saved in GRETEP format and retrieved at a later date; editing of the structure, cell, space group information via a GUI Menu; perform Mean Plane Determination; custom Addition and Deletion of Bonds via point and click; relocate the centre of rotation by clicking on a selected atom; handles organic, organometallic and inorganic/ionic structures; and Gretep can be passed a structure file via a command line so can be spawned by other software.

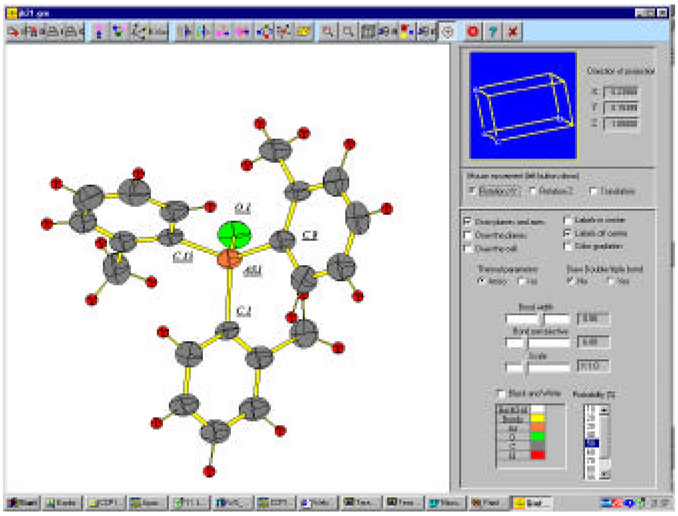
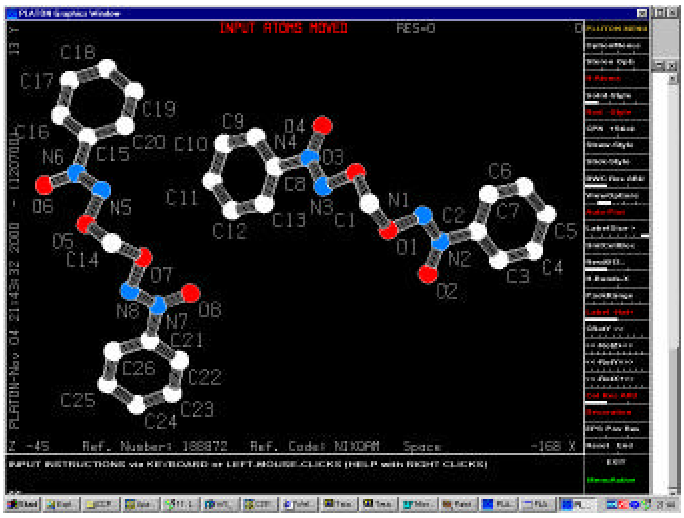


Fig 5: Gretep in action.

Platon and Addsym: Published example of finding missing symmetry using the Addsym function within Ton Spek's Platon.

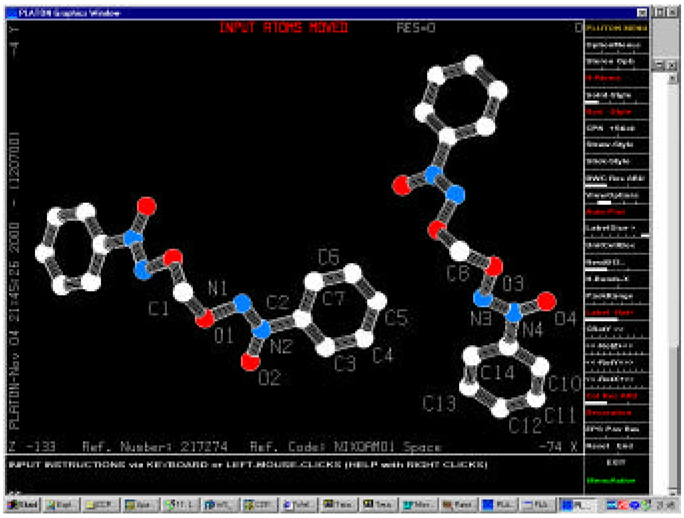
A recent journal article (Short Communication: "P1 or P-1? Corrigendum", Acta Cryst B56 (2000) pg 744, Richard E. Marsh) showed how Platon's Addsym can be extremely useful for finding missing symmetry and helping provide the correct space group. While Platon is becoming a standard tool for single crystal people, it is also just as relevant for assisting in accessing structures solved and refined using powder diffraction. The following series of screen images help tell the story.



Z -45 Ref. Number: 188872 Ref. Code: NIXDAM Space -168 X

INPUT INSTRUCTIONS via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

Fig 6a: Triclinic P1 structure as originally published (1997).



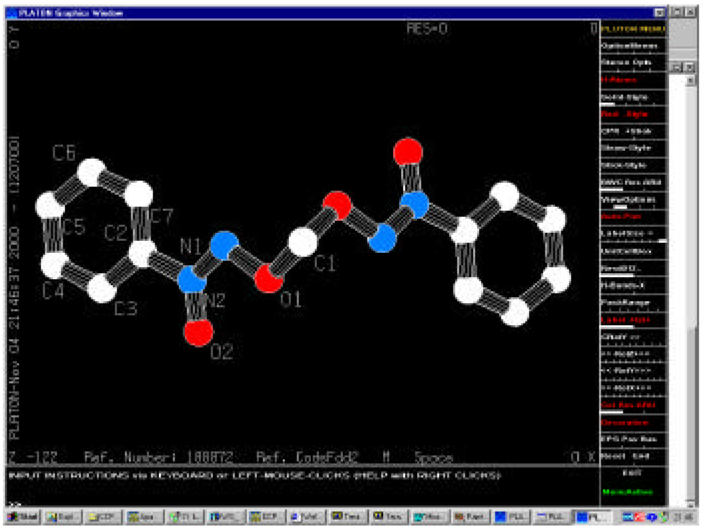
Z -133 Ref. Number: 217274 Ref. Code: NIXDAM01 Space -74 X

INPUT INSTRUCTIONS via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

Fig 6b: Monoclinic C2 structure as reinterpreted by Marsh (1999).

It is totally trivial to do run Addsym within Platon by opening a CIF, Shelx or Platon file. There is also the option to output a new Shelx coordinate file in the updated space group found by Addsym.

Platon, as mentioned previously, is also very useful forming other analysis including looking for non-bonding contacts, various crystallographic validation; and various options for finding the reduced cell (useful considering many powder indexing programs may not reliably be giving the "true" reduced cell – refer: 'Reduced Cells', M.J. Buerger, (Zeitschift fur Kristallographie, BD 109, S. 42-60 (1957) (summary on the CCP14: http://www.ccp14.ac.uk/solution/indexing/reduced_cell.html).



Z -122 Ref. Number: 188872 Ref. CodeFdd2 M Space 0 X

INPUT INSTRUCTIONS via KEYBOARD or LEFT-MOUSE-CLICKS (HELP with RIGHT CLICKS)

Fig 6c: Orthorhombic Fdd2 structure as revealed by running Platon's Addsym utility (2000).

Crystals for Windows Single Crystal Suite for structure refinement and user frienly DLS (Distance Least Squares) *by David Watkin, Richard Cooper and co workers*

The latest GUI version of Crystals for Windows can be very useful for aiding powder diffractionists. It is downloadable via http://www.xtl.ox.ac.uk/crystals.html (CCP14 Mirror: http://www.ccp14.ac.uk/ccp/web-mirrors/crystals/crystals.html). This includes performing quite user friendly DLS (Distance Least Squares) for optimisation of both organic and inorganic structures; generation of lists of bond length and angles for use in Rietveld refinement restraints; as well as assisting in structure refinement with such options as point and click placement of calculated hydrogens. Tutorials on performing some of the above functions, including user friendly DLS analysis is viewable via the web at:
http://www.ccp14.ac.uk/tutorial/crystals/.

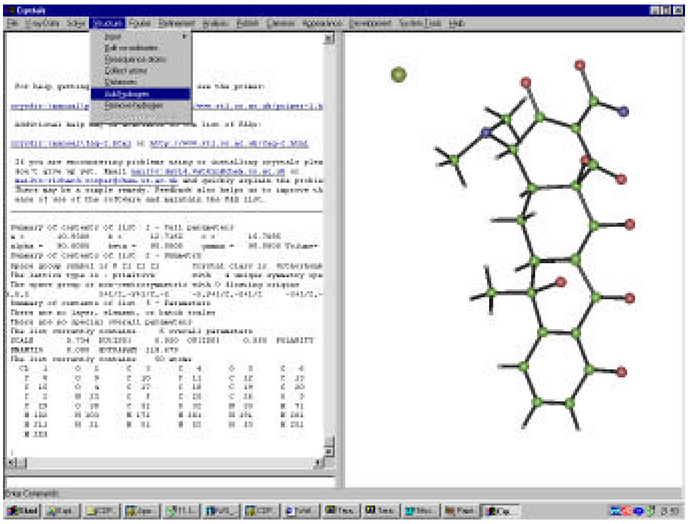


Fig 7: Crystals for Windows after adding calculated hydrogens to an organic structure.

Problems: Refining large organics solved from powder diffraction data.

During the recent Bayreuth Powder Diffraction Workshop, one of the main problems people seem to be encountering was in the ability to effectively perform restrained refinement on large organics solved from powder diffraction data. The present generation of Rietveld software seem more optimised for other areas making it difficult to perform what would be routine restrained refinement or organics with single crystal programs such as Shelx, CAOS, XTAL, Crystals, etc.

The implication is that Rietveld programs are presently lacking with respect of restrained refinement of organics compared to single crystal equivalents in the following areas:

- Lack of in-built routine Structure Visualization (though GSAS, Fullprof and LHPM-Rietica can get around this using Louis Farrugia's GUI WinORTEP - http://www.chem.gla.ac.uk/~louis/ortep3/)
- Lack of user-friendly graphical building up of the structure (Q peak finding - requiring appropriate algorithms for powder diffraction such as "maximum entropy")
- Lack of user-friendly structure refinement by interacting with the graphical structure on the screen
- Lack of easy to use powerful point and click restraints and rigid bodies.
- Lack of easy to use Fourier Map Generation and viewing (again requiring appropriate algorithms such as maximum entropy to clear up the electron density contour maps).
- Lack of automatic or "point and click" hydrogen placement and "riding hydrogen" refinement options.

Submissions, comments, rebuttals and objections to the above opinions are invited..

Rietveld Software Updates (as of late October 2000):

Hugo Rietveld website:
http://home.wxs.nl/~rietv025/
BGMN (11th September 2000)
http://www.bgmn.de/
Debvin (10th March 2000)
ftp://ftp.cc.uniud.it/DEBVIN/
GSAS (16th October 2000)
ftp://ftp.lanl.gov/public/gsas/
LHPM-Rietica (Xth October 2000)
ftp://ftp.ansto.gov.au/pub/physics/neutron/rietveld/Rietica_LHPM95/
MAUD for Java (9th October 2000)
http://www.ing.unitn.it/~luttero/maud/
Prodd (9th June 2000)
http://www.cus.cam.ac.uk/~jpw22/
Winplotr/Fullprof (29th June 2000)
http://www-llb.cea.fr/winplotr/winplotr.htm
ftp://bali.saclay.cea.fr/pub/divers/winplotr/
Winmprof (28th January 2000)
http://pecdc.univ-lemans.fr/WinMProf/WinMProf.htm
XND (29th May 2000)
http://www-cristallo.polycnrs-gre.fr/xnd/xnd.html
ftp://old-labs.polycnrs-gre.fr/pub/xnd/

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

New GPL'd ESPOIR 3.5 for Windows *by Armel Le Bail* with tutorial on setting up within 10 minutes to solve on an organic structure from powder diffraction data.

A new version of ESPOIR structure solution from powder diffraction software is available under the Gnu Public Licence and can be downloaded off the internet http://sdpd.univ-lemans.fr/sdpd/espoir/ (http://www.ccp14.ac.uk/ccp/web-mirrors/armel/sdpd/espoir/). The latest ESPOIR has a GUI of sorts as well as the ability to perform automatic analysis of the molecule connectivity to enable varying of torsion angles and performing pseudo-simulated annealing. A modified version of Rasmol is included for viewing animations of trial structures in XYZ format.

Armel has also created a web tutorial showing how it is possible to set up ESPOIR within 10 minutes for solving on organics using molecule location involving variable torsion angles:
http://sdpd.univ-lemans.fr/sdpd/espoir/10mn/
(CCP14 mirror: http://www.ccp14.ac.uk /ccp/web-mirrors/armel/sdpd/espoir/10mn/).

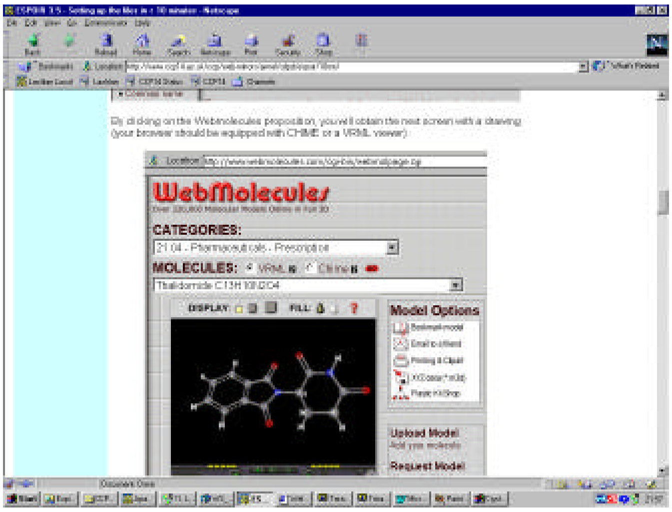

By clicking on the Webmolecules proposition, you will obtain the next screen with a drawing (your browser should be equipped with CHIME or a VRML viewer)

Fig 8: Part of the web tutorial explaining how to setup ESPOIR within 10 minutes to start solving on an organic with flexible torsion angles.

Some summary lists of Available Software at the CCP14 website:

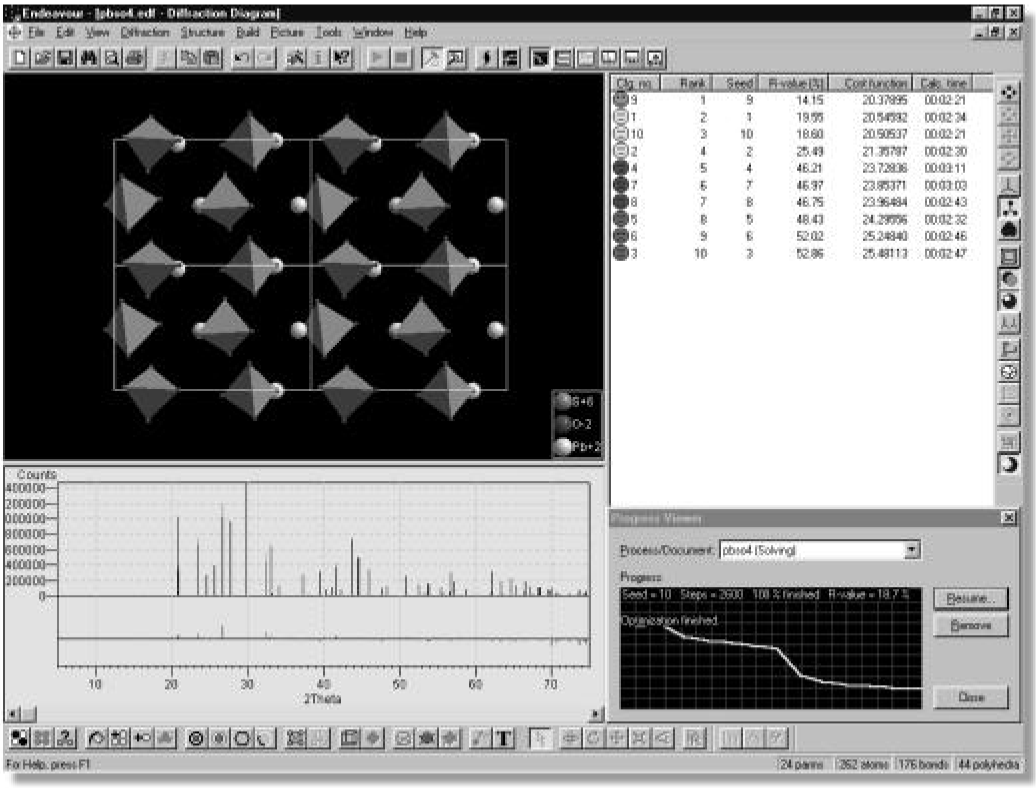
Anharmonic Thermal Refinement Software
    http://www.ccp14.ac.uk/solution/anharmonic/
Data Conversion for Powder Diffraction
    http://www.ccp14.ac.uk/solution/powderdataconv/
Image Plate Software
    http://www.ccp14.ac.uk/solution/image-plate/
Incommensurate Structure Software
    http://www.ccp14.ac.uk/solution/incomm.htm
Indexing Software for Powders
    http://www.ccp14.ac.uk/solution/indexing/
LeBail Method for Intensity Extraction
    http://www.ccp14.ac.uk/solution/lebail/
Pawley Method
    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 Analysis Software
    http://www.ccp14.ac.uk/solution/pole_figure/
Powder Diffraction Data Visualisation
    http://www.ccp14.ac.uk/solution/powder_data_visual/
Search-Match Phase Identification Software
    http://www.ccp14.ac.uk/solution/search-match.htm
Single Crystal Structure Solution Software relevant to Chemical Crystallography
    http://www.ccp14.ac.uk/solution/xtalsolution/
Single Crystal Structure Refinement Software relevant to Chemical Crystallography
    http://www.ccp14.ac.uk/solution/xtalrefine/
Single Crystal Suites linking to multiple programs relevant to Chemical Crystallography
    http://www.ccp14.ac.uk/solution/xtalsuites/pacegroup
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/

ENDEAVOUR

Structure Solution from Powder Diffraction

ENDEAVOUR is a powerful tool for the generation of structure models from powder diffraction data. Thus it closes the remaining gap in the process of structure solution from powder diffraction and leads to new dimensions in its routinely application on inorganic solid structures.

The structure solution is performed using a combined global optimization of the difference between calculated and observed powder diffraction data and the potential energy of the system. The method is described in J.Appl.Cryst. (1999), 32, 864-870



Cfg. no	Rank	Seed	R-value [%]	Cost function	Calc. time
9	1	9	14.15	20.37895	00:02:21
1	2	1	19.55	20.54592	00:02:34
10	3	10	18.60	20.50537	00:02:21
2	4	2	25.49	21.35787	00:02:30
4	5	4	46.21	23.72836	00:03:11
7	6	7	46.97	23.85371	00:03:03
8	7	8	46.75	23.96484	00:02:43
5	8	5	48.43	24.29556	00:02:32
6	9	6	52.02	25.24840	00:02:46
3	10	3	52.86	25.48113	00:02:47

Seed = 10 Steps = 2600 100 % finished R-value = 18.7 %

Optimization finished.

Download your free evaluation copy from:
http://www.crystalimpact.com/endeavour

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CRYSTAL IMPACT

MEETING AND SCHOOL REPORTS

Tenerife Powder Diffraction School

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e-mail: csilgo@ull.es

The ECA-sponsored 6th School "New trends in Material science: Computational Methods in Powder Diffraction" took place in July 2000. The school was supervised by C. Ruiz-Pérez, and the lecturers included C. Giacovazzo (Bari, Italy), D. Louër (Rennes, France), E. Matesanz (PHILIPS, Spain), J. Rodríguez-Carvajal (Saclay, Paris, France), and X. Solans (Barcelona, Spain). The school was made possible by the financial support of the University of La Laguna, and the Cabildo Insular de Tenerife, PHILIPS instrumental, as well as by the enthusiasm of the La Laguna LOC and 30 participants from 7 countries. Some of the participants presented short contributions.

Theoretical sessions included talks on conventional X-ray, neutron and synchrotron instrumentation, modelling and origins of diffraction line-profile shapes, powder pattern indexing, including modern methods, effect of errors and checking the validity with particular examples; contemporary methods of crystal structure determination from powders (Monte Carlo, simulated annealing and genetic algorithms methods); new implemented option for Rietveld refinement and microstructural effects in powder diffraction. Lecture notes were distributed and students were encouraged to participate actively during the hardworking practical sessions. A half-day excursion visited Instituto de Astrofísica de Canarias (IAC), Cañadas del Teide National Park and La Orotava village. The participants enjoyed La Laguna nights (La Bomba, summer song), canary typical food and Juan Rodriguez-Carvajal birthday cake.

The 7th School will be held in July, 2001, on the topic of molecular crystals, in La Laguna. For information contact Catalina Ruiz-Pérez (caruiz@ull.es).

NEWS FROM IXAS

International X-ray Analysis Society (IXAS)

The organizing committee for IXAS completed its work at the Spring 2000 EPDIC meeting in Barcelona and elected its first five officers. Bob Snyder will serve as the first president with Greg McCarthy as Treasurer, Peter Wobrauschek, Secretary, Hideo Toraya and Rene Van Grieken as the first two councilors. In August the next five officers were elected. The Vice President (President Elect for 2000) is George Havrilla, and the four additional Councilors are Eugene Antipov, Barbara Holynska, Brian O'Connor, and Paolo Scardi. The remaining five officers will be elected in the spring of 2001 with the first full membership e-election.

IXAS services are supported by contributions from equipment manufacturers so that the world community can access them at no cost is now in place. Programs and abstracts for all international X-ray analysis conferences will be on this site with all abstracts now indexed by Chemical Abstracts. In addition there are plans for a journal and the preparation of the full proceedings papers of the various conferences to be on the site with free access to all. All of this will be on a new server hosted by Ohio State University:

www.ixas.org.

The CPD Newsletter can be downloaded from the official web page:

http://www.iucr.org

Or

http://bragg.ing.unitn.it/cpd/Newsletters/index.html

See page 40 for "*How to receive the CPD Newsletter*", if you wish to be included in the mailing list.

WHAT'S ON

Conferences

22-25 April 2001
Gaithersburg, MD, U.S.A.

Accuracy in Powder Diffraction III

This is the third APD meeting after two very successful previous conferences, held in 1979 and 1992. It is intended to cover all important aspects of X-ray powder diffraction techniques, in order to present the state of the art in this field.

For further information contact:
James P. Cline
Ceramics Division
National Institute of Standards and Technology
100 Bureau Dr. stop 8523
Gaithersburg, MD 20899-8523 USA
Tel: 001 (301) 975 5793
Fax: 001(301) 975 5334
E-mail: Cline@credit.nist.gov
Web-site: bragg.ing.unitn.it/apd3; www.nist.gov

12-14 November 2001
Calcutta and Bangalore, India

Second ISPD--2001 and AsCA 2001

Second International School on Powder Diffraction (ISPD--2001)will be held in Calcutta, India from 12-14 November, 2001. Lecture sessions include contemporary topics in powder diffraction by X-ray, electron, neutron and synchrotron radiation, given by experts with hands-on computer sessions for young and active researchers in institutes, universities, and companies. This will be a satellite meeting of AsCA (Asian Crystallography Association) to be held for the first time in India in Bangalore from 18-21 November 2001. Participants may attend both meetings. Details will be announced shortly. The meetings are sponsored by IUCr, ICDD and other organisations.

For further information contact:

For ISPD 2001: Prof S P Sen Gupta, E-mail: msspsg@mahendra.iacs.res.in, Fax: 91-033-473 2805

For AsCA 2001: Prof M Vijayan , IISc, Bangalore, E-mail: mv@mbu.iisc.ernet.in, Fax: 91-080-3600683,3600535.

2 – 6 December 2001
Trento, Italy

Size-Strain III - Analysis of Microstructure and Residual Stress by Diffraction methods

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

For further information contact:

P. Scardi and M. Leoni,
Dipartimento di Ingegneria dei Materiali,
Università di Trento
38050 Mesiano (TN), Italy
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Fax: +39 0461 881977
E-mail: Paolo.Scardi@ing.unitn.it
Matteo.Leoni@ing.unitn.it
Web-site: bragg.ing.unitn.it/sizestrain

11-15 February, 2002

AXAA 2002

The AXAA 2002 Conference Organising Committee is pleased to announce the two day school and three day conference to be held from 11-15 February, 2002 in Newcastle, NSW, Australia.

Conference Objectives:

The schools program aims to provide training for early career professionals. The conference provides a unique opportunity for professionals with an interest in x-ray and surface analysis to come together over five days. The conference aims to:

- Recognise progress and highlight future directions for X-ray and surface analysis
- Develop knowledge and expertise in X-ray analysis practice and management
- Motivate participants to contribute to effective x-ray fluorescence, diffraction and surface analysis programs

Who Should Attend:

Academics, industrial lab professional staff, engineers, researchers, educators and leading professionals in other fields of X-ray and surface analysis technology

- There will be oral and poster presentations relating to: X-ray Fluorescence (XRF)
- X-ray Diffraction (XRD)
- Surface Analysis

For further information, please contact
Jane Yeaman
Tulips Your Conference Organiser
PO Box 116, Salamander Bay, NSW, 2317 Australia
Tel 02 4984 2554
Fax 02 4984 2755
E-mail: axaa@pco.com.au
Conference Website: www.pco.com.au/axaa2002

Workshops

ICDD clinics:

January 2001
Charles University, Praha, Czech Republic
X-ray Powder Diffraction Workshop
Topics include acquisition of good X-ray powder diffraction data and phase identification, set up and calibration of the diffractometer, specimen preparation, and semi-quantitative phase analysis.

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

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

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

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

For further information on the ICDD clinics contact:

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

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

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

ICDD Executive Director Position

The International Centre for Diffraction Data (see www.icdd.com), a scientific database corporation near Philadelphia, Pennsylvania, U.S.A., is seeking an Executive Director. The not-for-profit corporation operates from a modern headquarters facility and serves a world-wide scientific community. Required qualifications include proven managerial and business experience, a degree (minimum BS) in physical or materials sciences or engineering, and experience in X-ray diffraction, modern databases, and business and scientific use of the internet. Duties are interesting and diversified and include supervision of 40 employees, cooperation with about 300 international scientific volunteers, and teaching at workshops and conferences worldwide. The deadline for applications is 26 February 2001.

Send resumes and names of at least three references to:

Dr. Charles Prewitt, Search Committee Chair
c/o Ms. Theresa Maguire, Corporate Secretary
International Centre for Diffraction Data
12 Campus Boulevard
Newtown Square, PA 19073-3273, USA

WWW SITES OF GENERAL INTEREST TO POWDER DIFFRACTIONISTS

The Commission on Powder Diffraction (CPD): http://www.iucr.org/iucr-top/comm/cpd/
The International Union of Crystallography (IUCr): http://www.iucr.org
The International Centre for Diffraction Data (ICDD): http://www.icdd.com
The International X-ray Analysis Society (IXAS): http://www.ixas.org
CCP14: http://www.ccp14.ac.uk/index.html
General crystallography: http://www.unige.ch/crystal/w3vlc/crystal.index.html

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

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

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

Companies

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

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

Call for contributions to the next CPD Newsletter (No 25)

The next issue of the CPD Newsletter will be edited by *Bill David*, to appear in spring of 2001. Bill 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 25 (addresses are given below)

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