

**A1 - Structure Solution from Powder Diffraction - Methods****A1 - O1****REPLICATE, DIVIDE, MUTATE, SURVIVE: EVOLVING CRYSTAL STRUCTURES FROM PXRD****M. Tremayne<sup>1</sup>, S. Y. Chong<sup>1</sup>, C. C. Seaton<sup>2</sup>**<sup>1</sup>*School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK*<sup>2</sup>*School of Pharmacy, University of Bradford, Bradford, BD7 1DP, UK*

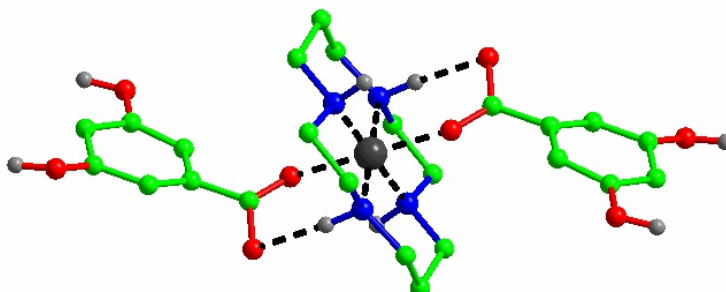
The crystal structure determination of molecular materials from powder diffraction data has been driven in recent years by the development of direct space methods of structure solution [1]. These approach structure solution by generation of trial crystal structures, often based on the known connectivity of the material, and assessment of the fitness of each structure by comparison with the experimental data. Global optimization methods are then used to locate the global minimum corresponding to the structure solution.

In this paper we present the implementation of a global optimization technique based on the differential evolution algorithm (DE) [2]. DE is an evolutionary process that maintains a population of structures (or members) that are mutated and recombined together over a number of generations until the population converges on the global minimum. The combination of mutation and recombination in a single step to create a child (eqn. 1), and the deterministic method of selection by comparison of a child with its parent, means that DE is both relatively simple and easy to implement, while offering robust searching of minima. It can be controlled using only three optimization parameters (ie.  $K$  and  $F$  – the levels of recombination and mutation respectively, and the population size  $N_p$ ) and has been used in the solution of structures of intermediate complexity without the need for multiple runs, and in some cases required the generation of less than a thousand trial structures.

$$\text{Child} = \text{Parent} + K(\text{Random}_1 - \text{Parent}) + F(\text{Random}_2 - \text{Random}_3) \quad (1)$$

Application of the DE method will be illustrated by the structure solution of a range of organic materials including new polymorphic forms [3], families of compounds in which the primary interest centres on intermolecular aggregation [4] and supramolecular materials (Figure 1). All examples have been solved from powder diffraction data collected on a conventional laboratory diffractometer, often significantly affected by preferred orientation. The limitations of direct-space methods when faced with such detrimental sample characteristics will also be discussed.

- [1] K. D. M.Harris, M. Tremayne & B.M.Kariuki (2001). *Angew. Chem., Int. Ed.*, 40, 1026.
- [2] K. V. Price (1999). *New Ideas in Optimization*, D.Corne, M. Dorigo, F.Glover (Eds), McGraw-Hill, London UK, 77.
- [3] C. C. Seaton & M. Tremayne (2002). *Chem. Commun.*, 880.
- [4] M.Tremayne, C.C.Seaton & C.Glidewell (2002). *Acta Cryst.* B58, 823.



**Figure 1:** The crystal structure of Ni(cyclam)dihydroxybenzoate solved from PXRD by the DE method.



A1 - O2

## A BAYESIAN APPROACH TO PHASE EXTENSION

D. S. Sivia, W. I. F. David and S. Hull

*Rutherford Appleton Laboratory*

The lack of phase information in diffraction data has always made the solution of crystal structures a challenging problem. While the difficulty can often be reduced by having several sets of measurements related by known changes, as in isomorphous replacement or anomalous dispersion, most experiments consist of a single data-set. The successful solution of a crystal structure then hinges on the use of additional information, in one way or another: this can range from a good initial estimate of the answer, or a general knowledge of the atomic connectivity, to just the physical positivity of the electron density distribution. In this talk, we consider the case when part of the structure is known, such as the location of the heavier atoms or a ring-fragment, and wish to use this knowledge to help

solve the remainder; in particular, we focus on the situation when the diffraction data are from a powdered sample.

We will begin with an elementary outline of the phase problem and a brief review of the conventional heavy-atom method. A Bayesian view of the situation will then be presented, with an emphasis on the case of powder diffraction data, and the theory illustrated with several examples.

Sivia, DS, and David, WIF, *J Phys Chem Solids* **62** (2001) 2119-2127.

Hull, S, Keen, DA, Sivia, DS, Berastegui, P, *J Solid State Chem* **165** (2002) 363-371.

A1 - O3

## COMBINED X-RAY POWDER DIFFRACTION AND DFT CALCULATION TO ELUCIDATE MOLECULAR AND CRYSTAL STRUCTURE OF FLUOROSTYRENES

M. Brunelli<sup>1</sup>, M.R. Johnson<sup>2</sup> and A.N. Fitch<sup>1,3</sup>

<sup>1</sup>*European Synchrotron Radiation Facility, B.P. 220, F38043 Grenoble Cedex, France*

<sup>2</sup>*Institute Laue Langevin, B.P. 156, F38042 Grenoble Cedex 9 France*

<sup>3</sup>*Department of Chemistry, Keele University, Staffordshire, ST5 5BG, UK*

An example will be presented in which combination of structural and numerical studies was applied to the investigation of the planarity of some fluorine derivative of styrenes, fluorostyrenes. The interest in this detail of the molecular geometry of fluorostyrenes came from some recent publications, [1, 2] in which a very complete study of both the 3 and the 4 conformers were carried out using IR, Raman, INS (Inelastic Neutron Scattering Spectroscopy) data combined with theoretical calculations. DFT (Density Functional Theory) calculations on the free molecule yield to the conclusion that these molecules are planar, while MO (Molecular Orbital) calculation might give torsions angle different from 0 or 180, which is a non-planar structure. In particular, in the INS data collected at 20 K, which is in the solid phase, some discrepancy could be observed between the observed and the calculated spectra at high wavenumbers. Therefore, more accurate DFT calculations required to be performed in a periodic system and hence information about their condensed state was needed.

We've performed a systematic study of the solid state structure of 2-, 3-, 4- fluorostyrene using X-ray powder diffraction in combination with numerical calculation. The

measurements were performed at the high resolution powder diffraction beamline, ID31, at the ESRF, Grenoble (France). After solification of the samples (at around 220 K, 212 K and 245 K, respectively), no more phase changes were observed in the temperature range 295 - 12 K. The three fluorostyrenes were found to have orthorhombic crystal structure at low temperature.

Here we report the final optimized values for the torsion angle from the DFT-VASP calculations, of 3- and 4-fluorostyrene. The results suggest that the three fluorostyrenes in the solid state have torsion angle different from zero.

[1] J. M. Granadino-Roldan, M. Fernandez-Gomez, A. Navarro, L.M. Camus and U.A. Jayasooriya. *Phys. Chem. Chem. Phys.* **4** (2002) 4890-4901.

[2] J. M. Granadino-Roldan, M. Fernandez-Gomez, A. Navarro and U. A. Jayasooriya. *Phys. Chem. Chem. Phys.* **5** (2003) 1760-1768.

## A1 - O4

**USING THE PARALLEL-TEMPERING ALGORITHM TO OVERCOME COMPLEX PROBLEMS IN STRUCTURE DETERMINATION OF INORGANIC MATERIALS WITH LABORATORY X-RAYS****T. Bataille<sup>1</sup>, N. Mahé<sup>1</sup>, E. Le Fur<sup>2</sup>, J.-Y. Pivan<sup>2</sup>, D. Louër<sup>1</sup>***Laboratoire de Chimie du Solide et Inorganique Moléculaire (UMR 6511 CNRS), Institut de Chimie*<sup>1</sup>*Université de Rennes, Avenue du Général Leclerc, 35042 Rennes, France*<sup>2</sup>*Ecole Nationale Supérieure de Chimie, Campus de Beaulieu, Rennes, France*

*Ab initio* structure solution of inorganic compounds from powder X-ray diffraction data still does not succeed in many cases. The major problem arises from the loss of information in terms of accurate integrated intensities, due to the projection of the three-dimensional reciprocal lattice onto the one-dimensional diffraction pattern. This feature is even enlarged with the use of conventional X-ray sources and with diffraction line broadening observed, for example, for nanocrystalline compounds obtained from solid state transformations. While the recent use of direct-space methods in organic chemistry is often successful, their application in inorganic chemistry remains difficult, due to the great number of degrees of freedom generated when starting from single atoms instead of large molecules. In the present study, we discuss the advantages of using a global optimisation procedure rather than the direct-methods and difference-Fourier syntheses for solving crystal structures of two inorganic powder compounds. In both cases, high quality powder data were collected with a Siemens D500 diffractometer using the Bragg-Brentano geometry and monochromatic  $\text{CuK}_{\alpha 1}$  radiation.

$\text{Na}_2[\text{VO}(\text{PO}_4)]_2(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$  was hydrothermally prepared in powder form in the course of the investigation of open-framework mixed vanado-phosphato-oxalate materials. Pattern indexing with DICVOL04 [1] led to a monoclinic solution with the unit cell dimensions  $a = 6.349(1) \text{ \AA}$ ,  $b = 17.144(3) \text{ \AA}$ ,  $c = 6.557(1) \text{ \AA}$ ,

$\beta = 106.59(2)^\circ$ ,  $V = 684.0 \text{ \AA}^3$  [refined zero-shift  $0.011^\circ$  (2 $\theta$ ),  $M_{20} = 48$ ,  $F_{32} = 79(0.007,56)$ ]. The conditions for non-extinction were consistent with space group  $P2_1/m$ . The direct methods revealed only the heaviest electron density peaks, but no O atoms were found in order to differentiate V and P atoms. The absence of preferred orientation effect allowed starting the structure solution using the parallel tempering algorithm available in FOX [2]. The initial model consisted in one  $\text{VO}_6$  octahedron, one  $\text{PO}_4$  tetrahedron, one rigid  $\text{C}_2\text{O}_4$  group, two Na atoms and two water O atoms. A reasonable model was found after 4.4 million trials (110 minutes with a PC equipped with a AMD Athlon 1.7GHz processor), except that one sodium atom needed to be replaced by the water molecule. The final Rietveld re-

finement converged to the satisfactory  $R$  factors  $R_{\text{wp}} = 0.067$ ,  $R_{\text{F}} = 0.071$ .

$\text{YK}(\text{C}_4\text{O}_4)_2$  was prepared from thermal treatment at  $240^\circ\text{C}$  of the inorganic precursor  $[\text{Y}(\text{H}_2\text{O})_6]\text{K}(\text{C}_4\text{O}_4)_2$  ( $\text{H}_2\text{C}_4\text{O}_4$ ). As for a majority of decomposition products, its powder pattern exhibits significant diffraction line broadening, i.e. five times larger than the instrumental resolution function of the diffractometer. The first 20 lines were indexed with DICVOL04 on the basis of a tetragonal symmetry, with unit cell dimensions  $a = 6.2011(5) \text{ \AA}$ ,  $c = 11.639(1) \text{ \AA}$ ,  $V = 447.6 \text{ \AA}^3$  [refined zero-shift  $0.007^\circ$  (2 $\theta$ ),  $M_{20} = 57$ ,  $F_{20} = 71(0.006,44)$ ]. The small number of Bragg peak positions available in the whole pattern, aggravated with the broadening of diffraction lines, was not sufficient for a thorough examination of the conditions for non-extinction. Thus, eleven space groups were retained in this symmetry. Structure determinations with the direct methods were attempted for each selected space group, leading to non reliable models. Consequently, a structure solution was carried out in the triclinic space group  $P1$  by means of the program FOX, starting from two Y and two K atoms and four squarate groups. The solution was found after 6.3 million trials (10 hours). From the atomic positions displayed by the program, symmetry-equivalent positions were deduced, which allowed to find out the correct space group  $P4/mcc$ . The final Rietveld refinement led to the  $R$  factors  $R_{\text{wp}} = 0.098$ ,  $R_{\text{F}} = 0.035$ .

It is shown from these two examples that global optimisation procedures may succeed when the direct methods fail. Finally, considering the crystal structure of the thermal decomposition product  $-\text{Zn}_2\text{P}_2\text{O}_7$  as starting model (determined *ab initio* from powder diffraction data [3]), we also discuss the influence of a few profile parameters affecting the quality of powder data on structure solution using the direct methods and a global optimisation algorithm.

1. A. Boulouf, D. Louër (2004), submitted for publication.
2. V. Favre-Nicolin, R. Cerny, *J. Appl. Crystallogr.* **35** (2002) 734-743.
3. T. Bataille, P. Bénard-Rocherullé, D. Louër, *J. Solid State Chem.* **140** (1998) 62-70.



A1 - O5

## POWDER OPTION IN JANA2000: REFINEMENT OF STANDARD AND MODULATED STRUCTURES FROM X-RAY AND NEUTRON POWDER DATA

M. Dušek, V. Petříček

*Institute of Physics, Academy of Sciences, Na Slovance 2, 182 21 Praha 8, Czech Republic*

Program Jana2000 is based on the generalized crystallography following from the superpace approach [1]. This provides a uniform access to both standard and modulated structures. Currently it can be applied to single crystal or powder data measured with X-rays or neutrons. The powder option was introduced in the year 2000 [2] in response to growing interest among users to refine modulated structures from powder data. After four years of development the program bears comparison with established powder systems.

The profile refinement includes refinement of cell parameters and  $q$  vectors, Gaussian, Lorentzian or Pseudo-Voigt profiles, correction for anisotropic particle and strain broadening, correction for asymmetry, preferred orientation, absorption and several kinds of background description. It should be noted that no indexing tool is available. As soon as the profile fitting is finished all tools hitherto available for single crystals are activated. Jana2000 works with structures up to 6 dimensions (three  $q$  vectors) and can refine all basic structure parameters, anharmonic ADP and coefficients of anomalous dispersion. It enables modulation of occupancy, position and ADP (including anharmonic ones). For standard structures multipole refinement is available, too. The symmetry restrictions of refined parameters are calculated automatically. Powerful constraints and restraints and a flexible rigid body access can be used to build very complicated structure models. The program can also calculate, visualize and

evaluate more dimensional Fourier maps, plot various parameters as a function of the internal coordinate  $t$ , calculate distances and angles, call external programs for direct methods or plotting crystal structures and many other things.

Jana2000 is free software available in [www-xray.fzu.cz/jana](http://www-xray.fzu.cz/jana) including the source code and user manual with solved examples. In the poster we present a program scheme and two examples. The first one concerns refinement of a complicated misfit layer structure of  $[\text{Ca}_2\text{CoO}_3][\text{CoO}_2]_{1.62}$  [3]. The another one shows result of rigid body refinement of  $\text{P}(\text{OC}_6\text{H}_5)_3$  [4].

### Acknowledgement

*This work was supported by the Grant Agency of the Czech Republic (GA 202/03/0430).*

- [1] Wolff de P.M., Janssen T & Janner A.(1981). *Acta Cryst.* **A37**, 625-636.
- [2] Dušek,M., Petříček,V., Wunschel,M., Dinnebier,R.,E. & Van Smaalen,S. (2001). *J.Appl.Cryst.* **34**, 398-404.
- [3] Grebille,D., Lambert,S., Bouree,F. & Petricek, V.(2004). *J.Appl.Cryst.* accepted.
- [4] Hernandez,O., Hedoux,A., Lefebvre,J., Guinet, Descamps,M., Papoular,R. & Masson,O. *J. Appl. Cryst.* (2002). **35**, 212–219.