morphous replacement (MIR) phases were determined by matching histograms of electron density. Accurate metal cluster geometries and the associated errors in atomic positions can be determined from refinement against anomalous differences using normal scattering phases from a refined structure. When applied to MAD data collected on SiRHP, these methods confirmed the 4Fe-4S cluster asymmetry initially observed in the refined 1.6 Å resolution structure and resulted in a MAD-phased, experimental, electron-density map that is of better quality than the combined MAD/MIR map originally used to solve the structure.

PS02.04.14 SIMPROT: A PROGRAM IN DEVELOPMENT FOR CRYSTAL STRUCTURE DETERMINATION OF PROTEINS.

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An overview will be presented of the Direct Methods program SIMPROT that is designed to deliver ab initio an initial model of a protein structure if isomorphous data sets are available, e.g. from SAS, MAD or SIR experiments. Basically, SIMPROT follows the same methodology as employed in the Direct Methods software package SIMPEL [1]. However, is has been suitably modified in accordance with the difference structure factor formalism that has been developed recently [2], [3], [4].

The latter formalism is based on using the difference between two isomorphous structure factors as variable in the derivation of the Joint Probability Distributions upon which Direct Methods are based. It has been shown that this approach leads to accurate phasesum invariant estimates. A graphical overview of SIMPROT is given and some preliminary results will be discussed.

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[3] C.E. Kyriakidis, R. Peschar and H. Schenk. (1993). Acta Cryst.A49, 557-569.
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Structure Determination Using Powder Data

MS02.05.01 SUPRAMOLECULAR STRUCTURES FROM HIGH RESOLUTION POWDER DIFFRACTION.

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Over the past few years, the feasibility of determining crystal structures ab initio from powder diffraction data has been steadily improved. Although a number of complicated inorganic crystal structures have been solved by this method, very little has been done in the field of supramolecular structure determination, namely for organic- and organometallic compounds. Assuming the material itself is well crystallized, the use of Synchrotron radiation is necessary to get a resolution as high as possible over the entire angular range of the powder pattern. Besides the higher resolution, advances in the computational aspects of the problem are also crucial for structure determination. Especially the development of more sophisticated grid search techniques of molecular fragments, considering geometrical and physical aspects of the crystal, is an important step forward in finding the right solution. The structure solutions presented here stand for some of the most complicated organic and organometallic structures which have ever been solved ab inito from high resolution powder data. They include the high and the low temperature phase of the Ru-sawhorse dimer $[Ru_2(O_2PMe_2)_2CO)_4]n$ (1), the industrial important (Kolbe-Schmitt-synthesis) phenolates C_6H_5OA (A= K, Rb, Cs) (2), $C_6H_5OK\ 2(C_6H_5OH)$ (2), $C_6H_5OK\ 3(C_6H_5OH)$ (2), Na-Para-Hydroxy-Benzoate $NaC_7H_5O_3$ (2), base free alkaline-cyclo-pentadienide C_5H_5A (A=Li,Na,K,Rb) and the triclinic low temperature form of $C_{60}Br_{24}(Br_2)_2$ (3). In addition to well known techniques such as direct methods, difference Fourier synthesis, Patterson maps and Rietveld analysis, the newly proposed pseudo-atom method proved to be a very efficient tool to solve all structures containing well defined molecular fragments. In the case of $C_{60}Br_{24}(Br_2)_2$ the orientation of the well defined $C_{60}Br_{24}$ molecules in a triclinic distorted fcc lattice could be found unambiguously by maximizing of nearest neighbor distances. The structural motive of the high temperature form of the Ru-sawhorse dimer was found by conventional direct methods. The similarity criterion for the low temperature phase resulted in a restricted 4-dimensional grid search.

It can be shown that the precision is comparable to that achievable with single crystal techniques, and, therefore, allows for the interpretation of binding mechanism and reactions. Nevertheless, much more work is required in developing these structure solution methods further.

(1) Dinnebier, R.E. et al., NSLS annual report (1994), Beamline X3B1, Brookhaven National Laboratory
(2) Dinnebier, R.E. et al., NSLS annual report (1995), Beamline X3B1, Brookhaven National Laboratory
(3) Dinnebier, R.E. et al., J. Appl. Cryst. (1995), 28, 327-334

MS02.05.02 SOLUTION AND REFINEMENT OF DRUG STRUCTURES FROM POWDER DATA.

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The vast majority of pharmaceuticals used in everyday life are moderately sized organic compounds. Usually, their molecular structures are known from single crystal X-ray experiments. However, polymorphism (which is frequently found in pharmaceuticals) often makes the determination of a particular crystal form very difficult. In such cases, obtaining a structure solution from powder data is an attractive option, but one which presents a considerable challenge given that most of the compounds of interest will crystallise in low symmetry space groups with large unit cells, leading to complex diffraction patterns with lots of peak overlap. Model building is usually precluded due to conformational flexibility in the molecules, so *ab initio* methods offer the best hope of a solution.

Computational strategies such as standard direct methods, combined maximum entropy / log-likelihood gain and optimal extraction of structure factors will be discussed, but a particular emphasis will be placed on using sample preparation and data collection strategies to maximise the chance of obtaining a structure solution.

MS02.05.03 ZEOLITE STRUCTURE DETERMINATION FROM POWDER DATA: COMPUTER-BASED INCORPORATION OF CHEMICAL INFORMATION.

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Many technologically and industrially important materials, including zeolites, are synthesized and used in polycrystalline form. Since the crystal structures of such phases often determine their useful properties, it is essential that methods to study their structures are available.

The FOCUS method, which incorporates the use of chemical information into the structure determination process, has been developed. FOCUS combines automatic Fourier recycling (using integrated intensities extracted from a powder pattern and random starting phases) with a specialized framework search specific to zeolite structures, which can be described as 3-dimensional 4-connected topologies. The capabilities of FOCUS have been tested with six examples of medium to high complexity (zeolite topologies DOH, LEV, RSN, AFR, LTA, EMT), and the method was then applied to three novel zeolite structures - the two zincosilicates VPI-9 and VPI-10, and the beryllosilicate B2 - and a promising model was obtained in all cases. The structure of VPI-9 has since been confirmed with a full Rietveld refinement, and the code VNI has been assigned to that topology. Refinements for VPI-10 and B2 are in progress.

Experience shows that the approach of using chemical and geometrical knowledge can compensate for some of the information that is lost as a result of the overlap problem. At the same time, there is an intrinsic disadvantage: any method based on assumptions of certain structural properties is also limited to materials which conform to these assumptions. Examples which show the consequences of relaxing the structural assumptions were investigated, and it was found that the computing time requirements of FOCUS grow very rapidly with the number of different possible connectivity types. Suggestions for further developments to overcome this problem are outlined.

MS02.05.04 POWDER STRUCTURES FROM LIMITED DATA SETS.

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Structures of compounds which can be obtained only in the polycrystalline form depend mainly on the use of their powder diffraction data. Substantial progress has been made in instrumentation and computational aspects during the last decade for the application of powder diffraction techniques to solve unknown structures. One of the crucial steps involved in this process is to acquire the best possible diffraction data. Synchrotron sources, with their high brightness, excellent collimation and wavelength tunability provide optimum conditions for extracting individual intensities in the powder pattern. In most cases we have been able to arrive at the solution using data from a rotating X-ray source. However, synchrotron data was required to complete the structures in some cases.

This talk focuses mainly on the structure determination of metal phosphonates and phosphates. These compounds are difficult to obtain in single crystalline form and in most cases even their powder samples are poorly crystalline. The compounds yield only weak diffraction peaks whose intensities fall off very rapidly at higher scattering angles. Despite these difficulties, we have been able to solve the structures of a large number of compounds. Generally, the structures of these compounds are layered, where the metal-phosphate inorganic framework forms a two-dimensional layers which are separated by the organic groups on either side. In some cases metal phosphonate interactions led to unusual linear or porous structures. General methods used in solving the structures will be discussed using some representative examples.

In many cases the structures were solved by the use of 30-70 low angle(CuKα; $2\theta<60^\circ$) reflections by a combination of direct methods and heavy atom methods. The success comes from experience both in the structural aspects of these materials as well as the systematic application of efficient methods. It is equally important to use the results from other methods like spectroscopy, thermogravimetry, electron diffraction, etc. to arrive at the solution when only a limited number of powder diffraction data are available.

MS02.05.05 DETERMINATION OF MOLECULAR CRYSTAL STRUCTURES FROM X-RAY POWDER DIFFRACTION BY MONTE CARLO METHODS.

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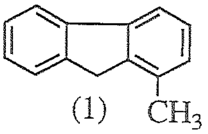
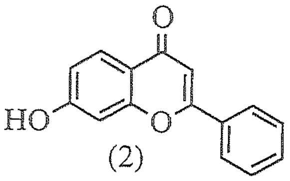
Many important crystalline solids cannot be prepared in the form of single crystals of sufficient size and quality for single-crystal X-ray diffraction studies, and in such cases it is essential that structural information can be extracted from powder diffraction data. We have developed and applied a method employing a Monte Carlo algorithm for crystal structure determination from powder diffraction data. In this method, a series of structural models is generated by random movement of a collection of atoms within the unit cell, and each trial structure is accepted or rejected on the basis of the agreement between the experimental powder diffraction pattern and the powder diffraction pattern calculated for the structural model. This technique differs considerably from the normal approach for structure determination from powder diffraction data, in that intensity information is not directly extracted from the diffraction pattern, and hence the problems of assigning intensities to overlapping reflections are avoided. The success of this method for *ab initio* crystal structure determination from X-ray powder diffraction data has been demonstrated by its application to the solution of several crystal structures including p-$BrC_6H_4CH_2CO_2H$ [K. D. M. Harris, M. Tremayne, P. Lightfoot, P. O. Bruce, *J. Am. Chem. Soc. (1994)*, **116**, 3543] and the γ-phase of 3-$ClC_6H_4CHCHCO_2H$ [B. M. Kariuki, D. M. S. Zin, M. Tremayne and K. D. M. Harris, *Chem. Mat.* (1996), in press]. In the work presented here, we have extended the Monte Carlo method to structure solution by a) simultaneous translation and rotation of a rigid structural fragment within the unit cell - illustrated by the structure determination of 1-methylfluorene (1) - and b) simultaneous translation and rotation with additional rotation about intramolecular bonds - illustrated by the structure determination of 7-hydroxyflavone (2).



(1)



(2)

MS02.05.06 CRYSTAL CHEMISTRY FROM POWDER DATA.

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A strength of structure analyses using powder data is the relatively short time required to obtain high quality data sets. This makes powder diffraction analysis particularly suitable for systematic structural studies on series of related compounds such as solid solutions in minerals and their synthetic equivalents. The high precision obtained when collecting and processing powder data sets under identical conditions allows the detailed study of subtle crystal chemistry correlations, for example variations in cation site occupancies, anion vacancies and bonding interactions.

The use of variable counting time (VCT) data collections (Madsen and Hill, 1994) enhances the capability to analyse subtle structure variations using X-ray data collected using a conventional laboratory configuration. In particular it yields more consistent thermal parameters, more accurate site occupancies and more stable refinement of light atoms.