

# POWDER DIFFRACTION

## Structure Solution from Powder Diffraction at the NSLS

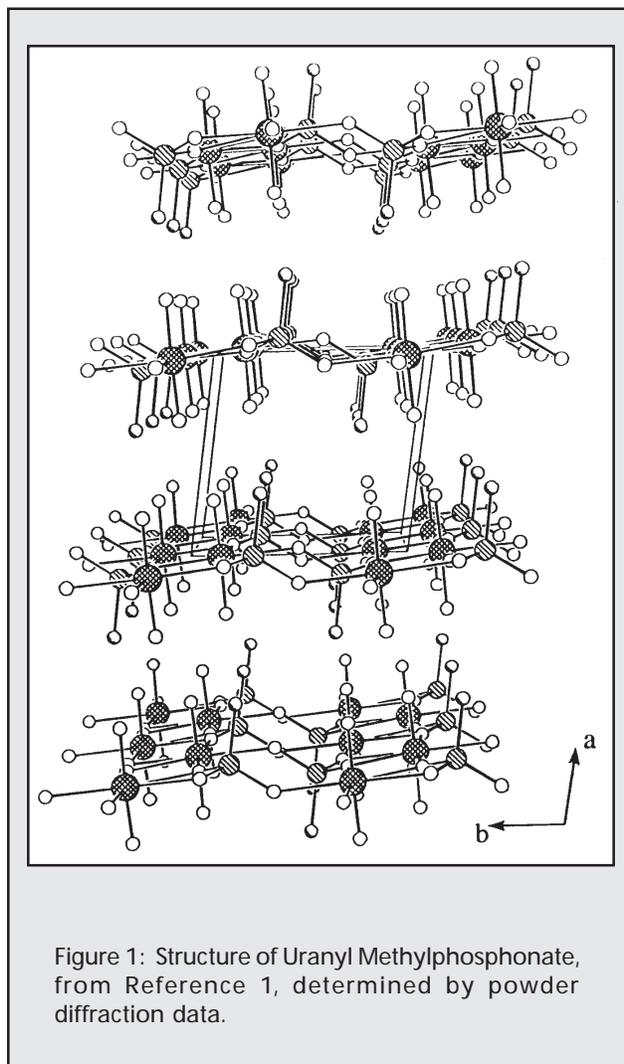
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### INTRODUCTION

Over the last few years, there has been a rapid growth in the development and application of methods for the *ab initio* solution of unknown crystal structures from powder diffraction data. Although conventional laboratory techniques have been successful in solving many heavy-atom inorganic structures, the most exciting recent advances have centered around the use of synchrotron x-ray powder data for the solution of molecular and organic structures, and framework structures such as zeolites. For structure solution problems, synchrotron radiation offers two outstanding advantages: the very high instrumental resolution that can be achieved with the use of a crystal analyzer mounted in the diffracted beam (about an order-of-magnitude better than that of a conventional diffractometer), and the feasibility of using samples loaded in thin-walled capillaries (which can be up to 2 mm in diameter depending on the sample transparency) without any loss in resolution. Other significant advantages are accurate peak positions, improved peak-to-background discrimination, wavelength tunability, well-characterized peak shapes, and the ease with which data can be collected at low temperatures in order to minimize thermal disorder.

Most *ab initio* powder studies at the National Synchrotron Light Source (NSLS) are carried out at the bending-magnet beam lines X3B1 and X7A, which have a long and productive history in this field. In a typical experiment, a double-crystal Si or Ge (111) monochromator is used in conjunction with a flat Si or Ge analyzer crystal, usually in the wavelength range 0.7-1.3 Å. The capillary sample is rotated or rocked during data collection (which in favorable circumstances might extend to a d-spacing of 0.8 Å), and the raw data converted to a diffraction histogram. The standard procedure at this point is to: (1) index the unit cell using one of several powerful auto-indexing programs, (2) extract the structure factors, (3) solve at least part of the structure using traditional methods, and (4) locate the rest of the atoms by a combination of Rietveld refinement and difference Fourier synthesis.

At stage (3) the problem is basically reduced to a single crystal structure determination with a limited and noisy data set, and can be tackled by the application of traditional Patterson and direct methods. The powder technique has been successfully exploited for a number of structures containing 30 to 50 atoms in the asymmetric unit, and in the future may perhaps be extended to 70-100 atom problems. Some examples are described below.

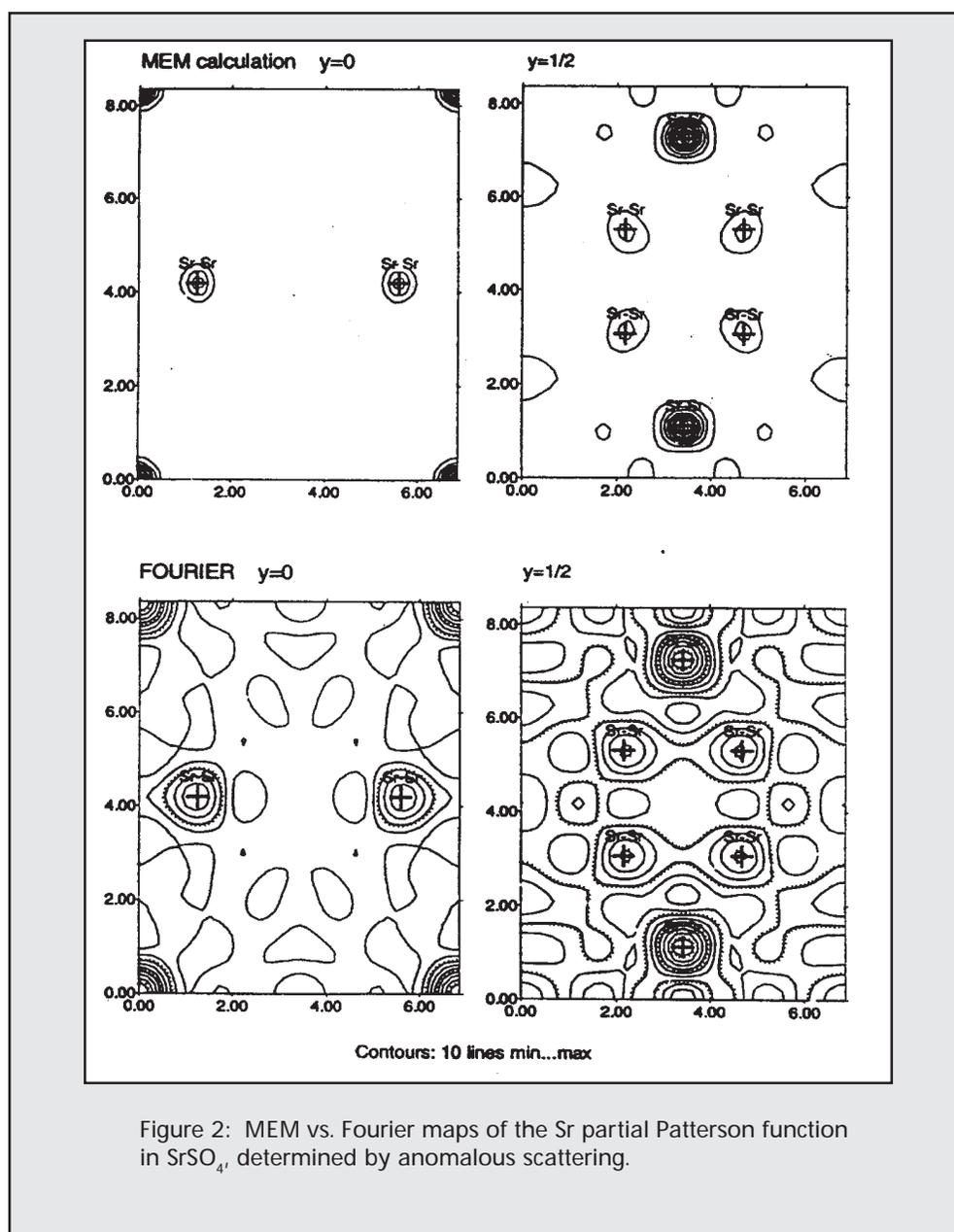


Although the powerful multiple anomalous diffraction techniques increasingly being used for protein crystallography cannot be exploited in the same way for powder data, anomalous scattering can nevertheless be applied in principle to the solution of unknown structures through the generation of partial Patterson maps of the anomalous scatterer, and a test case is described below.

The most recent developments in the application of powder techniques have focused on more novel approaches to the solution of organic compounds, molecular crystals and other light-atom structures such as zeolites. These approaches include Monte Carlo procedures, simulated annealing techniques, global optimization based on a genetic algorithm, entropy

maximization and maximum likelihood, Fourier recycling with a specialized topology search specific to zeolites, and the use of periodic nodal surfaces. Several of these methods operate in direct rather than reciprocal or Patterson space, and rely on random displacements of structural fragments to generate an acceptable fit to the diffraction pattern, thereby avoiding the necessity of extracting structure factors in step (2) above.

A one-day workshop, "Using Powder Data to Solve Crystal Structures," reviewing this area of crystallography was held at the NSLS 1998 Annual Users' Meeting. There were eighty participants, testifying to the exceptionally high level of interest in this topic.



## TRADITIONAL METHODS

Some of the traditional methods used to phase single-crystal diffraction patterns have been adapted to powder data sets, and are in productive use. Structure solutions from powder data are never as routine as single-crystal experiments, because the collapse of the diffraction pattern into one dimension generally requires close human supervision and evaluation of the quality of the raw data, determination of the unit cell, extraction of integrated intensities, etc. Patterson methods are very powerful for cases in which there are a few heavy atoms. One recent example is the structure of uranyl methylphosphonate,

$\text{UO}_2(\text{O}_3\text{PCH}_3)$ , illustrated in **Figure 1**.<sup>[1]</sup> This layered compound is of interest because metal phosphonate systems can be synthesized with a variety of functional groups, and are able to self-assemble into lattices with interesting potential materials properties, in this case, luminescence. The approximate structure was solved from laboratory x-ray data using Patterson methods, and completed by successive Fourier difference calculations, but synchrotron data were necessary to obtain a stable refinement.

Direct methods constitute the current workhorse technique for phasing single crystal diffraction patterns, based on statistical relationships of the phases and the intensities of combinations of three or more diffraction peaks. Powder data would seem to be ill-equipped to meet the condition of the number of independent observations much greater than the number of atom coordinates for any but the simplest problems, but the combination of high resolution experiments with advances in software has increased the power of this technique. Several recent examples of newly-solved structures, drawn from this year's experimental abstracts, include  $\text{Rb}_3\text{PbCl}_5$ , the charge-transfer complex  $[\text{Ni}(\text{dmit})_2]^{2-} \text{DPD-Me}^{2+}$ , and the alkali salicylates  $\text{C}_7\text{H}_5\text{O}_3\text{Rb}$  and  $\text{C}_7\text{H}_5\text{O}_3\text{K}$ .

In contrast to macromolecular crystallography, anomalous scattering techniques have not yet been used for *ab initio* structure solution from powder data. The key to the use of anomalous dispersion in phasing single crystal diffraction patterns lies in the fact that it produces a different intensity for the two members of Bijvoet pairs  $hkl$  and  $\bar{h}\bar{k}\bar{l}$ . The technique is not directly transferable to powder diffraction, because all such pairs of reflections are superimposed, but it is nevertheless possible in principle to determine the difference Patterson density of the anomalously scattering atom from two measurements, close to and far from the absorption edge. The application of this technique to the test case of  $\text{SrSO}_4$  is illustrated in **Figure 2**, which shows the partial Patterson density of Sr.<sup>[2]</sup> A notable feature of this work is the obvious superiority of maximum entropy methods over conventional Fourier synthesis in the reconstruction of the density maps.

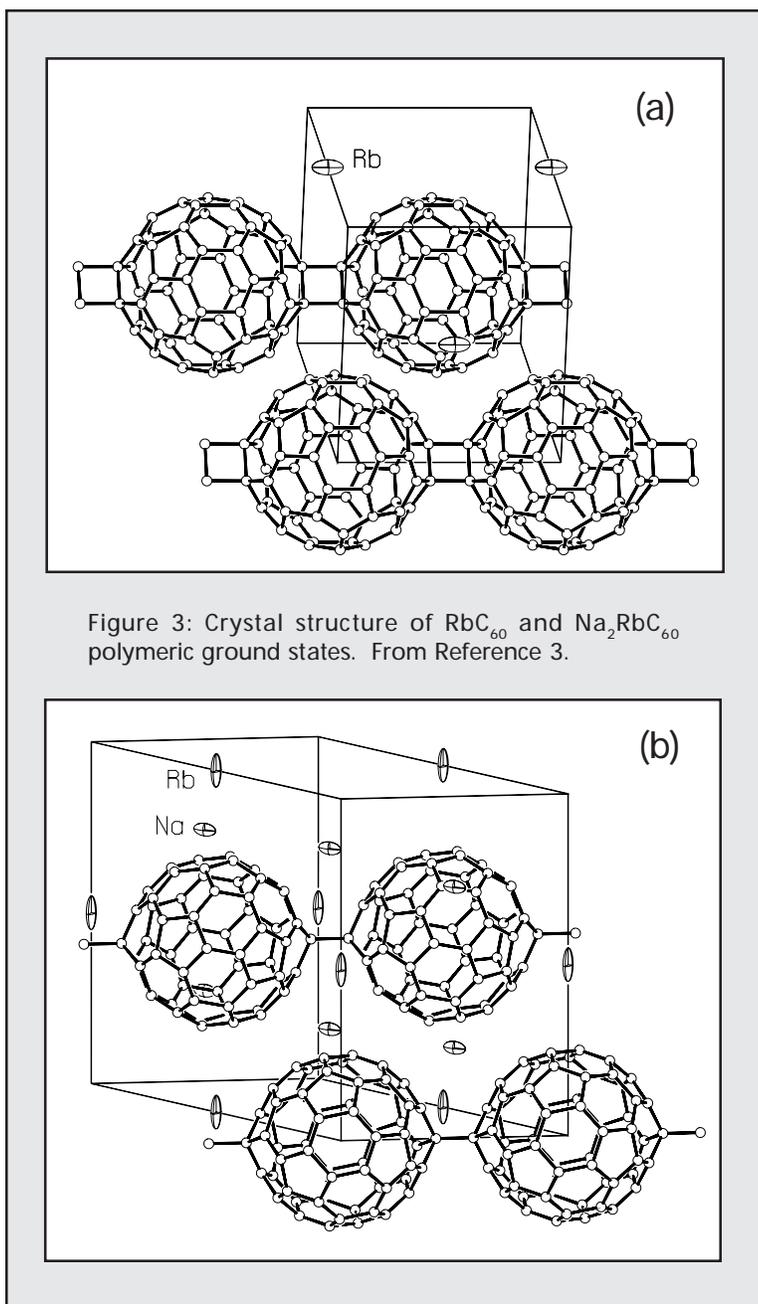
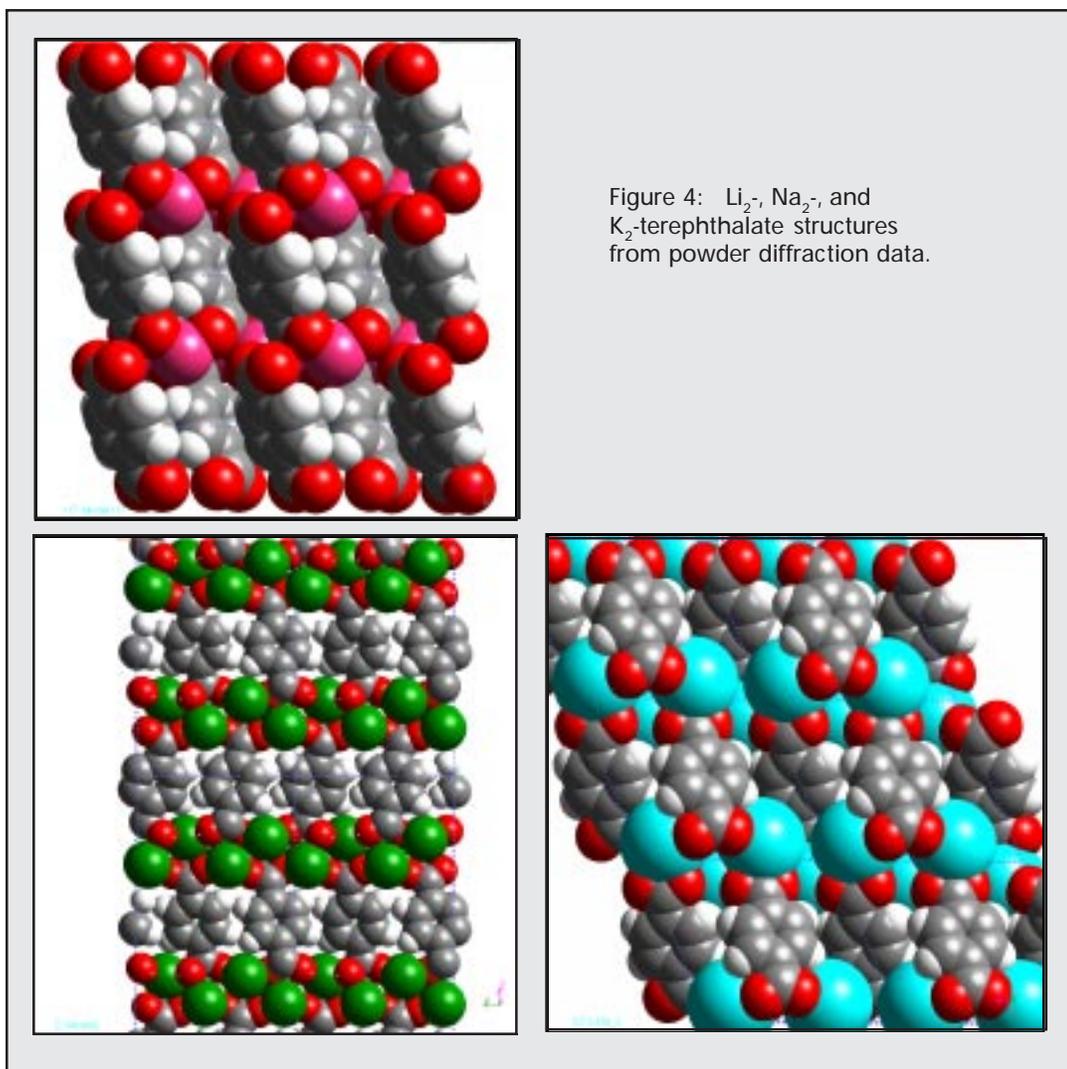


Figure 3: Crystal structure of  $\text{RbC}_{60}$  and  $\text{Na}_2\text{RbC}_{60}$  polymeric ground states. From Reference 3.

## **SIMULATED ANNEALING TECHNIQUES FOR MOLECULAR SOLIDS**

In the cases of organic solids, one can usually make a fairly good guess of the molecular structure from chemical principles (bond lengths and angles) and so there are only a few degrees of freedom in determining how the molecules might pack into a lattice. Organic molecules typically occupy the general position of a lattice, and so a structure is specified by six real numbers to locate the position and orientation of the molecule's center, plus however many internal degrees of freedom are described by torsion angles. In these techniques, the agreement between a calculated diffraction pattern and the observed data is regarded as an energy to be minimized, and exhaustive searches or simulated annealing algorithms are applied to determine the best fit between model and data. There are several interesting new results from recent experiments at the NSLS.

The developing story of polymerization of  $C_{60}$  has been full of surprises. In 1994, experiments at the NSLS showed that  $RbC_{60}$  and  $KC_{60}$  had different low-temperature states depending on their thermal history. If cooled slowly, they polymerized spontaneously into the ground state structure illustrated in **Figure 3a**, with two single bonds (a [2+2] cycloaddition) linking adjacent fullerenes into chains. If quenched, the fullerenes paired off into dimers; surprisingly, it was found that the dimers were linked by a single carbon-carbon bond, different than the polymer. More recently, it was found that if the fullerene charge state is increased to 3-, in  $Na_2RbC_{60}$  or  $Na_2KC_{60}$ , it has a polymeric ground state (**Figure 3b**) connected by the same single bond as the singly charged fullerenes in quenched  $Rb_2(C_{60})_2$  and  $K_2(C_{60})_2$ .<sup>[3]</sup> These results imply that the charge state has a crucial effect on determining the available routes of interfullerene bonding. In this work, the fullerenes were previously known to be centered at special positions of the crystal lattice, but the



orientation had to be determined in order to find the plausible bonding geometry. The high angle part of the diffraction pattern suffered from such severe peak overlap that no progress could be made with extracted intensities, but the problem could be attacked by comparing the entire calculated diffraction profile. This would only work for a molecule that largely retains its rigid identity in different crystal structures, but the successful refinements prove that this premise is correct.

A very different example comes from the chemical industry. Amoco technology produces over four million tons annually of purified terephthalic acid (1,4-benzenedicarboxylic acid). Understanding the natures of terephthalate complexes of catalyst and corrosion metals will lead to process insights and improvements. Nothing, however, is known about the solid state structures of such complexes, because they are intractable solids, available only as powders. Despite the importance of this problem, there has been little progress from applying conventional crystallographic techniques to the powder patterns of transition metal terephthalates. There are a great number of possible metal-carboxylate binding modes, and so it is

worthwhile to develop skills and techniques for solving the structures of such coordination compounds, and to gain insight into how terephthalate anions pack in the solid state. Toward that end, J.A. Kaduk at Amoco has studied a number of terephthalate salts of non-transition metal cations. Combinations of Monte Carlo simulated annealing, molecular mechanics, and crystallographic techniques have proven successful in obtaining the structures of such salts. The structures of dilithium, disodium, and diammonium terephthalates have been solved *ab initio* using synchrotron powder data and simulated annealing software from Molecular Simulations Inc., and can be compared to the structure of dipotassium terephthalate, determined using conventional single-crystal techniques. The structures of the three alkali salts are shown in **Figure 4**, which illustrates large differences between the structures of these closely related compounds. For example, the terephthalates in the Li, K, and ammonium salts are nearly planar, but the carboxylates are rotated approximately  $20^\circ$  out of the ring plane in disodium terephthalate. These four structures provide enough of a “database” to begin to understand the

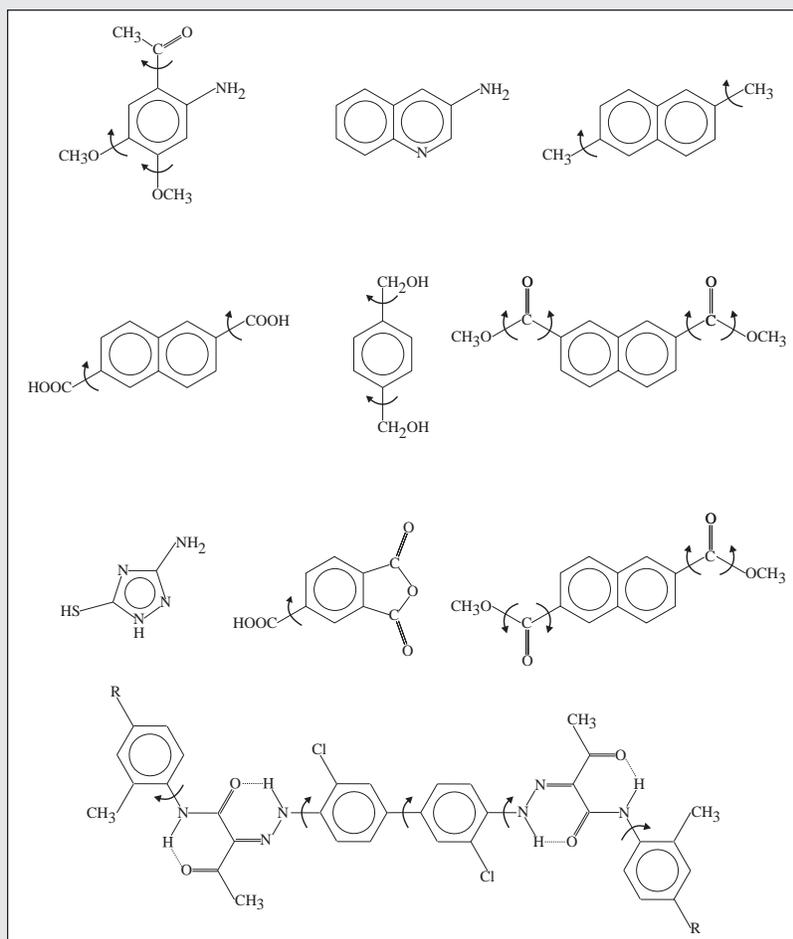


Figure 5: An assortment of molecules whose crystal structures have been determined by *ab initio* powder diffraction techniques. Circular arrows indicate molecular torsion angles that must be determined experimentally.

energetics of these structures. Such understanding is proving useful in determining the structures of more process-related salts.

Simulated annealing techniques, both as developed by users and in commercial software, and with varying degrees of input from calculations of the conformational and packing energetics, have been applied to first determine the solutions of a large number of different molecular solids. The range of complexity is illustrated in the molecular diagrams in **Figure 5**. More details on all of these structures are available in the experimental abstracts from beamlines X3B1 and X7A.

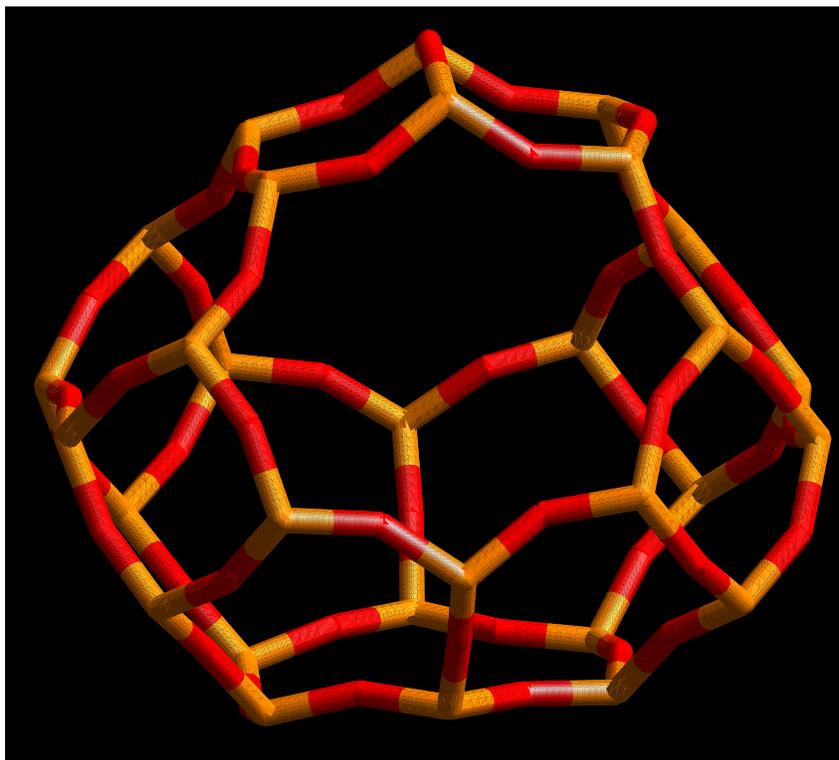
It is worth pointing out that synchrotron data is often crucial for solving organic structures, not only because it yields better structure factors, but because it permits determination of the correct unit cells and space groups. The systematic errors inherent in a laboratory Bragg-Brentano experiment, particularly peak shifts due to the penetration of x-rays into weakly absorbing samples, make it difficult to index the laboratory patterns. One often thinks of the determination of the unit cell as mechanical, but it is crucial to obtaining the correct structure. Furthermore, the high angular resolution and high signal to background ratio of data sets usually collected with synchrotron radiation are of great importance in the determination of systematic absences and therefore of the correct space group.

## FRAMEWORK COMPOUNDS

Framework compounds such as zeolites are very widely used as catalysts, adsorbents and ion-exchangers in industrial processes. The catalytic activity and selectivity of zeolites depend upon active sites which are accessed by reactant organic molecules through pores of about the same size as the molecules. Understanding zeolite structures is thus of utmost importance in optimizing the properties of these materials for industrial use. Since most zeolites are synthesized via the use of organo-cation templates under hydrothermal conditions which typically yield crystals less than 5 microns in size, powder techniques are vital in structural studies, and many such structures have been successfully solved by industrial and academic groups in the past decade. The techniques to solve zeolite structures from powder data are somewhat different than molecular structures. Instead of a distinct molecule which can be moved around in the unit cell (by computer), one has a highly connected framework, with a large number of tetrahedrally coordinated (Si,Al) atoms. It is therefore necessary to generate and test a number of different framework topologies against the experimental data, and several recently developed algorithms have extended the utility of these techniques.

A striking recent example is the structure of a new small-pore zeolite, ERS-7, with the approximate

Figure 6: The 17-sided "picnic-basket" cage element in the structure of the new zeolite ERS-7, determined by powder diffraction.



composition  $\text{Na}_x\text{R}_y(\text{Si}_{1-z}\text{Al}_z)\text{O}_2$ , where R is the template ion, N,N-dimethylpiperidinium and  $x \sim 0.03$ ,  $y \sim 0.09$ , and  $z \sim 0.1$ . The correct structure was identified as one of 373 unique framework topologies generated by a simulated annealing technique using MSI software, and was verified by Rietveld refinement and lattice energy minimization calculations.<sup>[4]</sup> The orthorhombic framework has twenty atoms in the asymmetric unit, and consists of 17-sided cages with a “picnic-basket” shape connected by an eight-membered ring system such that the ring channels run through the “handles” of the picnic basket, depicted in **Figure 6**.

Many groups are actively seeking new zeolites with even larger pores, consisting of rings of twelve or more tetrahedral atoms, for catalysis or absorption on large organic molecules. Materials with a high-silica content are particularly desirable because of their high acidity and thermal stability. The structure of a novel compound with a 14-membered ring, CIT-5, was recently determined at the NSLS by an iterative process of model building, distance-least-squares refinement of the model parameters, and comparison of the simulated and experimental patterns until the closest match was found<sup>[5]</sup>. Rietveld refinement was carried out on this structure, which is orthorhombic with 5 Si and 8 O atoms in the asymmetric unit, and is composed of one-dimensional extra-large pores of nearly circular cross-section (**Figure 7**).

Another interesting example is the *ab initio* solution of the structure of two closely-related large-pore high-silica molecular sieve materials, SSZ-44 and SSZ-35. The first was solved by application of the Fourier recycling and topology search (FOCUS) method,<sup>[6]</sup> followed by Rietveld refinement. The structure is monoclinic with 8 Si and 17 O atoms in the asymmetric unit, and consists of unusual one-dimensional straight channels containing pore openings that oscillate between rings of ten and eighteen tetrahedral atoms in layer-like units<sup>[7]</sup>. An interesting feature of this structure is that the powder diffraction experiments revealed that SSZ-44 and SSZ-35 are very similar, with ABAB and ABCABC stacking, respectively, of layers along the pore direction. It was previously known that SSZ-44 and SSZ-35 had similar catalytic properties, and this new structural information shows that they are the pure end-member polymorphs of a new fault series, which allow investigation of the relationship between the organic structure-directing agent and the stacking fault structure of the zeolite framework.

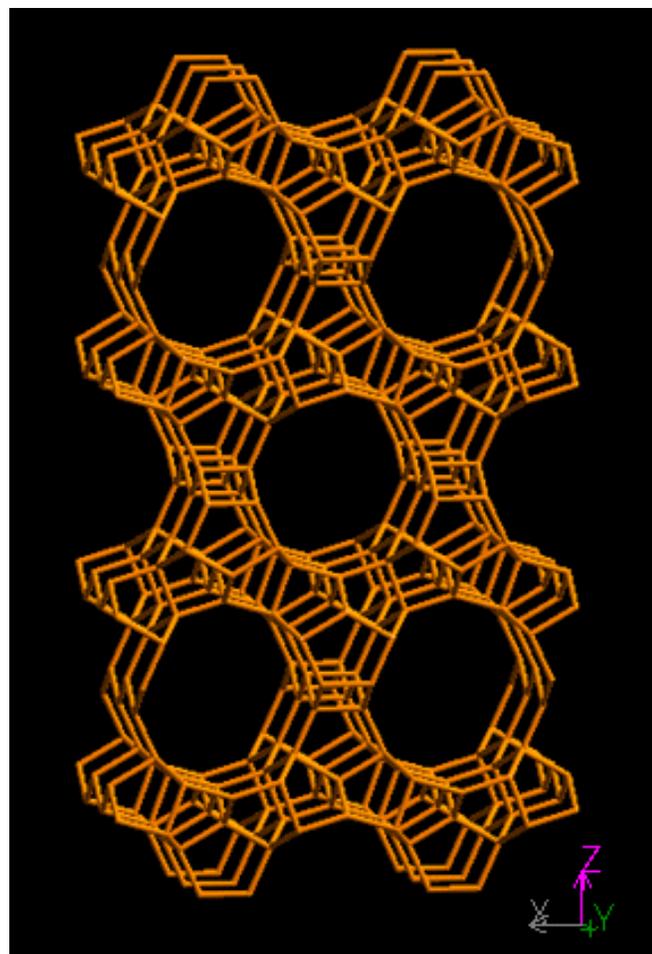
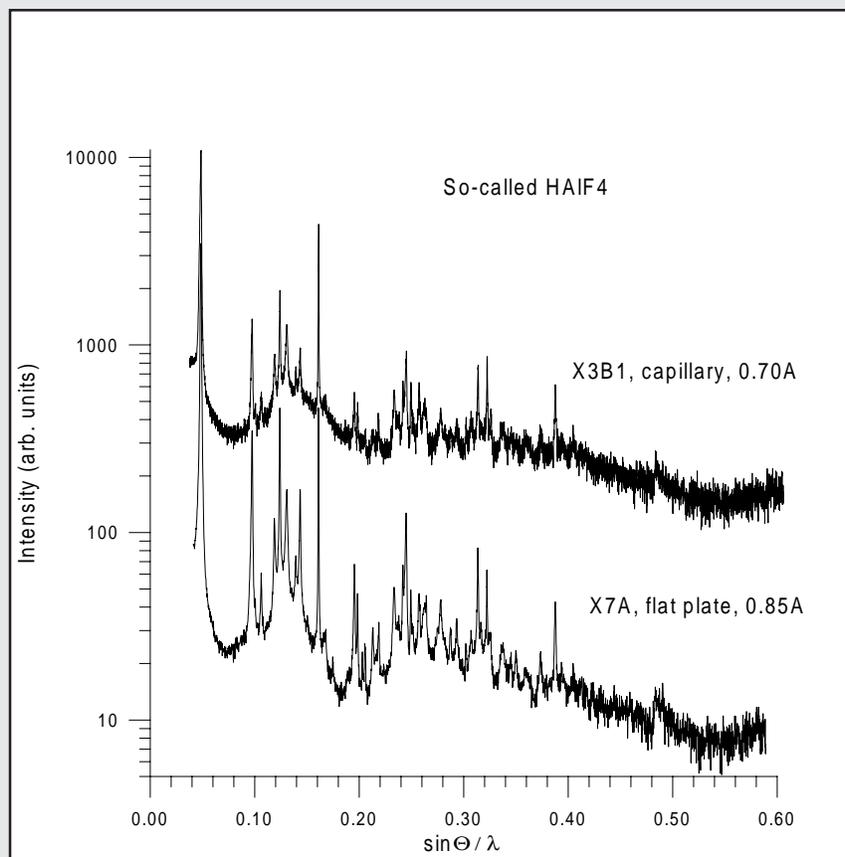


Figure 7: Structure of CIT-5 viewed down the [010] axis, showing the large pores circumscribed by 14-membered rings of tetrahedral Si atoms.

## MARGINAL MATERIALS

Du Pont Corporate Research and Development is working on new families of catalysts for Freon® replacements, and this has prompted work in various aluminum fluoride preparations. Compounds which are industrially useful catalysts often give very poor diffraction patterns which make them difficult to attack. One well-publicized example was the DuPont powder challenge. Data sets collected at two NSLS beamlines of a material alleged to be  $\text{HalF}_4$  proved to be intractable, and so Richard Harlow issued a \$1000 cash challenge to the crystallographic community for the first acceptable solution from the data plotted in **Figure 8**.<sup>[8]</sup> Relative to other work described here, this data is of extremely poor quality, having broad, overlapped peaks, with a limited range of *d*-spacings. Several entries (including the proposer) correctly found part of the structure, layers of

Figure 8: Diffraction data for alleged HAIF<sub>4</sub>. Upper trace, in a capillary to minimize preferred orientation, at beamline X3B1; lower trace, on a flat plate to maximize signal to noise ratio, at beamline X7A.



edge- and corner-sharing AlF<sub>6</sub> octahedra, but the credit for a complete solution goes to Leonid Solovyov and Sergei Kirik from the Institute of Chemistry and Chemical Engineering, Russian Academy of Sciences in Krasnoyarsk, Russia. By chemical tests on samples provided by DuPont, they suspected the presence of organic material, and so converged to the correct solution, with pyridinium counterions. This brings us back to a

theme that runs through much of the work reviewed here: chemical information beyond the diffraction data is often crucial to solve a structural problem, but that information had better be correct! It also shows that if one is sufficiently motivated, one can solve significant problems from rather poor samples, and that we can expect to see considerable further progress in the utility of *ab initio* powder techniques to interesting problems. ■

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