



## DISORDERED MATERIALS

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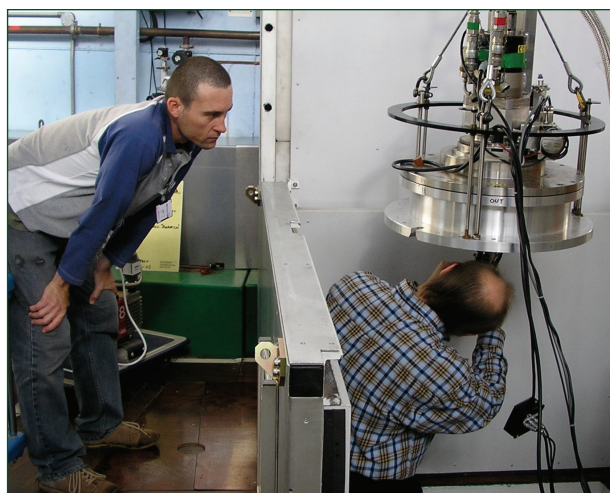
This group combines diffuse X-ray scattering methods with computer simulation to deduce the arrangement of atoms and molecules in disordered crystals. Conventional crystal structure determination reveals only averaged arrangements, inadequate to explain some of the basic properties of many minerals, inorganic compounds, organic compounds and alloys that exhibit crystalline disorder. Diffuse scattering gives information on how neighbouring atoms or molecules interact with each other. Quantitative studies of diffuse scattering are, however, still rare because of the intrinsically very low intensities involved.

The group uses dedicated diffuse-scattering diffractometer systems based on curved position-sensitive wire detectors. These allow high quality diffuse scattering data to be efficiently recorded over large regions of diffraction space and provide a unique facility for tackling a whole range of complex structural problems. The group also has access to the most advanced synchrotron radiation and neutron source facilities in the world and methods are being developed to utilise these for diffuse scattering measurements.

The group's interests span a wide range of fields, each presenting problems for which this specialised technique can give unique information. Areas in which we have applied the techniques include: disordered molecular crystals, guest/host systems such as urea inclusion compounds, non-stoichiometric inorganic materials and minerals (for example, the cubic stabilised zirconias, mullite and wüstite), flexible framework structures such as silica polymorphs and their analogues, alloys, and quasicrystal phases.

Much of the current effort of the group is concerned with the further development and exploitation of the least-squares method, which was developed in the group for directly fitting a Monte Carlo (MC) simulation to observed X-ray diffraction data.

### Refinement of Monte Carlo Models of Disordered Molecular Crystals



PhD student Andrew Beasley helps Dr Matthias Gutmann with a neutron experiment at ISIS.

We have now extended the automatic refinement method to use neutron diffuse scattering data in addition to X-ray data. Deuterated benzil,  $C_{14}D_{10}O_2$ , has been studied. The neutron data, collected using the SXD instrument at the ISIS facility in the UK, has the advantages of being sensitive to light atoms, such as hydrogen (although to reduce absorption of the neutron beam, deuterium is used instead) and of giving three dimensional data over a very wide region of reciprocal space. The neutron data successfully constrained the magnitudes of the displacements of the atoms in a way that the X-ray data had failed to do. The first simultaneous refinement of neutron and X-ray diffuse scattering data showed that the two techniques can be as successfully combined in the study of diffuse scattering as they are, routinely, in conventional crystallography. *(With D J Goossens, A Beasley, A P Heerdegen, and M J Gutmann [ISIS, Oxon, UK])*

## Diffuse Neutron Scattering from Crystals

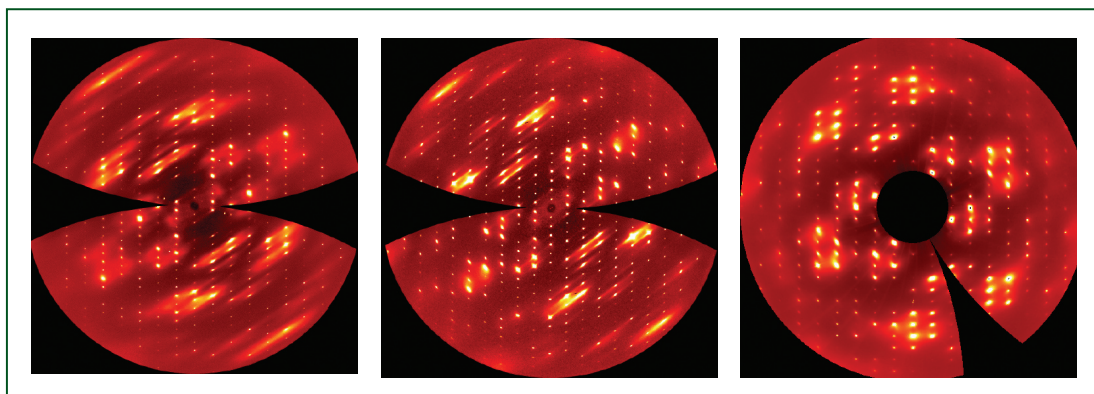
We have carried out experiments using the time-of-flight (tof) Laue technique instrument, SXD, at ISIS in order to collect diffuse scattering data for the molecular crystal d-benzil,  $C_{14}D_{10}O_2$  from a complete 3D volume of reciprocal space out to very high  $Q$  ( $30 \text{ \AA}^{-1}$ ). The aim in this work is to obtain a PDF (pair distribution function) in three dimensions. PDFs in 1D have recently become accepted as a valuable tool for probing local structure in materials from powder diffraction data and the thesis of our work is that a 3D PDF that is obtainable from single crystal data should provide a much more detailed view of this local structure, since there is no orientational averaging. Our work on neutron diffuse scattering has featured as a 'Science Highlight' in the ISIS Annual Reports for 2004 and 2005.

Neutron diffuse scattering data have also been collected at ISIS for deuterated *para*-terphenyl at temperatures above and below the structural phase transition near 200K. The study reveals details about the phase transition and is our first example of using neutron data on a molecular system containing static disorder. Below the phase transition temperature the static disorder vanishes and only the thermal motion remains. (With D J Goossens, A Beasley, A P Heerdegen, and M J Gutmann [ISIS, Oxon, UK], Th Proffen, [LANSCCE, Los Alamos, USA])

## The Influence of Disorder on Polymorphism

Polymorphism is of key importance in the pharmaceutical industry since the properties of different polymorphs of the same compound may differ considerably e.g. the rate of uptake of pharmaceutical molecules by the human body is often strongly dependent on which polymorphic form of the material is present. There are many patenting issues that arise from this. The aim of the study is to use diffuse scattering methods to investigate the crystal structures of polymorphic systems in a level of detail that goes beyond the average structures that are revealed by conventional crystallography. A particular aim is to investigate the role that molecular flexibility plays in determining crystal packing and the conformations and dynamics of the molecule that occur in different polymorphs.

As a first step we are studying the model compound *p*-(*N*-methylbenzylidene)-*p*-methylaniline (MeMe), which is known to crystallise in at least three polymorphic forms. Two of these have orientational disorder in which the molecules are "flipped" either end-to-end and/or side-to-side, but the third appears, in conventional crystallographic studies, to be completely ordered. We have collected three-dimensional diffuse scattering data from all three polymorphs at the Advanced Photon Source (APS), and are now attempting to model the features in their diffuse diffraction patterns. Even the 'ordered' polymorph II shows highly structured diffuse scattering, which should reveal a wealth of detail of the local structure and dynamics. (With A Beasley, D J Goossens, A P Heerdegen, and P L Lee [APS, Argonne, USA])



From left to right, the (*h*0*l*) sections of the three polymorphs I, II and III of MeMe.