



Disordered Materials

Professor Richard Welberry

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 that are 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 utilize these for diffuse scattering measurements.

The group's interests span a wide range of different fields, each presenting problems for which this specialised technique can give unique information. These include: disordered molecular crystals, guest/host systems such as urea inclusion compounds, nonstoichiometric 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.

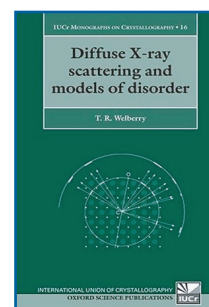
Much of the current effort of the group is concerned with the further development and exploitation of the least-squares method for directly fitting a Monte Carlo (MC) simulation to observed X-ray diffraction data, proposed for the first time in 1997. This work is supported by an ARC Discovery Grant. A second ARC Discovery Grant is held jointly with the Withers Group and supports work to investigate the role of strain in disordered systems.

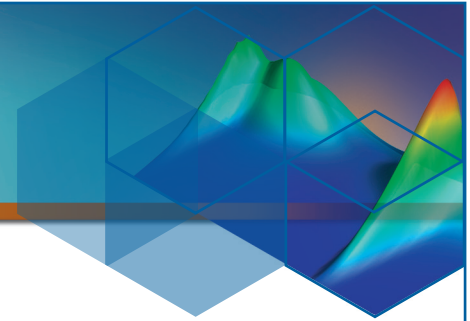
Diffuse X-ray Scattering and Models of Disorder

A highlight of the year was the publication of the book entitled "Diffuse X-ray scattering and models of disorder" by the Group leader, published by Oxford University Press in the International Union of Crystallography Series of Monographs on Crystallography. The book details the work of the group in developing methods of recording, interpreting and analysing diffuse X-ray scattering.

Refinement of Monte Carlo Models of Disordered Molecular Crystals

The current main emphasis of this work is to develop the techniques whereby the diffuse scattering from a molecular crystal can be measured and analysed on a routine basis. Such analyses provide information on how the molecules interact with each other that is not available from conventional crystal structure determinations. The need to measure very weak intensities in the presence of the very strong Bragg peaks presented nontrivial problems when the synchrotron data that had been collected at the APS in Chicago in 2003 was processed. Considerable effort was required to overcome these problems. The main source of the difficulties was that when Bragg peaks impinge on the detector, locally generated fluorescence produces a 'blooming' artefact. After much work we now have good 3D data sets for the series of flexible molecules 2,2'-, 3,3'- and 4,4'-dimethoxybenzil, each of which has five internal degrees of flexibility.





A number of software tools have been developed to aid the setting up, model design and running of the Monte Carlo (MC) simulation program that is used to analyse the diffuse scattering data. Whereas previously each new project required the setting up of a purpose-built MC program involving many weeks of development, it is now feasible to use a generic program that can be tailored to suit different systems in a much shorter time.

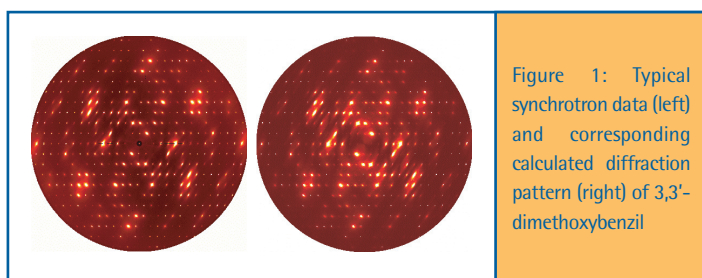


Figure 1: Typical synchrotron data (left) and corresponding calculated diffraction pattern (right) of 3,3'-dimethoxybenzil

Most effort this year has gone into the analysis of 3,3'-dimethoxybenzil. A model that gives excellent agreement with the observed synchrotron data has been developed and the study has provided invaluable experience of how modelling of this kind of system should be carried out. Some preliminary work on the 2,2'-dimethoxybenzil system has also been carried out. This system has presented some unusual new diffraction features which will present new

challenges to the methodology. (With D J Goossens, A P Heerdegen, and D R Haeffner, P L Lee, J Almer [APS, Argonne, USA])

Diffuse Neutron Scattering from Crystals

Further diffuse neutron scattering data have been recorded for d_{10} -benzil, $C_{14}D_{10}O_2$ using the time-of-flight (tof) Laue technique instrument, SXD, at the ISIS Neutron Source, UK. Data covering a large fraction of the total 3D reciprocal space out to a Q of 15 \AA^{-1} has been recorded at four different temperatures. Work has now begun to re-refine the structural model including this new neutron data alongside the original X-ray data. Our work on benzil was featured as a 'Science Highlight' in the ISIS Annual Report for 2004.

Our collaborations with ISIS staff have also led to our involvement with a study of diffuse scattering in the relaxor ferroelectric material PZN ($PbZn_{1/3}Nb_{2/3}O_3$). A renewed interest in the field of ferroelectricity has taken place in recent years since the finding of exceptional piezoelectric properties in the lead-oxide class of relaxor ferroelectric (RF) materials typified by PZN. We have developed a model for PZN that explains the diffuse scattering that is observed. This is based on the supposition that the origin of its properties is the lone-pair electrons of the Pb atoms. (With D J Goossens, A P Heerdegen, and W I F David, M J Gutmann, M J Bull [ISIS, Oxon, UK])

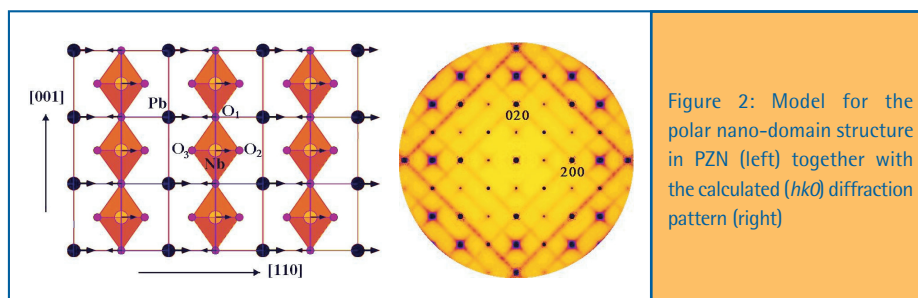


Figure 2: Model for the polar nano-domain structure in PZN (left) together with the calculated $(hk0)$ diffraction pattern (right)

<http://rsc.anu.edu.au/research/welberry.php>