Final report on GR/M05362/01, Structure of disordered materials (MT Dove and DA Keen)

The main purpose of this grant was to develop the technique of total neutron scattering for the study of disordered materials, based on the time-of-flight instruments at the ISIS source. We have developed a new RMC-based analysis tool that explicitly incorporates the Bragg reflections, so that the resultant configurations are consistent with both long-range and short-range structural order. We have used the methodology for a number of studies of crystalline materials with disordered phases, focussing particularly on structures that are networks of polyhedral groups of atoms and molecular crystals.

1. Background

The traditional method to study the atomic structure of materials is through Bragg diffraction. This gives the average positions of atoms, and if it is possible to account for all sources of error in the data, it is also possible to obtain the distribution functions that describe the range of positions of all atoms. This method is ideal for reasonably well ordered materials, but can fail to give real insights into the atomic structures of disordered crystalline materials. The problem is illustrated by the high-temperature cristobalite polymorph of silica, which is one of the materials studied in this project. The average structure of the cubic phase obtained from analysis of Bragg diffraction appears to have linear Si–O–Si bonds, but such a configuration of these atoms is known to be energetically unfavourable. Detailed analysis of Bragg diffraction data shows that this structure has anomalously short Si–O bond lengths, and large amplitudes of motion of the oxygen atoms in the direction normal to the Si–O–Si vector. The reasonable conclusion is that the Si–O–Si bond is actually usually bent, and only appears to be linear when averaged over all bonds in the crystal. It therefore appears that there is considerable structural disorder, and this interpretation also explains why the Si–O bond appears to be short. Using this insight it is then possible to refine the crystal structure assuming a more reasonable model for the distribution of positions of the oxygen atoms. However, although this gives a reasonable fit to the diffraction data, there is an apparently insurmountable problem. Even with the best diffraction instruments, the maximum value of Q for which Bragg peaks can be measured with reasonable resolution, $Q_{\max}$, is usually not large enough to give a resolution in real space, $\Delta r = 2\pi/Q_{\max}$, that is good enough to distinguish between different models of the structural disorder. For example, for X-ray diffraction with Cu Kα radiation, the best Δr that could be obtained is 0.77 Å, which is just less than half the Si–O bond.[1] Moreover, even if it is possible to obtain the distribution functions for the positions of individual atoms, Bragg diffraction contains no direct information about the correlations between the positions of pairs of atoms, and it is these correlations that are often associated with the onset of the structural disorder.

By contrast, for structural studies of materials with no long-range order (glasses, fluids) the concept of a distribution of atom positions has no meaning. Instead, the structure is defined by the very correlations between atom positions that cannot be determined by analysis of Bragg diffraction. Instead, structural studies of these disordered materials is performed using analysis of the total diffraction measurement, $S(Q)$, which includes elastic and inelastic scattered radiation, and which explicitly includes information only about pair correlation functions in the formalism. One important aspect of total scattering experiments is to be able to obtain data to high values of Q in order to obtain the best spatial resolution on the pair distribution functions. Typically with the best data from reactor sources, $Q_{\max} \sim 20$ Å^{-1}, but with time-of-flight sources such as ISIS, $Q_{\max}$ can exceed 50 Å^{-1}.

The *main focus of our proposal* was to develop the use of total scattering methods for the study of structurally disordered crystalline materials. The experimental task is to obtain data over a wide range of Q with a resolution sufficient to be able to extract the maximum information from the Bragg peaks (which are δ-functions broadened by the instrumental resolution). The more challenging task concerns the analysis of the data. Typically the goal of a total scattering experiment is the determination of the pair distribution functions, from which it may be possible to obtain information about the structure around the first few neighbouring shells of atoms. Recently there have been significant attempts to obtain more detailed models of liquids and glasses using the Reverse Monte Carlo (RMC) modelling method. A number of criticisms have been levelled against the RMC method, particularly concerning the possibility that the RMC methods generate models with too much structural disorder. An alternative approach is to use least-squares fitting methods to adjust a configuration of atoms to give best agreement with the pair distribution functions. *Our project is concerned with developing these methods* for the case where there is structural disorder within materials with some degree of long-range crystallographic order. *The novel feature of our work* is to use the information in *both* the total scattering and Bragg scattering to give information about both long-range *and* short-range structure simultaneously. *We have developed a version of the RMC method* that enables us to construct atomic models that are consistent with both the Bragg diffraction data (constraining the distribution functions for individual atoms) *and* the total scattering data and associated pair distribution functions (giving information about local structure).

This programme of work has been particularly timely since it ties in with the development of the EPSRC-funded GEM (General Materials) diffractometer at ISIS. This is a new-generation ISIS that is designed for both diffraction and total scattering measurements. Most UK users are concerned with either one type of measurement or the other, but for our work the GEM instrument is ideal since we always want both types of measurement. GEM came on line just over halfway through our project, and for the first part of the project we worked with the now-decommissioned LAD diffractometer. This changeover between instruments determined the timing of the different stages of our work.

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[1] Even with better experiments, such as HRPD at ISIS, information that could improve Δr is lost through considerable overlap of diffraction peaks

2. Technical achievements

2.1 GEM total scattering data reduction

Data reduction is a critical aspect of total scattering measurements, since analysis requires that the $S(Q)$ data be on an absolute scale. For our work on the LAD diffractometer, we followed previously established methods. These were relatively easy to port to the reduction of GEM data, and early experiments on GEM taught us how best to measure the corrections required for the data reduction. It should be noted that our experience is that data reduction procedures are actually more accurate on GEM owing to the greater stability of the instrument. One factor is worth remarking on. We have found that for some samples, trace impurities have noticeable resonance absorption at high energies (e.g. Hf impurities in Zr-containing compounds). Because different detectors are positioned with different scattering angles, these resonances occur in spectra corresponding to different values of Q, and the spectra from a single bank of detectors summed over all detectors will contain a dip in $S(Q)$ that is broad in Q. To solve this problem, it is possible to exploit the fact that there are many detectors by subtracting the affected region from the spectra of all individual detectors before summing. This procedure was developed in collaboration with Dr Raedelli, the instrument scientist for GEM, using the IDL Ariel data-reduction software for GEM.

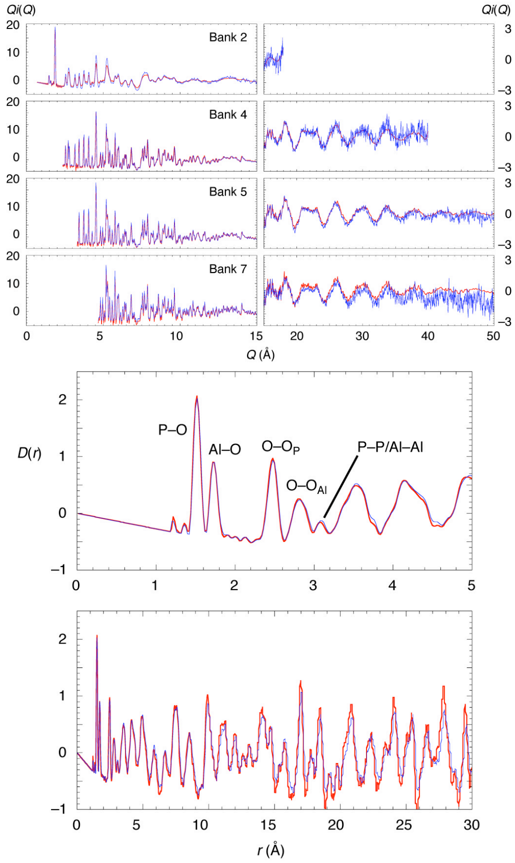

Figure 1. Fitted diffraction patterns and resultant pair distribution functions of AlPO$_4$ analysed using MCGRtof.

2.2 Pair distribution functions

The pair distribution functions are obtained from the Fourier transforms of the measured $S(Q)$ functions. The immediate problem faced in this procedure is that the measurement of $S(Q)$ is obtained using different sets of detectors with different scattering angles. Each set of detectors will cover a different range of values of Q with a different resolution function. If one is not concerned with the effects of instrument resolution, it is possible simply to splice together data from different detectors and Fourier transform the resultant $S(Q)$. This is the procedure we followed with our treatment of data from LAD. The effect of neglecting resolution is to attenuate the pair distribution function, particularly at higher values of r, and this can be seen as difficulties in obtaining a perfect match between experiment and calculation when building atomic models.

In order to incorporate experimental resolution into the Fourier transform of $S(Q)$ in a way that treats all banks of detectors separately, we have developed the inverse transform method previously implemented by Pusztai & McGreevy (*Physica B*, **234–6**, 357, 1997) in their `MCGR` program (usually used for constant-wavelength data). We have reworked this program for analysis of GEM time-of-flight data incorporating the resolution function for this type of data. Our new program is called `MCGRtof`, and is now available for routine use (and has been supplied to other workers). An example of its use for AlPO$_4$ is shown in Figure 1.

2.3 RMC method with integrated Bragg intensities

One of the primary aims of our project was to develop the RMC method to incorporate the information contained within the Bragg peaks.[2] As noted in §1, by taking account of the information within the Bragg peaks the structural models constructed from total scattering data will be consistent with the long-range order as well as the short-range structure. There is another advantage of taking account of the Bragg peaks. Total scattering measurements provide one-dimensional data, namely data as functions of the modulus of the scattering vector, Q, and the direct interpretation is in terms of the modulus of the interatomic distance, r. Although with polycrystalline samples the Bragg peaks are projected onto a one-dimensional representation of reciprocal space, the fact that the Bragg peaks retain their $hk\ell$ indices in the data analysis means that they retain their information about the three-dimensional long-range order in the crystal structure (which is why Rietveld refinement is so successful for analysing crystal structures). It is not sufficient to simply assume that the information within the Bragg peaks is contained within the analysis of the total scattering signal. That information is actually degraded by the finite size of the simulation sample,[3] the indexing of the Bragg peaks is not brought into the analysis, and there is no direct analysis based on the distribution of atom positions. Because the LAD diffractometer was scheduled to be decommissioned during the project, and replaced by the new GEM diffractometer, we chose to start by using integrated Bragg peak intensities obtained from the diffraction patterns by the Pawley method.

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[2] After the start of our project, we became aware that this problem is also being tackled by Mellergård & McGreevy (*Chem Phys* **261**, 267, 2000). However, their solution is only appropriate for data with low values of Q_{max}, and cannot be ported to time-of-flight data with large values of Q_{max}.

[3] In order to compare the measured $S(Q)$ with the Fourier transform of the calculated pair distribution function, t is essential to convolve the $S(Q)$ data with a function that describes the finite range of the

The idea of the RMC method is to define an agreement factor for comparing a calculated quantity with experimental data:

$$\chi^2 = \sum_j (\Delta y_j)^2 / \sigma_j^2$$

where Δy is the difference between a data point and calculated quantity, and σ^2 is a weighting factor. χ^2 is treated as an energy function in a Monte Carlo sense, and the RMC method works by adjusting the positions of all atoms in the configuration through random steps until a minimum value of χ^2 is reached. In traditional RMC, χ^2 is calculated for either $S(Q)$ or the pair distribution functions. For our preliminary work on silica, we also incorporated a term in χ^2 to allow us to incorporate structural constraints on bond lengths and angles, with weightings that are adjusted to ensure that the model gives the correct widths of the nearest-neighbour peaks in the pair distribution functions.

In our first implementation of RMC for crystalline materials, we defined a term in χ^2 for the extracted Bragg intensities, comparing them with the Bragg intensities calculated from the RMC configurations via

$$I_{\mathrm{Bragg}} = \left| \sum_j b_j \exp(i\mathbf{Q} \cdot \mathbf{r}_j) \right|^2$$

With large samples, this can be calculated with only small fluctuations between different configurations. The main difficulty with this approach is handling overlapping peaks. The Pawley method takes account of overlap, but only by introducing some degree of uncertainty in a formally correct way. In the second stage of the project (§2.4) we subsequently developed a total-pattern fitting method for the analysis of the Bragg peaks, properly accounting for instrument resolution, but there was no value in beginning this second stage until GEM was in operation. The advantage for our work in starting with extracted Bragg peaks is that we used the initial LAD data to assess the effects of including the Bragg diffraction data in χ^2 relative to the other terms, both on the accuracy of the final model and the speed of convergence of the RMC method. We also assessed the relative contributions of terms based on $S(Q)$, pair distributions and constraints. We found that the best RMC simulations, both in terms of accuracy and speed to convergence, were those in which we incorporated all terms. Although $S(Q)$ and the pair distribution functions contain the same information in principle, this information is weighted differently in the two functions, and a more balanced picture could be obtained by including both functions.

The program we developed is called `RMCBragg`. It is available for other workers.

This approach was developed in a detailed study of the structural disorder in the cristobalite and tridymite polymorphs of silica, together with a detailed series of tests of accuracy and performance.

2.4 RMC method with total-pattern fitting of Bragg diffraction data and optimised for GEM data

The second stage in the development of the RMC method was to develop a total pattern fitting treatment of the Bragg diffraction. In this case, the agreement factor is between the calculated and experimental diffraction patterns, with the calculated pattern constructed from the structure factors and the instrument resolution function. We now treat each bank of detectors separately, as in our inverse fitting of the pair distribution function. Although we still have overlapping Bragg peaks, the problem is circumvented, as in the Rietveld method, by treating the whole diffraction pattern, not just the Bragg peaks alone.

We also now define a separate χ^2 for $S(Q)$ for each data bank, and in our calculations of $S(Q)$ from the configuration we now take account of the experimental resolution function (although there is a considerable computational overhead).

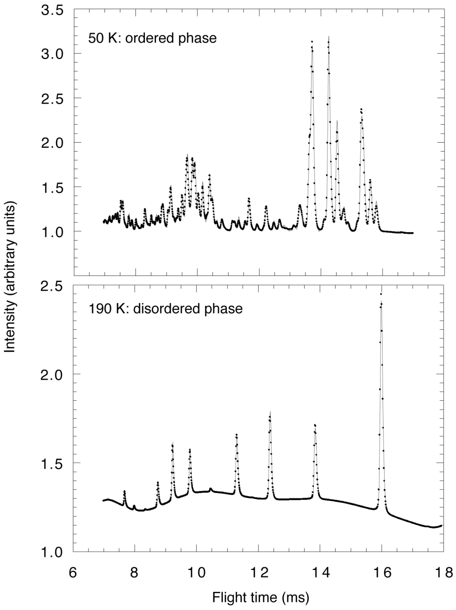

Figure 2: Total pattern fitting of Bragg diffraction data for two phases of SF_6.

The program we have developed for this work is called `RMCprofile`, and is available for other workers. Although developed for time-of-flight data, it can be used equally well for $S(Q)$ data obtained on a constant-wavelength source. A sample fit to the diffraction pattern is shown in Figure 2.

2.5 Reconstruction of three-dimensional diffuse scattering

As noted in §2.3, total scattering is a one-dimensional technique. We have explored the extent to which it is possible to use the RMC configurations, which by nature are three-dimensional, to reconstruct three-dimensional diffuse scattering. Patterns constructed for quartz are shown below. These show streaks of diffuse scattering that correspond to soft phonon modes, consistent with theory, and change on cooling through the displacive phase transition. We have quantified the picture by performing measurements of the temperature-dependence of the diffuse scattering in quartz and comparing with calculations from the RMC configurations. The agreement is striking, showing that can RMC give quantitatively correct three-dimensional patterns of diffuse scattering. The results are shown in Figure 3.

2.6 Analysis of rigid unit motions

Many of the materials we have looked at (silica, tungstates, perovskites) contain structural polyhedra. We had previously developed theoretical models based upon the existence of phonon modes in which the polyhedra can move without distortion, which we call "rigid unit modes" (RUMs). These models are appropriate for studies of displacive phase transitions and negative thermal expansion. We have recently developed a real-space version of the RUM theory based on the mathematical technique of geometric algebra, and used this to analyse the RUM structures of our RMC configurations. This approach enables us to separate rigid unit motions from distortions of polyhedra, and has enabled us, for the first time, to quantitatively determine the extent of the contribution of the RUMs to structural disorder in these materials. Some representative results will be shown below.

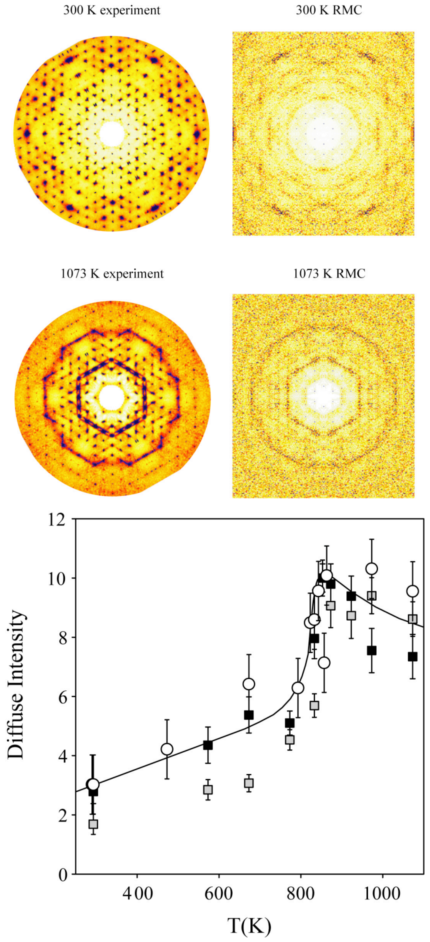

Figure 3. Top: Reconstructed maps of diffuse scattering for the two phases of quartz, compared to data we obtained on a single-crystal spectrometer. Bottom: comparison of temperature dependence of RMC diffuse intensity (circles) with single crystal measurements (squares).

3. Science achievements

3.1 Range of measurements

We have performed total scattering measurements on a wide range of systems. Our initial work concerned a series of studies of silica polymorphs, quartz, tridymite and two siliceous zeolites, augmenting our earlier series of measurements on cristobalite. We also obtained new data on silica glass for benchmarking (particularly as we now have good atomic models). The main features of these systems are the existence of networks of linked polyhedra, tying in with our ongoing research programme into the physics of network materials. Similarly, we have obtained extensive sets of data on the negative-thermal expansion network materials ZrW_2O_8 and ZrP_2O_7, and on several perovskite phases (PZT, $SrTiO_3$). We have also obtained data on molecular systems, including SF_6, C_4F_8 and $NaNO_3$, and on the combined network/molecular system Na_2CO_3. The common factor in all these studies has been to look at the phase transitions in these materials, particularly focussing on the increase in structural disorder in the high-temperature phases.

3.2 Displacive phase transition in quartz

Quartz provides a nice example of what can be achieved with our methodology. This is actually the first detailed study ever of a phase transition that considers the behaviour across short-range and long-range length scales simultaneously. Figure 1 shows the measured $T(r)$ functions as a function of temperature. These data show that the structural disorder increases gradually on heating, and there are not marked changes at the transition temperature T_c.

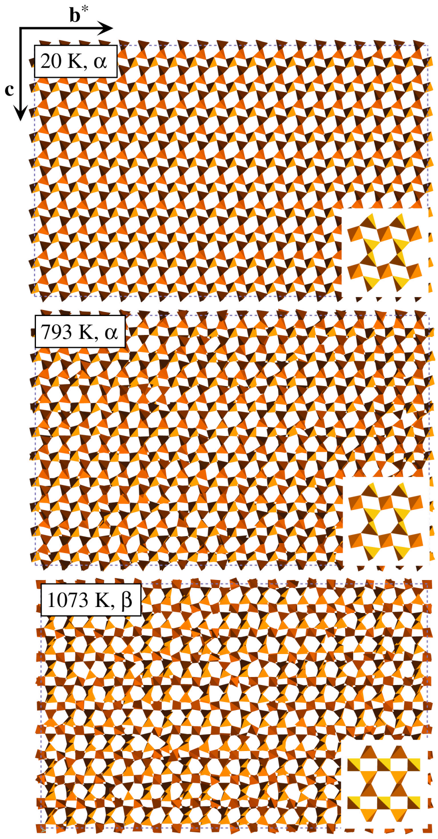

Figure 4: Three configurations of quartz from the RMC analysis. The average structure is shown in the insets. The configurations show progressive disorder on heating, with no evidence for domains of ordered structure at high temperature.

Figure 4 shows three RMC configurations, one at very low temperature, one just below the phase transition, and one in the high-T phase. The low-T configuration has a high degree of order, the intermediate-T one has the average structure of the low-temperature phase but with considerable disorder in the orientations of the SiO_4 tetrahedra, and the high-T configuration shows a high degree of disorder. The main result from analysis of the configurations is that the structure of the high-T phase does not consist of a patchwork of domains of the low-temperature ordered phase, contrary to the viewpoint (unsubstantiated) of many workers. We are confident that these configurations are consistent with experiment because of the good agreement between calculated and measured diffuse scattering, §2.5.

Based on these results, we have provided an explanation of the behaviour of quartz through the phase transition. There is considerable orientational disorder of the SiO_4 tetrahedra, which can arise from low-frequency phonons in which the tetrahedra rotate as rigid units, which we call Rigid Unit Modes, RUMs[7]. The phase transition allows the excitation of a whole spectrum of RUMs that provides a background of orientational disorder in the crystal structure at high temperatures. The phase transition involves an instability in just one of these RUMs.

We have performed a detailed quantitative analysis of a number of structural correlations from these configurations. One interesting correlation is the Si–Si–Si angular distribution function, which shows the effects of both changes in long-range order and the onset of disorder that grows on heating towards the high-temperature phase.

Using our geometric algebra methods, we have quantified the degree of disorder between configurations. Figure 5 shows the result of this analysis. At high temperatures, the largest part of the atomic displacements is due to the RUM motions, and on cooling through the phase transition the RUM component is reduced quite markedly. This result is in agreement with theoretical estimates.

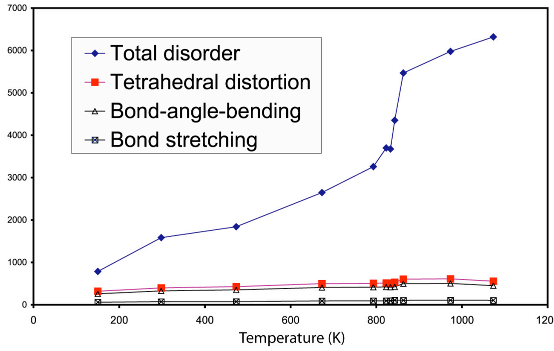

Figure 5. Geometric analysis of the temperature-dependence of the contributions to the structural disorder in quartz. It is clear that most of the disorder at high-T arises from RUMs, with the fraction of modes that are RUMs decreasing on cooling through the phase transition.

The result of this study has been a completely new view of the phase transition in quartz, which excludes domain models and incorporates the conventional soft-mode picture. In this view we see the importance of large-amplitude fluctuations that are generated by the phase transition but which are not associated with the fluctuations in the order parameter. We have obtained similar results for phase transitions in the other polymorphs of silica. Our results on quartz have now been used for comparisons with molecular dynamics simulation models by Müser & Binder (*Phys Chem Min* **28**, 746, 2001).

The RMC analysis, including the geometric algebra analysis, has also been used to interpret the negative thermal expansion in one of our zeolite samples. The same approach has been used for the study of the negative-thermal expansion materials ZrW_2O_8 and ZrP_2O_7. A part of one of the configurations of ZrW_2O_8 is shown in Figure X, showing the large amplitude orientational disorder of the structural polyhedra.

The conclusion from this work is that we now have a tool that can provide unique data-based information about displacive phase transitions, and which is free from any artefacts of interatomic potential models.

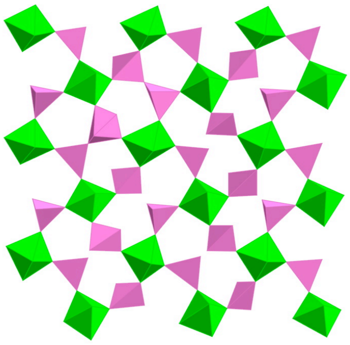

Figure 6. Part of the RMC configuration of ZrW_2O_8, showing orientational motions of ZrO_6 and WO_4 polyhedra that give rise to negative thermal expansion.

3.3 Molecular disorder in SF_6

SF_6 is an octahedral molecule, which crystallises in a simple bcc structure. On average, the S–F bonds point along the <100> axes, but there has long been experimental and simulation evidence for the existence of rotational disorder. Some years ago we proposed on the basis of our simulation results that the origin of this disorder arises from orientational frustration interactions. The interactions between nearest-neighbour (<1/2,1/2,1/2>) molecules act to order their orientations with respect to the crystal axes, but with the F…F closest neighbours on next-nearest neighbour (<100>) molecules strongly opposing this orientational order. As a result, the molecules tumble to avoid close F…F contacts. The use of total scattering with RMC has given us the first opportunity to test this idea experimentally. This was also one of the first experiments we performed using GEM during its commissioning phase.

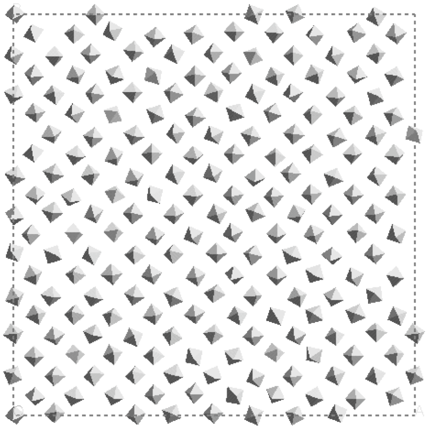

Figure 6. (100) configuration of SF_6 in its disordered phase, showing the molecules as octahedra.

An RMC configuration is shown in Figure 6. This shows that the molecules are oriented with the S–F bonds close to the <100> directions, but with considerable orientational disorder. The important analysis concerns the F…F contact distances for nearest and next-nearest neighbour molecules. The distribution function is shown in Figure 7. The important feature is the peak in the second-neighbour distribution function at 3.2 Å. This is at a significantly larger distance than if the molecules were vibrating independently (2.5 Å), and is clear evidence of the repulsive interaction that drives the existence of the orientational disorder seen in the RMC configurations. The molecular correlations have also been analysed using correlation functions with symmetry-adapted rotational coordinates.

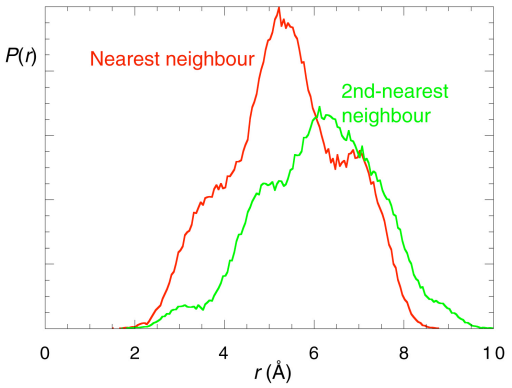

Figure 7: Intermolecular F..F distance distribution function for nearest and next-nearest neighbour molecules.

Similar types of results have been obtained for the other molecular systems we have investigated.

The importance of this aspect of our work is that Bragg diffraction is notoriously difficult for the analysis of rotationally disordered crystals. Usually the number of Bragg peaks is tiny – for example, for the high-*T* phase of C_4F_8, there are only 4 Bragg peaks in our data (even with the high quality of data that can be obtained on GEM). Moreover, the structural analysis cannot be undertaken on the basis of atoms having average positions. Instead, it has been common to analyse data in terms of molecular orientational distribution functions expanded in terms of the symmetry-adapted rotational variables (linear combinations of spherical harmonics). These expansions cannot usually be taken to high order, and as a result the derived orientational distribution functions are often found to be non-positive definite. The RMC approach automatically constrains the functions to be positive definite, and properly takes account of correlations between the orientations of neighbouring molecules, which is often central to understanding the physics of these materials. Our tools will now enable better structural studies to be undertaken on these materials.

4. Summary

The main outcomes from this work are of two types. First is the development of RMC methods for studies of disordered crystalline materials, where we exploit the existence of Bragg peaks to provide simultaneous information about structural order on both long-range and short-range length scales. This is a unique tool for the study of disordered crystalline materials; all other tools provide information only about one of these two aspects. Our tools not only provide both aspects, but also give the link between them. Furthermore, for disordered materials, the RMC analysis overcomes some of the shortcomings of standard crystallographic analysis due to limitations in the information contained within the usual Bragg diffraction pattern. In order to develop the RMC analysis to take account of the unique features of the new GEM diffractometer at ISIS, we have developed new codes for the calculation of pair distribution functions. Both the RMC and pair distribution function codes are available for the wider community to use. But wider than this, we are now offering the neutron scattering community a new approach to the study of disordered crystalline materials, which is closely tied to the unique capabilities of the GEM diffractometer. With the EPSRC support for this project, we have been the main group to exploit the capability of this instrument for obtaining both Bragg diffraction and total scattering data simultaneously. Other groups are now picking up on the possibilities that we have opened up.

The second outcome is the science we have been able to carry out with our methodologies. We have focussed mostly on structural disorder that arises from the existence of structural phase transitions. The unique information that can be obtained from our methods has enabled us to obtain new views of structural phase transitions. For quartz, for example, we have been able to understand the origin of the disorder in the high-temperature phase, cutting though previous attempts to understand the phase transition that had only been able to account for part of the picture. We have incorporated new analysis tools (based on geometric algebra) we have developed to give a detailed analysis of the atomic configurations generated by the RMC simulations, tying the results with theory. We only have space to report on a small subset of the systems we have studied, but similar types of results have been obtained for other systems.

4. References arising from this project

1 Application of the Reverse Monte Carlo method to crystalline materials. MG Tucker, DA Keen and MT Dove. Journal of Applied Crystallography **34**, 630–638, 2001

2 Dynamic structural disorder in cristobalite: Neutron total scattering measurement and Reverse Monte Carlo modelling. MG Tucker, MD Squires, MT Dove and DA Keen. *J Phys: Cond Matter* **13**, 403-423, 2001

3 A detailed structural characterisation of quartz on heating through the □–□ phase transition. MG Tucker, DA Keen and MT Dove. *Mineralogical Mag* **65**, 489–507, 2001

4 Direct measurement of the thermal expansion of the Si–O bond by neutron total scattering. MG Tucker, MT Dove and DA Keen. *J Phys: Cond Matter* **12**, L425–L430, 2000

5 Rigid Unit Modes in framework structures: theory, experiment and applications. MT Dove, KO Trachenko, MG Tucker and DA Keen. *Rev Min & Geochem* **39**, 1–33, 2000

6 Simultaneous analyses of changes in long-range and short-range structural order at the displacive phase transition in quartz. MG Tucker, MT Dove and DA Keen. *J Phys: Cond Matter* **12**, L723–L730, 2000

7 A comparison of various commonly used correlation functions for describing total scattering. *J Appl Cryst* **34**, 172–177, 2001

8 MCGRtof: Monte Carlo *G*(*r*) with resolution corrections for time-of-flight neutron diffractometers. MG Tucker, MT Dove and DA Keen. *J Appl Cryst* **34**, 780–782, 2001

9 Neutron total scattering method: simultaneous determination of long-range and short-range order in disordered materials. MT Dove, MG Tucker and DA Keen. *European Journal of Mineralogy* (in press)

10 Total scattering and Reverse Monte Carlo modelling of disordered crystalline materials. MG Tucker, MT Dove and DA Keen. In *From semiconductors to proteins: beyond the average stucture* (ed SJL Billinge and MF Thorpe) (in press)

11 Finding best-fit polyhedral rotations with geometric algebra. SA Wells and MT Dove. *J Phys: Cond Matter* (submitted)

12 Real-space rigid unit mode analysis of simulations of framework structures. SA Wells, MT Dove and MG Tucker. *J Phys: Cond Matter* (submitted)

13 MG Tucker, MT Dove, and DA Keen. Profile refinement in Reverse Monte Carlo analysis of total scattering data from polycrystalline materials. *J Appl Cryst* (submitted)

A number of other papers on systems we have looked at are being prepared for publication. Due to the staging of key components of the research project, the main flow of analysis of results came right at the end of the project.