

# SXD: Novel Single Crystal Studies using the Time-Of-Flight Laue Technique

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## Abstract

Some of the novel applications of time-of-flight Laue diffraction performed on the SXD instrument at ISIS are discussed. The power of the technique both in structural refinement and in diffuse scattering studies is stressed.

## Introduction

SXD, the single crystal diffractometer at ISIS (Figure 1), uses the Laue time-of-flight diffraction technique (Wilson, 1993a) for structural studies. This method exploits the ability of an instrument equipped with a 2D position-sensitive detector (PSD) on a pulsed neutron source to access large volumes of reciprocal space in a single measurement and has significant advantages in many areas of structural work.

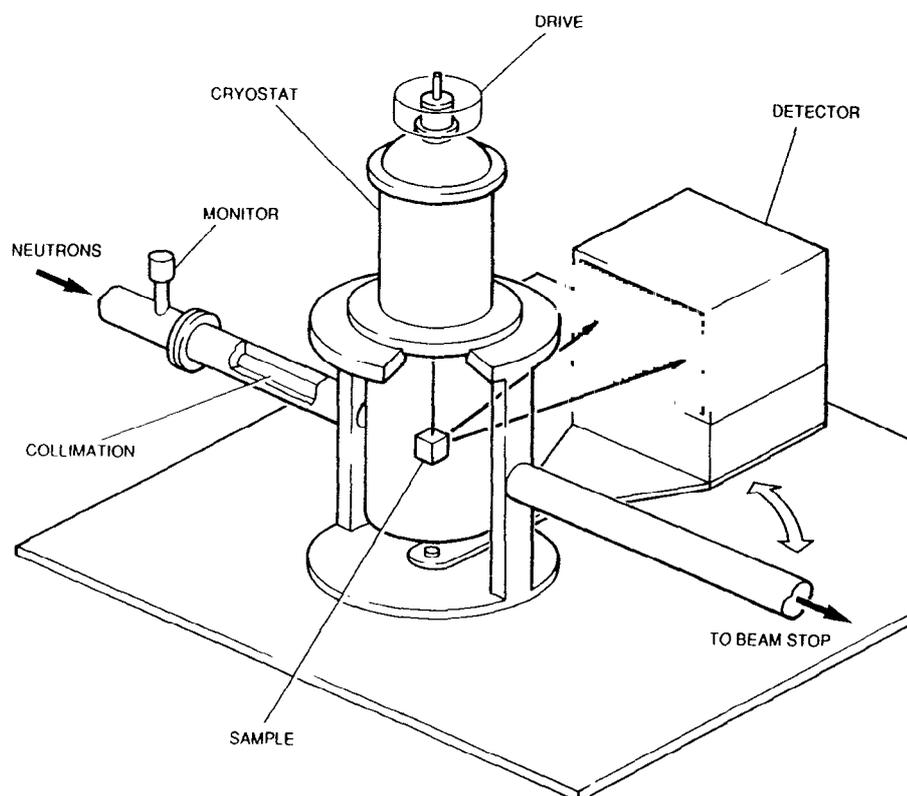


Figure 1 - The time-of-flight Laue instrument SXD at ISIS.

The first areas in which SXD was successful (Wilson, 1990) were those of the examination of incommensurate structures and the more qualitative aspects of diffuse scattering, these being the most obvious areas in which an ability to conveniently measure the regions between Bragg peaks is especially useful.

More recently, however, improvements in the instrumentation, especially the provision of larger, more reliable PSDs, have enabled the extension of the scientific programme. SXD is now fully capable of routinely performing a full range of single crystal studies, for example:

- Structural studies - chemical crystallography, the location of hydrogen atoms (Wilson, Stewart and Keen, 1992; Wilson, 1993b), the study of long range static disorder (Artioli et al, 1993), the exploitation of the high  $\sin \theta/\lambda$  measurements possible on a spallation source (Keen, Hannan and Wilson, 1993);
- Diffuse scattering studies - the study of short range order and disorder, quantitative atomic level cluster modelling (Hull and Wilson, 1992), quantitative Reverse Monte Carlo type modelling (Li et al, 1993).
- Incommensurate structures and phase transitions - the study of magnetic structures, the monitoring of structural changes from single data histograms (Wilson, 1993c).

### **Structural Studies**

The application of time-of-flight Laue diffraction in routine structural studies broadly mirrors that of any neutron single crystal diffractometer, primarily involving the location of hydrogen atoms or the differentiation of atoms with similar atomic numbers. The nature of the time-of-flight Laue technique, however, is such that the data collection and reduction are significantly different from traditional techniques. By using the wide wavelength range available from a pulsed source such as ISIS, which with time-of-flight is uniquely non-prejudicial in terms of overlap, and combining this with large area PSDs, an instrument such as SXD is found to measure many reflections simultaneously (see Figure 2). Thus the coverage of reciprocal space is achieved in a series of histograms, typically a dozen or so, rather than by scanning individual reflections. The angle- and wavelength-dependent corrections are more severe (but occasionally, in favourable cases, more informative) than in the fixed wavelength case, and this tends to lead to slightly poorer agreement factors than are available from a fixed wavelength, step scanning instrument. In addition, there is some evidence that the non-uniform statistical distribution of intensities measured using time-of-flight Laue can also adversely affect the resulting crystallographic R-factor (Wilson, 1993d). Nonetheless, both accuracy and precision can be obtained in structural studies on SXD, as shown in the following examples:

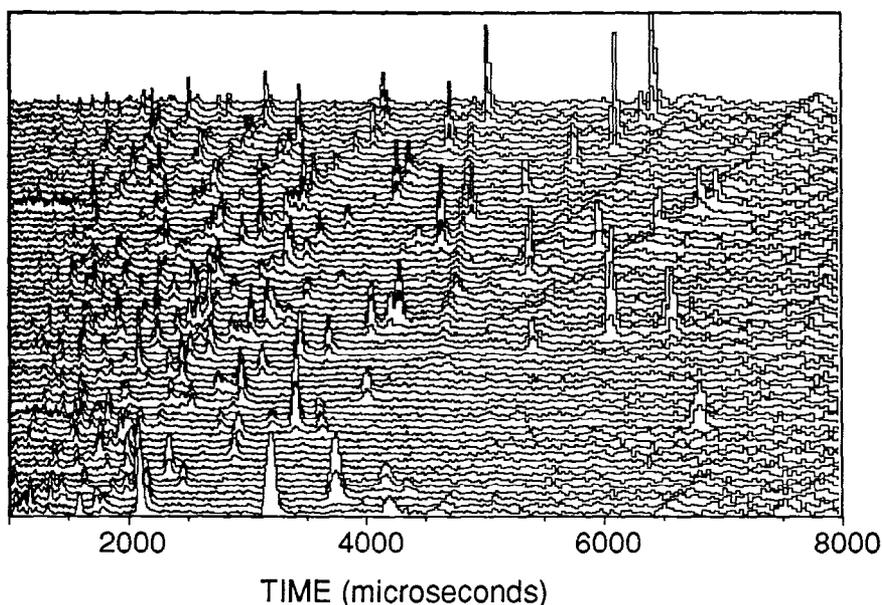


Figure 2 - Representation of the large number of reflections (around 400) measured in a single histogram on SXD from urea phosphoric acid.

**(i) Hydrogen atom location in the organic structure 3-deazauracil**

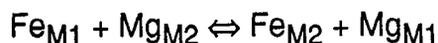
X-ray studies of this material had yielded the heavy atom framework and indicated a strong ( $\sim 2.5 \text{ \AA}$ ) O-H...O hydrogen bond. However, the combination of the poor visibility of hydrogen atoms for X-rays and the obviously high non-bonding electron density in this region precluded hydrogen atom location. As this hydrogen bond is thought to play a crucial role, in the cytostatic properties of the parent drug 3-deazauridine, location of this hydrogen atom is important. Two experiments were carried out on SXD to investigate this material. In the first, using a smaller area PSD, a "quasi-equatorial" data set was collected, roughly equivalent to one or two layer lines in Weissenberg geometry, and the resulting 80 neutron structure factors were used in combination with the earlier X-ray data in a joint X-n refinement. This revealed unambiguously the location of the vital H atom on O4, rather than the alternative O2 site (Wilson, Stewart and Keen, 1992). A subsequent full data set collected on SXD using the larger detector led to neutron-only refinements which agreed well with the joint refinement (Wilson, 1993b). In addition to confirming the obvious utility of neutron data in cases such as this, the ability of even a limited data set to reveal correct and useful information in combination with other data, was extremely encouraging.

**(ii) Fe/Mg ordering in olivine at high temperatures**

Olivine,  $(\text{Mg,Fe})_2\text{SiO}_4$ , is the most constituent of the upper terrestrial mantle and a common rock forming mineral. In the structure of olivine, Mg and Fe can be distributed over two structural sites, M1 and M2, which have slightly different octahedral configurations. There are, however, conflicting crystallochemical factors which influence the Mg-Fe ordering onto the two sites, which superficially seem to

suggest that there is more likelihood of Fe<sup>2+</sup> occupying M1. There are also, however, other effects such as composition, oxygen fugacity, pressure and especially temperature, which can affect the relative distribution of the two cations.

The determination of the equilibrium in the exchange reaction



as a function of temperature can provide important information on the cooling history of the host rocks. Recent X-ray experiments on olivine samples quenched from various temperatures seem to indicate that iron tends to concentrate in site M1 as the temperature increases. However, olivines quenched from temperatures above 800°C show the same equilibrium constant as those of crystals quenched from 700°C, indicating that the maximum temperatures which can be determined by this technique is in the region of 700-800°C. This is because the rate of cooling, even for very rapid quenching techniques, is lower than the speed of the exchange reaction at temperatures above 800°C. The only way to truly monitor this equilibrium above 800°C is to carry out an *in situ* experiment at these temperatures. The convenience of high temperatures experiments using neutron diffraction allows a single crystal neutron scattering experiment to measure this equilibrium.

The sample used in the SXD experiment (Artoli et al, 1993) was an olivine single crystal of volume some 5 mm<sup>3</sup> taken from a pallastic meteorite from Kansas, whose iron content (> 10%) is sufficient to allow a reliable determination of the site content. Data were collected at two temperatures (880°C and 1060°C) and the results of the refinements at the two temperatures are shown in Table 1. All atoms were refined with anisotropic temperature factors, with the site occupancies refined both with Mg/Fe temperature factors fixed and with these parameters varying, with essentially identical results. The Fe temperature factors were fixed to be identical with those of the equivalent Mg atom and the overall site occupancies were constrained to add up to one on each site.

<b>Table 1</b>	
Neutron refinement parameters for olivine	
T=880°C, R <sub>w</sub> =0.058 for 319 data, 42 refined parameters	a=4.788(3), b=10.349(3), c=6.061(2) Å; V=300.3 Å <sup>3</sup>
K <sub>D</sub> =1.45, Fe(M1)=0.140(26), Fe(M2)=0.100(26)	
T=1060°C, R <sub>w</sub> =0.062 for 238 data, 42 refined parameters	a=4.792(3), b=10.361(3), c=6.082(2) Å; V=302.0 Å <sup>3</sup>
K <sub>D</sub> =0.47, Fe(M1)=0.081(40), Fe(M2)=0.159(40)	

The most remarkable result is that, while the Fe occupies the site M1 preferentially at 880°C as expected from the previous experiments on quenched samples, there are clear indications that at the higher temperature Fe preferentially occupies site M2. This result, unexpected from all previous X-ray results, indicates that there is a significant alteration in the Fe/Mg equilibrium above 880°C. This shift in equilibrium occupancy is obviously masked in studies of quenched samples by the speed of the exchange reaction, and is therefore only accessible in an experiment performed at

the higher temperature. This shift in preferential occupancy will also have implications for the position of the equilibrium in those samples quenched from above 800°C. Such a conclusion has significant implications for our understanding of rock-forming processes.

**(iii) High  $\sin\theta/\lambda$  measurements - the exploitation of epithermal neutrons**

In previous measurements on the fluorite material  $\text{SrF}_2$  on SXD (Forsyth, Wilson and Sabine, 1989) it was found to be possible to refine the anharmonic thermal vibrations in this structure to high precision even at room temperature, where the effect is obviously smaller than at elevated temperatures. However, even at room temperature there remains a significant contribution to the scattering at and around the Bragg peaks from thermal diffuse scattering (TDS). The simplest way to reduce TDS effects is to reduce the temperature but unfortunately this will also reduce the thermal vibrations of the atoms and hence make any anharmonic effects still more difficult to measure. However, the effect of anharmonicity on structure factors and hence on reflection intensities, increases with  $Q$  (and hence  $\sin\theta/\lambda$ ) and given that higher  $Q$  data ought to be accessible at lower temperature as the Debye-Waller factors reduce, it may be possible to measure and refine anharmonic effects, uncorrupted by TDS, even at low temperatures. SXD is an ideal instrument with which to attempt this, as the combination of the favourable properties of the neutron (no form-factor fall-off with  $Q$ ) and of ISIS (high flux of epithermal neutrons, especially on the ambient water moderator on which SXD is sited) should allow very

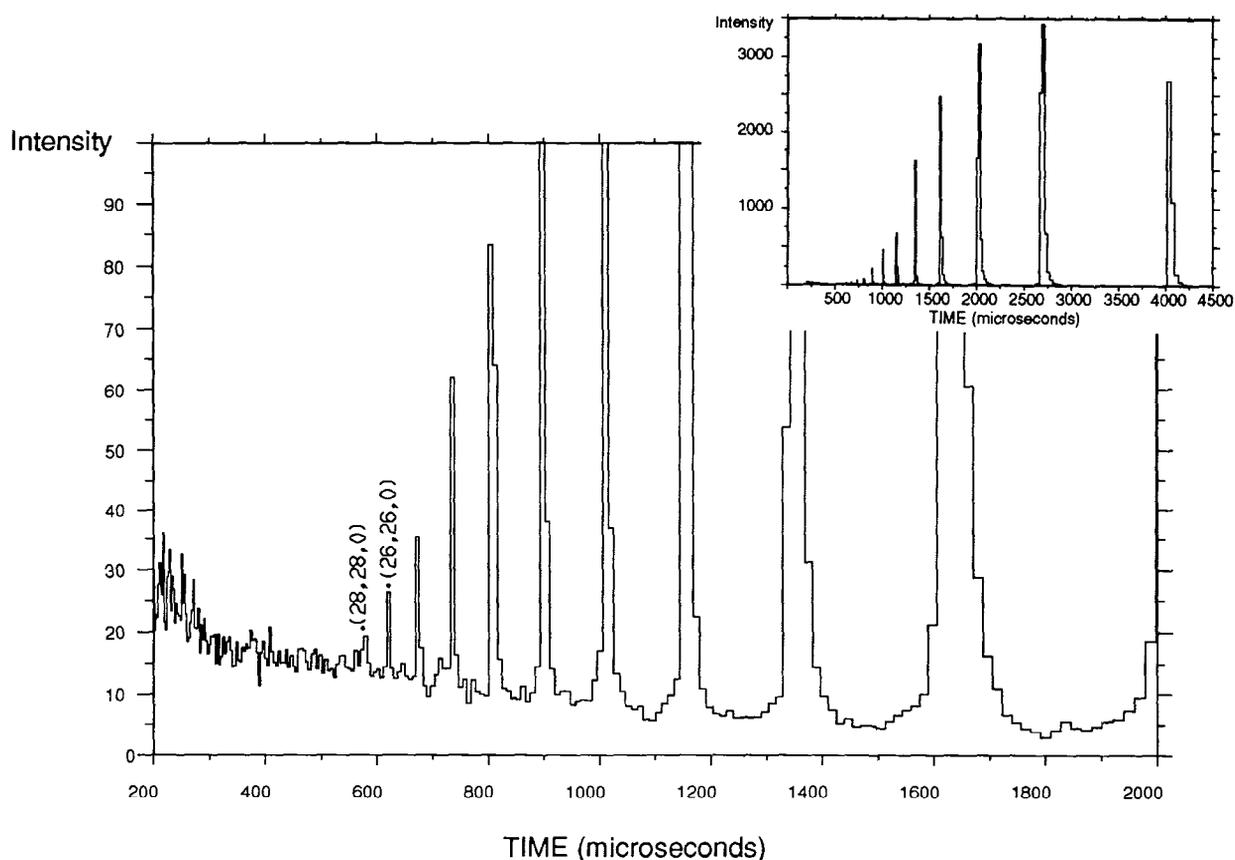


Figure 3 - The  $(hh0)$  row of reflections in  $\text{SrF}_2$  measured at 25 K on SXD, showing the  $(28,28,0)$  reflection at  $\sin\theta/\lambda$  of  $> 3.3 \text{ \AA}^{-1}$ .

high resolution data to be accumulated. Accordingly, a data set was measured from SrF<sub>2</sub> at 25 K on SXD. The data are in the process of being analysed, but the promise of this approach is indicated by the observation of the (28, 28, 0) reflection (from a cubic crystal, with  $a = 5.8 \text{ \AA}$ ; Figure 3), representing a  $\sin\theta/\lambda$  value of  $> 3.3 \text{ \AA}^{-1}$  ( $Q > 40 \text{ \AA}^{-1}$ ). Since the earlier work extended the  $\sin\theta/\lambda$  range to  $< 1.7 \text{ \AA}^{-1}$ , the prospects for analysing detailed thermal effects at this low temperature seem realistic, and work is continuing on this (Keen, Hannan and Wilson, 1993).

### Diffuse scattering studies

While SXD remains an extremely powerful surveying instrument for examining diffuse and/or incommensurate scattering patterns, the emphasis of the diffuse scattering programme has now shifted from elegant demonstrations of this capability to much more quantitative applications of the technique. Unlike routine structural refinement, interpretation of results in this field is still difficult, but is extremely rewarding and informative when successful. Detailed results have now been obtained using both cluster modelling and Reverse Monte Carlo type analysis. The rapid, accurately quantitative results obtained using SXD, and in particular the combination of these with simultaneous Bragg reflection measurements, are extremely favourable for further advances in these areas.

#### (i) *Defect clusters in (Ca,Y)F<sub>2+x</sub> as a function of temperature*

Structural information concerning defect clusters within non-stoichiometric compounds can be obtained from both Bragg and diffuse scattering measurements. The average unit cell structure is determined from the Bragg scattering, while direct information concerning the local arrangement of the defect cluster is obtained from the coherent diffuse scattering, which often exhibits broad maxima between the Bragg peaks. Both types of data are readily accessible on SXD.

The defect structure of the anion-excess fluorite Ca<sub>0.94</sub>Y<sub>0.06</sub>F<sub>2.06</sub> was investigated using both Bragg and diffuse scattering measurements on SXD at 20° and 900°C. It is found that the best agreement with both Bragg and diffuse scattering information at low temperatures (Figure 4) is obtained by adopting a defect cluster which results from the conversion of six edge-sharing (Ca,Y)F<sub>8</sub> cubes into corner-sharing square antiprisms (Hull and Wilson, 1992). These cuboctahedral clusters are a general feature of ordered anion-excess yttrifluorites, and the SXD results, by combining the two types of diffraction information, indicate that these clusters are also present, but randomly distributed, in the disordered solid solution of (Ca,Y)F<sub>2+x</sub>.

At higher temperatures, approaching the fast-ion transition, the diffuse scattering has a radically different appearance (Figure 5). Again both Bragg and diffuse scattering data were used in the analysis and clearly indicate that at 900°C the cuboctahedral clusters have broken up and the main type of defects in the structure are now Frenkel type anions, with further relaxation of anions into positions previously unoccupied at 20°C (Hull, Hoffmann and Wilson, 1993). The high temperature pattern thus closely resembles that from stoichiometric CaF<sub>2</sub> in which these Frenkel defects are the medium for fast-ionic conductivity. The availability of such **quantitative** information from a combination of Bragg and diffuse scattering lends great power to this area of application.

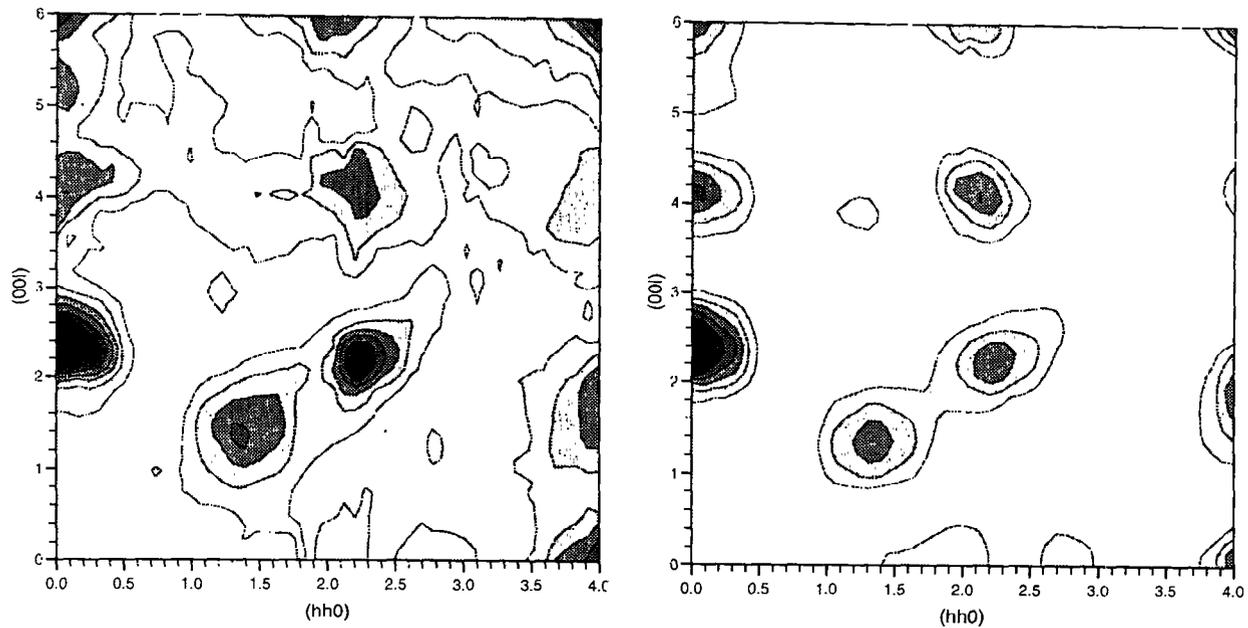


Figure 4 - Observed (left) and calculated (right) coherent diffuse scattering from  $(\text{Ca}, \text{Y})\text{F}_{2.06}$  at  $20^\circ\text{C}$ . The latter is calculated using isolated cuboctahedral clusters to accommodate the excess fluorine atoms.

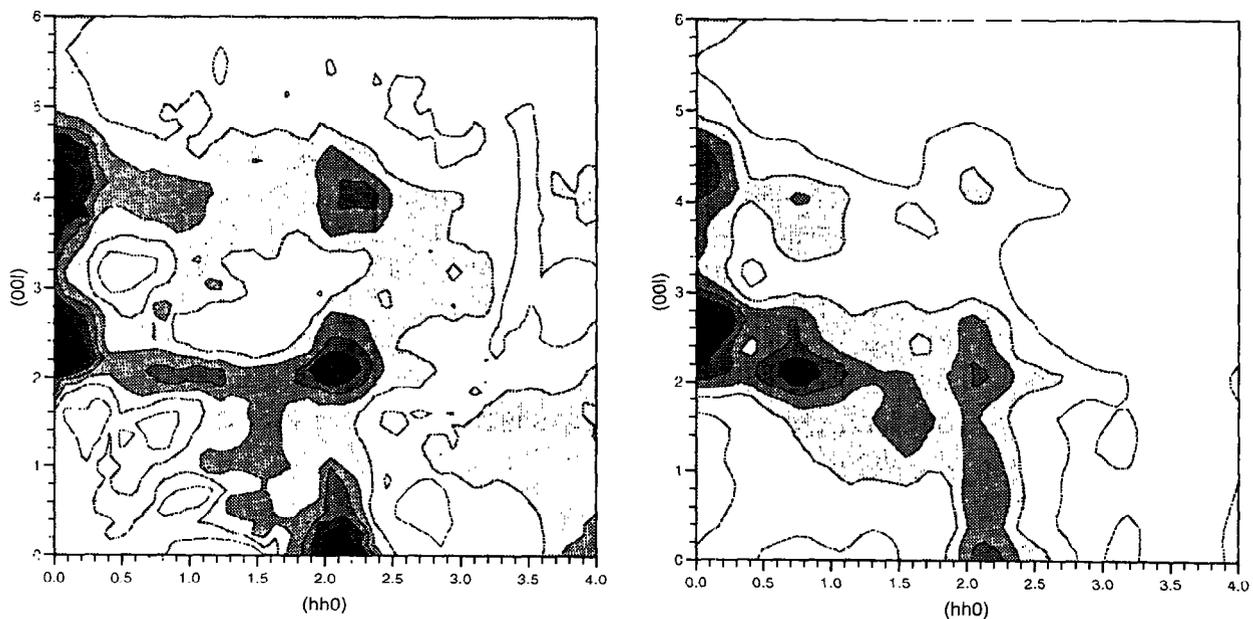


Figure 5 - Observed (left) and calculated (right) coherent diffuse scattering from  $(\text{Ca}, \text{Y})\text{F}_{2.06}$  at  $900^\circ\text{C}$ . The latter is calculated using isolated Frenkel defect-like excess fluorine atoms.

## (ii) Short range proton ordering in Ice Ih

The normal form of ice, ice Ih, consists of a tetrahedrally coordinated oxygen network, with the hydrogen atoms arranged so as to obey the Bernal-Fowler 'ice rules'. These state that each oxygen is bonded to two hydrogens, with one hydrogen on each O...O bond. In ice Ih the hydrogens obey these rules but are disordered with respect to one another. In order to examine this disorder and to see whether there is any local ordering of the protons a comprehensive study of the diffuse scattering from single crystal D<sub>2</sub>O ice Ih has been made on SXD, where the large region of reciprocal space measured is of particular benefit. To date the diffuse scattering has been measured in the (hhl) and (h0l) planes at 20 K and in the (hk0) plane at 10, 20, 110, 160 and 250 K.

The scattering in the (hhl) plane is shown in Figure 6. This is found to be very structured as the most significant features result from static disorder. A simulation in which the standard crystallographic positions for the atoms were used with the hydrogens completely disordered within the Bernal-Fowler rules (Figure 6) clearly reproduces the hexagonal rings. However, it fails to pick up the very strong diffuse streak stretching along (00l) from the (330) position. Further investigation suggests that this feature originates from a slight change in the H-O...H bond angle. No evidence has yet been found for any local ordering of the hydrogens beyond that expected from the 'ice rules'. Simulations are continuing using various innovative fitting techniques, such as RMC, and this work again stresses that the possibility of quantitative analysis of such diffuse scattering patterns is adding to our understanding of the underlying structural processes.

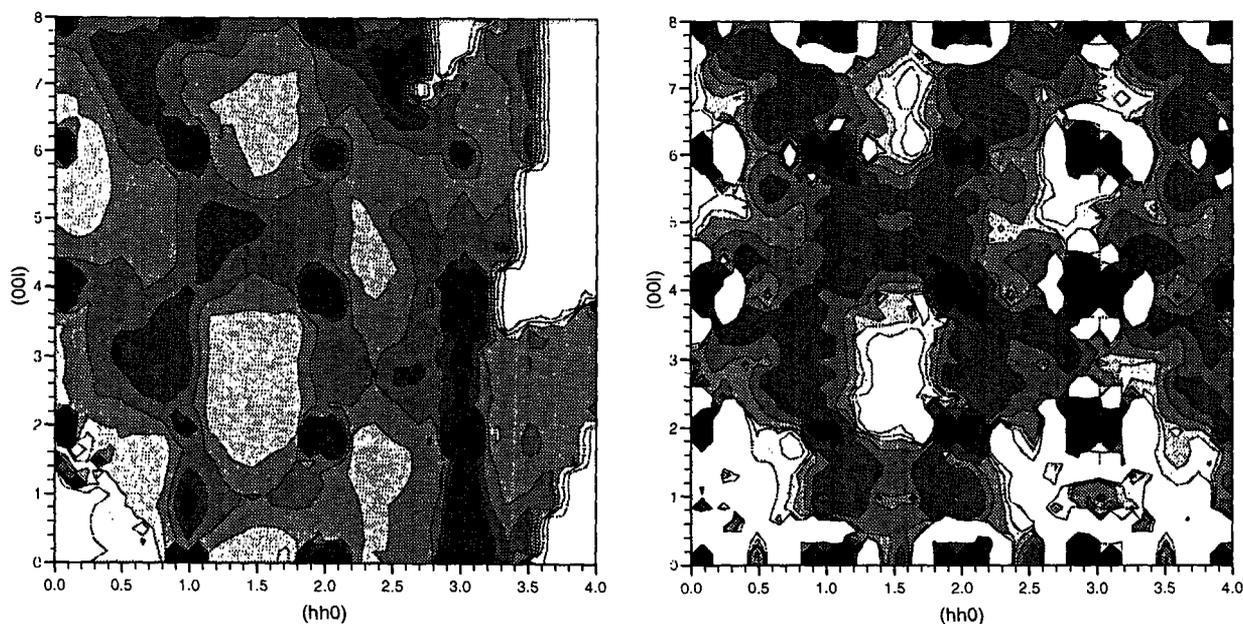


Figure 6 - Observed (left) and simulated (right) scattering in the (hhl) plane of Ice Ih at 20 K.

## Phase transitions

The study of phase transitions can be carried out in two ways using time-of-flight Laue diffraction. The first is the conventional manner in which full data sets are collected under each set of physical conditions, from which full refinements can yield the significant changes. This is most convenient for high symmetry systems if a single crystal sample is used, as then the amount of data comprising a more or less complete data set can be minimised. The alternative is to take advantage of the fact that frequently a phase transition can be characterised by the changes in a small subset of reflections - in this case the use of relevant  $\Delta(F)/\Delta(\text{parameter})$  methods (Wilson, 1993c) on this subset can yield sufficient information. Ultimately, for the time-of-flight Laue method, the aim is to reduce the amount of data collected to a single histogram, with optimisation of the sample orientation to maximise the amount of unique information available in this single shot. In this way the experimental set-up is the most convenient for the alteration of sample environment parameters as the sample and detector can remain completely stationary throughout the entire experiment.

### *(i) Single histogram dynamic scanning of the simulated dehydration of cytosine monohydrate*

Single crystals of the nucleic acid base cytosine monohydrate ( $\text{C}_4\text{H}_5\text{N}_3\text{O}_2 \cdot \text{H}_2\text{O}$ ) undergo an unusual dehydration reaction in which the water of crystallisation is lost while leaving the crystal structure essentially unaltered. The dehydration reaction occurs over a period of some 50 hours at  $40^\circ\text{C}$ , and thus "real-time" crystallographic monitoring of the reaction would require data collection periods of the order of 1-2 hours. This means there would be time for only histogram snapshot at each set of conditions (in this case elapsed time). In this respect time-of-flight Laue diffraction has a major advantage in that the group of reflections measured in a single shot are measured at genuinely the same time and under the same conditions - the usual scanning restriction that conditions change as a set of scans are performed does not affect this type of measurement.

The unit cell of this material is moderately complex, and more importantly in the context of extracting useful structural information from limited data, is of low symmetry. The cell is monoclinic,  $P2_1/c$ ,  $a = 7.78$ ,  $b = 9.82$ ,  $c = 7.67 \text{ \AA}$ ,  $\beta = 99.6^\circ$ , and there are some 656 reflections accessible to a  $d_{\text{min}}$  of  $1.0 \text{ \AA}$ .

This system is thus ideal for an investigation of the possibilities for single histogram dynamic scanning in time-of-flight Laue diffraction as the end points of the refinement will be well fixed. The general strategy is to perform full structural refinements on the end members of the reaction and use these to fix appropriate parameters within the necessarily limited refinements from the single histogram data. In an ideal case the experiment can also be designed to focus on a histogram in which the structure factor changes throughout the transition are maximised, that is the optimal  $\Delta F - \Delta(\text{parameter})$  path can be exploited. Thus it might be possible to focus on rather subtle changes in reaction path, reaction rate etc, given this optimal set of  $\Delta F$  values.

To date only a simulated experiment has been performed, to test the principle. Structure factor sets were generated for various  $\text{H}_2\text{O}$  occupancies in the range 1.0

(monohydrate) to 0.0 (fully dehydrated). The generated structure factors were allocated quasi-random errors based on their magnitudes (not at this stage on intensity statistics) and extinction was assumed not to be present. For each of the six occupancy levels generated, there were some 605 reflections in the full data set, with some 83 of these in the single histogram selected for the limited data set. This histogram was selected essentially at random - it was not chosen in this case to optimally reflect the expected structure factor changes during the reaction.

The structure chosen as the starting point was that reported by McLure and Craven (1973) for cytosine monohydrate. It was assumed that any cell contraction during the dehydration reaction would be isotropic and that the only significant changes in the structure would be to the scale factor and the occupancies of the water molecule. Variations in the scale factor were taken account of in the simulated data, and all other parameters were fixed at their values from the monohydrate structure. In the refinements, therefore, there were three parameters related to the dehydration reaction, the occupancies of the oxygen and two hydrogen atoms. All refinements commenced from full H<sub>2</sub>O occupancy and converged in five or fewer refinement cycles. The data from the refinements are summarised in Table 2 and Figure 7.

	Full data			Limited data		
	<i>O1 occ</i>	<i>H1 occ</i>	<i>H2 occ</i>	<i>O1 occ</i>	<i>H1 occ</i>	<i>H2 occ</i>
<i>OCC=1.0</i>	0.999(2)	1.001(4)	1.006(4)	0.999(4)	1.021(12)	0.978(11)
<i>OCC=0.8</i>	0.801(2)	0.811(4)	0.805(4)	0.779(5)	0.811(8)	0.828(9)
<i>OCC=0.6</i>	0.605(2)	0.606(4)	0.616(4)	0.589(5)	0.585(9)	0.623(9)
<i>OCC=0.4</i>	0.406(2)	0.412(4)	0.398(4)	0.387(5)	0.404(8)	0.414(8)
<i>OCC=0.2</i>	0.208(2)	0.224(4)	0.196(4)	0.196(5)	0.182(8)	0.204(8)
<i>OCC=0.0</i>	0.001(2)	-0.005(4)	-0.003(4)	0.007(4)	-0.002(8)	0.015(7)

It can be seen from these that the results from the limited data show great promise. In spite of necessarily reduced precision, the values obtained for the occupancies are in good agreement with those from the full data refinements. This illustrates that it is in fact possible to obtain useful structural information from single histogram 'dynamic' scanning measurements from single crystals on a time-of-flight Laue instrument. While the precision of such dynamic refinements will necessarily be limited, as a consequence of the limited data accessed in a single shot, substantive information can be obtained, yielding important transitory structural information. Further investigations are in progress on this system, including optimising the  $\Delta F$ - $\Delta(\text{parameter})$  path and further refinements in which the temperature factors and positional parameters are perturbed (Wilson, 1993c).

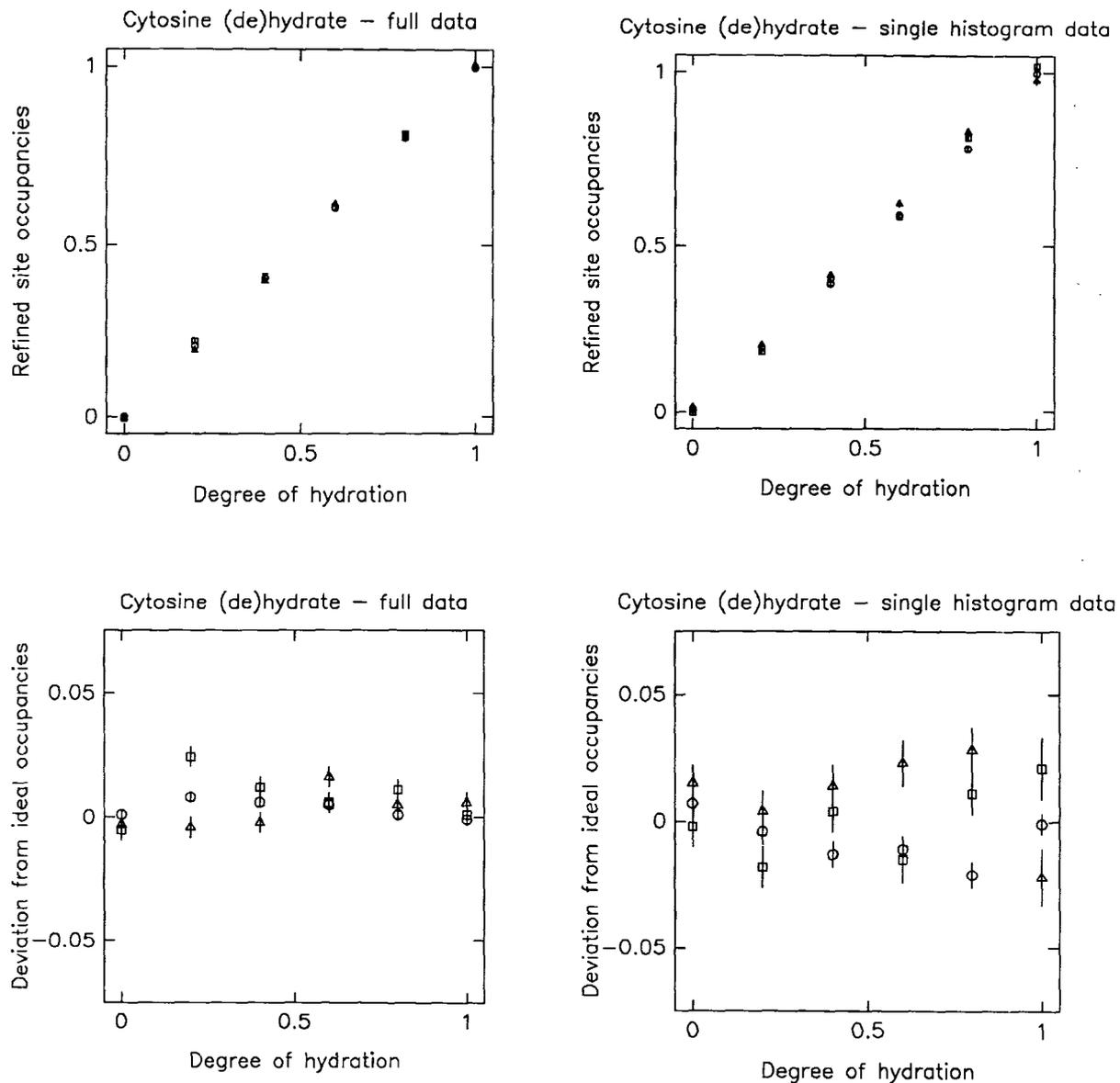


Figure 7 - Dehydration of cytosine monohydrate. (top) Refined site occupancies from full (left) and single histogram (right) data sets. (bottom) The deviations of these occupancies from the ideal values in the full (left) and single histogram (right) data sets. Key: (O) - O7 occ; (□) - H11 occ; (Δ) - H12 occ.

## Conclusions

It is clear that the time-of-flight Laue technique has useful and often quite original contributions to make in the field of neutron single crystal diffraction. While those applications involving more routine structural refinement remain of general interest and the high Q capability of SXD promises to yield great insight into the basic physics of simple materials, the use of the surveying capability of the technique in either diffuse scattering or the study of phase transitions remains the most exciting area of application.

## References

- G Artioli, R Rinaldi, P-F Zanazzi and C C Wilson (1993) *High temperature Fe/Mg partitioning in olivine crystals: ordering reversal above 1000°C*. Nature, submitted.
- S Hull and C C Wilson (1992) *The defect structure of anion-excess  $(Ca_{1-x}Y_x)F_{2+x}$  with  $x=0.06$* . J Sol State Chem **100** 101-114.
- S Hull, M Hoffmann and C C Wilson (1993) *The defect structure of  $(Ca,Y)F_{2.06}$  at high temperature*. In preparation
- D A Keen, L R Hannan and C C Wilson (1993), work in progress.
- J-C Li, V M Nield, D K Ross, R W Whitworth, C C Wilson and D A Keen (1993) *Disorder in  $D_2O$  ice Ih studied using pulsed neutron single crystal diffraction*. Phil Mag B, submitted.
- R J McLure and B M Craven (1973) *New investigations of cytosine and its monohydrate*. Acta Cryst B**29** 1234-1238.
- C C Wilson (1990) *The data analysis of reciprocal space volumes*. in "Neutron Scattering Data Analysis 1990", ed M W Johnson, pp 145-163, IOP Conf Series **107**, Adam Hilger, Bristol.
- C C Wilson (1993a) *Understanding the time-of-flight Laue diffraction technique - interpretations and comparisons*. J Appl Cryst, submitted.
- C C Wilson (1993b) *A pulsed neutron single crystal diffraction study of the structure of 3-deazauracil*. J Cryst Spect Res, submitted.
- C C Wilson (1993c) *Monitoring phase transitions using a single data histogram in neutron time-of-flight Laue diffraction*. J Appl Cryst, in preparation.
- C C Wilson (1993d) *Reflection statistics in single crystal diffraction on a pulsed neutron source*. Acta Cryst A, in preparation.
- C C Wilson, N S Stewart and D A Keen (1992) *On hydrogen atom positions in 3-deazauracil*. Chem Comm **1992** 1160-1162.