ICANS-XI International Collaboration on Advanced Neutron Sources
KEK, Tsukuba, October 22-26, 1990

Diffuse scattering studies on SXD

C C Wilson, S Hull and D A Keen
ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK

ABSTRACT
The application of the ISIS time-of-flight single crystal Laue diffractometer SXD to the study of diffuse scattering is discussed. The ability of such an instrument to access large volumes of reciprocal space in a single measurement is shown to be of great benefit, making the instrument ideal for the observation of such scattering. Examples are given of the use of the instrument in this field and the simultaneous use of diffraction and diffuse scattering data in structural determination discussed.

I. INTRODUCTION

The Single Crystal Diffractometer SXD at ISIS is ideally suited to the study of diffuse scattering. This is a consequence of the instrument being designed as a time-of-flight Laue diffractometer, exploiting the pulsed, polychromatic ISIS beam along with large area detectors to provide continuous coverage of large reciprocal space volumes. The combination of continuos coverage with large detected volume makes SXD an ideal probe for surveying reciprocal space, measuring between the Bragg peaks being as straightforward in this geometry as measuring the Bragg peaks themselves. In addition, it is straightforward on SXD to sample the desired measurement space without the necessity for accurate crystal alignment or complex angular scans of crystal and/or detector. During the actual measurement of a data histogram, all parts of the instrument remain fixed.

The ability to scan on SXD in this way without knowing precisely what one expects to observe is of great benefit in the study of novel systems where the scattering between Bragg peaks may be unknown. In addition, the collection of a large reciprocal space volume of data in a single run is ideally suited to observing changes with temperature etc, which can be achieved without alteration of any other instrument parameters.

In its first year of scheduled operation, a major part of the SXD programme has been devoted to this surveying aspect of the single crystal field, with special emphasis on diffuse scattering. There have been several systems studied successfully, two examples of which are given below to illustrate the technique.

II. DEFECT CLUSTERS IN THE ANION EXCESS FLUORITE $(Ca,Y)F_{2+x}$

Compounds with the fluorite crystal structure provide one of the simplest examples of 'fast-ion' conductors. At temperatures well below the melting point fluorite compounds such as CaF_2 undergo a broad transition to the fast-ion phase, characterised by a rapid increase in the ionic conductivity, and associated with the onset of dynamic disorder within the anion sublattice (Hayes, 1980). The addition of trivalent cations to the halide fluorites introduces excess anion interstitials into the fluorite lattice which maintain electrical neutrality. To understand the profound effect which this doping has on the ionic conductivity (Catlow et al, 1981) it is important to understand the nature of the disordered structure.

Structural information concerning defect clusters within nonstoichiometric compounds can be obtained from both Bragg and diffuse scattering measurements. In a Bragg diffraction experiment the reflection intensities enable the average unit-cell structure to be determined, indicating the atomic positions and occupancies of various crystallographic sites. However, to

obtain direct information concerning the local arrangement of the defect cluster, it is necessary to investigate the coherent diffuse scattering, which often exhibits broad maxima between the Bragg peaks. A single crystal diffractometer on a pulsed neutron source, such as SXD at ISIS, allows large volumes of reciprocal space to be investigated in one crystal orientation. It is possible, therefore, to simultaneously measure a large number of individual Bragg intensities and determine the distribution of the diffuse scattering intensity within reciprocal space.

A combined diffraction and diffuse scattering study has been undertaken, using a single crystal sample of CaF_2 doped with ~5%YF_3, with the aim of constructing a complete, and consistent, model of the defect structure within this anion excess fluorite. Analysis of the experimental data is currently in progress, using defect clusters proposed in the literature on the basis of various experimental and theoretical techniques. To date, the defect cluster which best fits the experimental data for both Bragg intensities and diffuse scattering is that suggested by previous studies using single crystal diffraction alone and is shown in Figure 1. The fluorite lattice can be considered as a simple cubic array of anions, with the cations occupying the alternate cube centres. The excess interstitial F^- anions are then situated at positions (y, -y, 1/4) and (-y, y, 1/4), with respect to the origin on an anion site, and produce relaxations of the two nearest neighbour anions in <111> directions away from the interstitials towards cube centres which are not occupied by cations. These neighbouring relaxed ions cause further, but progressively smaller, relaxations (not shown in Figure 1) of the 6 next nearest neighbours and the 16 3rd nearest neighbours, again in <111> directions towards empty cube centres.

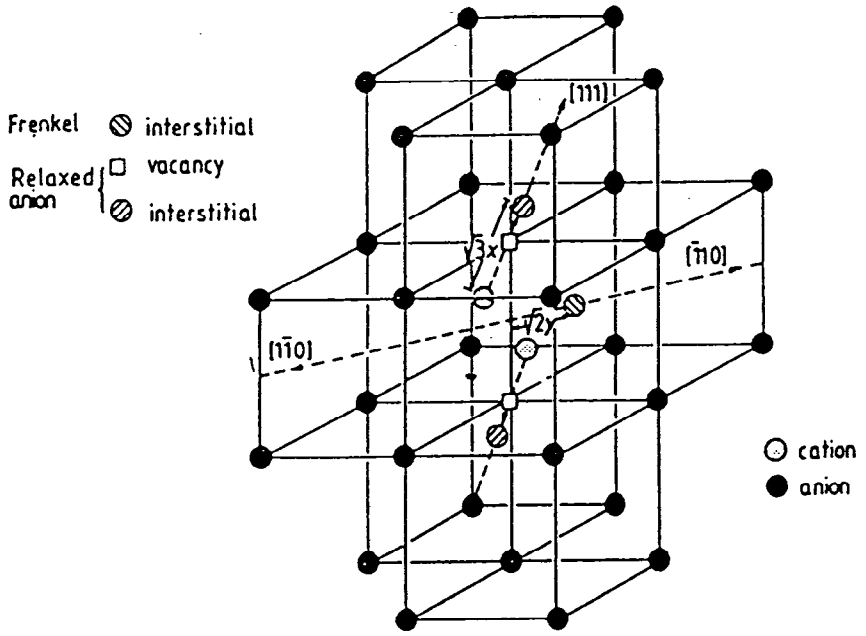


Figure 1 – A model for the defect cluster in $(Ca,Y)F_{2+x}$, showing the interstitial F' ion positions and the relaxed interstitials F".

Values for the positional parameters describing the location of the disordered anions within the defect cluster have been determined by performing a least-squares fit of the diffuse scattering data in the (hhl) plane of reciprocal space using the model described above. Scale and background parameters are also included, plus an overall isotropic temperature factor for the disordered anions. The measured diffuse scattering data and the fitted calculated pattern are shown in Figures 2 and 3. Preliminary refinements of the Bragg intensities support the defect cluster model obtained from the fit to the diffuse scattering data. A comparison of the positional parameters obtained by each approach is shown in Table 1. In view of the encouraging agreement obtained, software for simultaneous least squares refinement of the diffuse and diffraction data is currently being developed at ISIS.

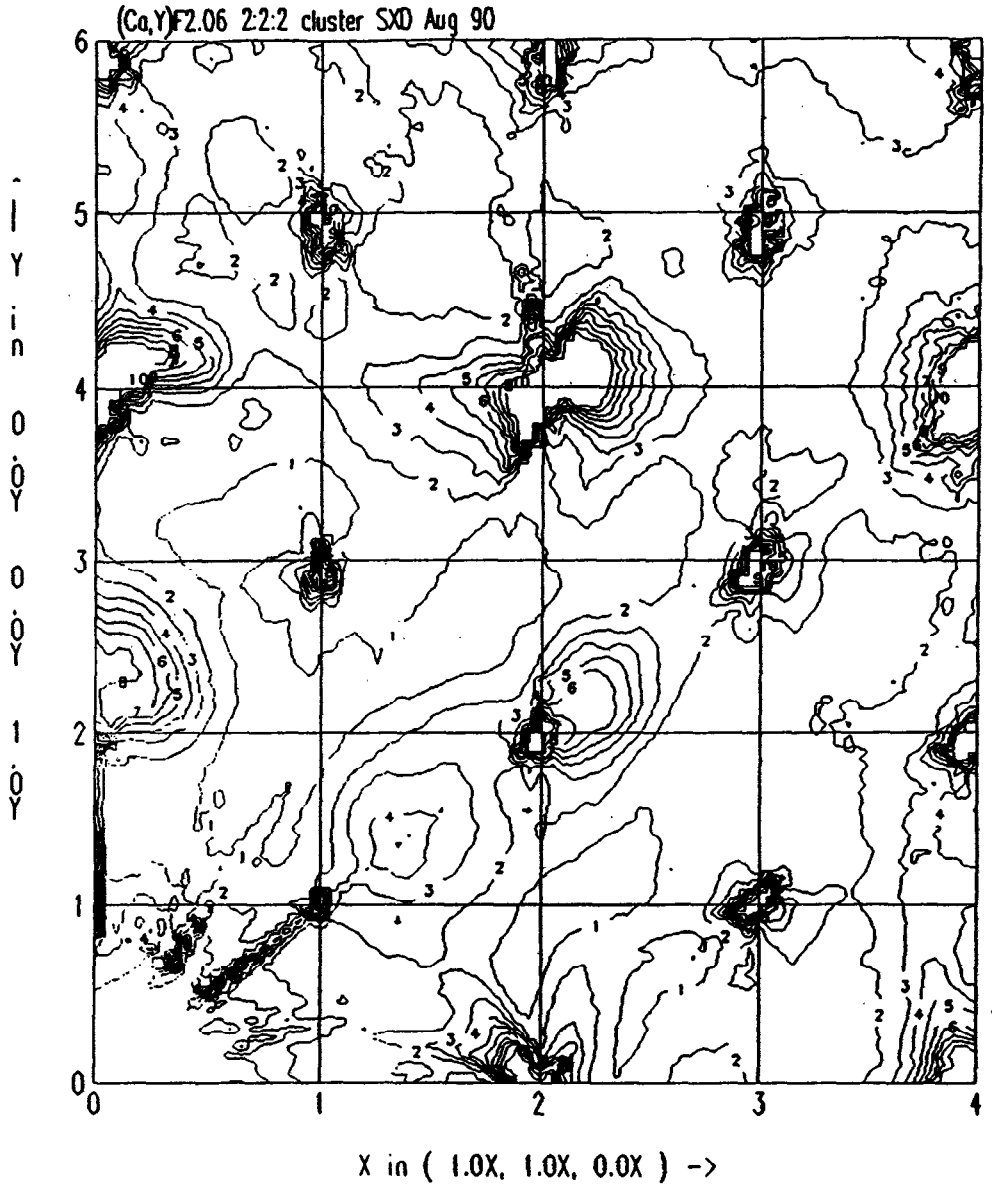
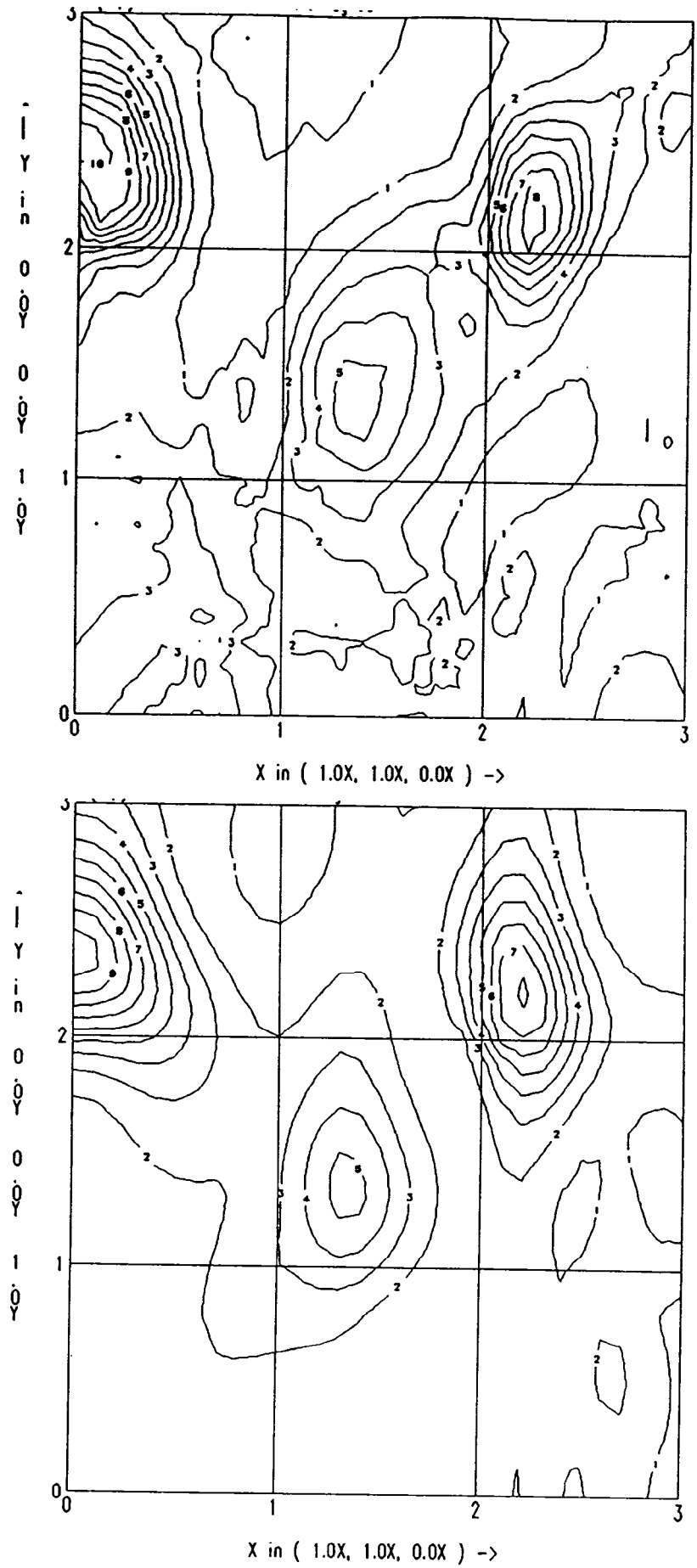


Figure 2 – The Bragg and diffuse scattering data collected on SXD from $(Ca,Y)F_{2.05}$.

TABLE 1 – Refined positional parameters from diffuse and diffraction data refinements

Atom	Position	Parameter	Diffuse	Diffraction
F'	(0.5,a,a)	a	0.442	0.370(9)
F"	(b,b,b)	b	0.419	0.403(11)
$F"_b$	(c,c,c)	c	0.284	0.266(3)
$F"_c$	(d,d,d)	d	0.262	0.258(5)

Figure 3 – The observed (top) and calculated (bottom) coherent diffuse scattering in $(Ca,Y)F_2$ from the defect cluster described. The Bragg and thermal diffuse (TDS) scattering have been removed from the observed data in a semi-empirical way, leaving only the diffuse scattering due to the defects.



III. PRE-MELTING IN LEAD

Although the solid to liquid transition is familiar to us all, the microscopic mechanism of the melting process is not well understood. Materials which show 'pre-melting' effects, when the solid shows signs of structural disorder prior to melting, have been investigated to try to determine what happens when a solid melts. Lead is one such material, having the advantages of a reasonably low melting point ($T_m = 601K$), a simple fcc structure and readily available single crystals. Conductivity measurements show changes around 60K below T_m which are attributed to the formation of liquid-like defects in the crystal structure. Phonon linewidth measurements also indicate a change in behaviour above 500–550K.

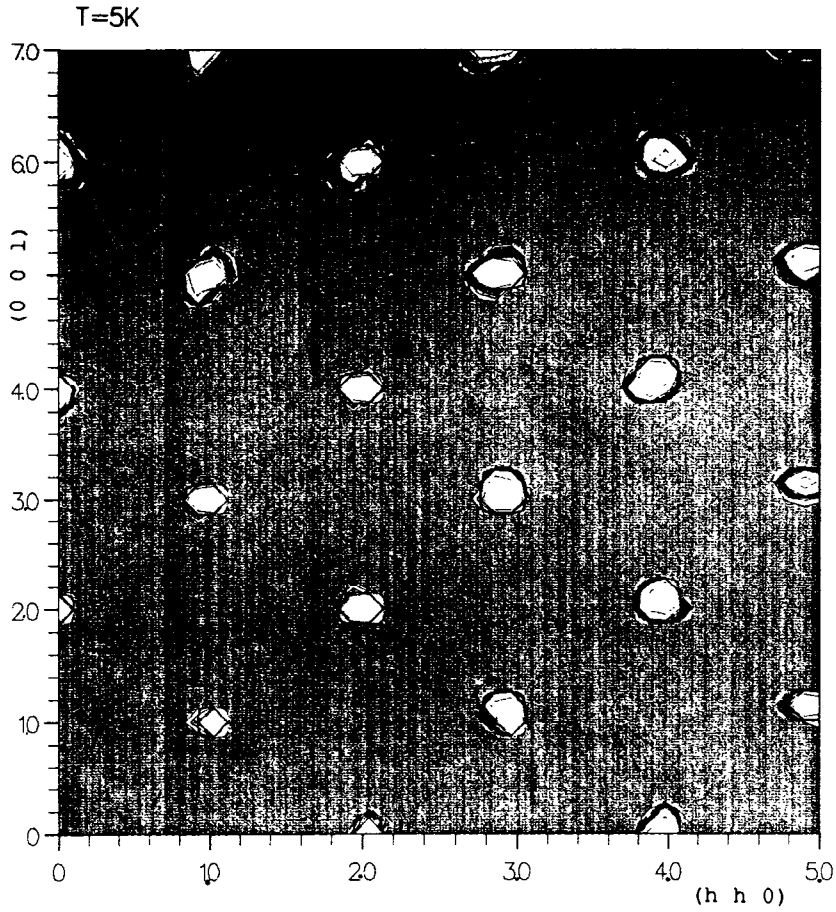
The diffuse neutron scattering has been measured on SXD from a single crystal lead sample at 5K, 293K, 373K and 548K in the (hhl) plane (Figure 4). This scattering shows the development of the thermal disorder in the material as the temperature is increased towards the melting point. There is considerable diffuse scattering even at room temperature, which becomes more pronounced as the temperature is raised still further. At 548K, the high-Q Bragg peaks are barely visible in these plots, demonstrating the high disorder in lead at these high temperatures. The thermal disorder in a crystalline material may be determined via Debye-Waller factors calculated from Bragg scattering (Merisalo, Lehmann and Larsen, 1984). However, in a material where the dominant scattering is diffuse rather than Bragg, this may not be appropriate. Using Reverse Monte Carlo simulation (Keen, Hayes and McGreevy, 1990) the whole structure factor may be modelled and the thermal disorder assessed from both the diffuse and Bragg scattering. The patterns shown here will be analysed in this way.

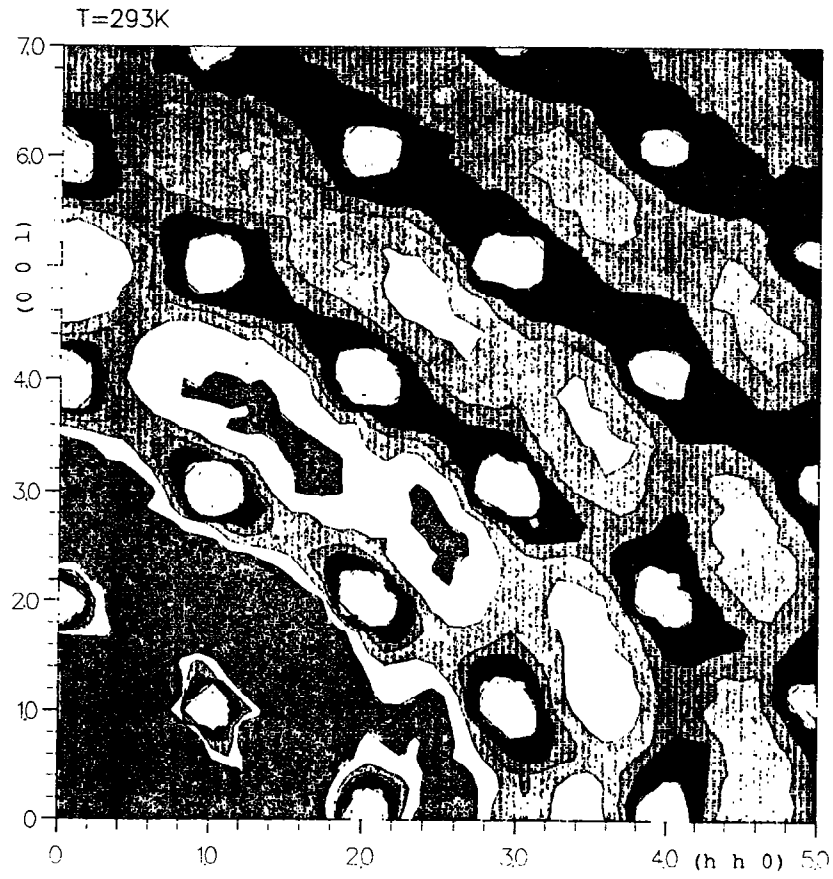
Having demonstrated that SXD is ideally suited to this sort of measurement, further experiments are planned to measure the diffuse scattering up to the melting point in order to allow the determination of changes in the disordered structure associated with the 'pre-melting' in the material.

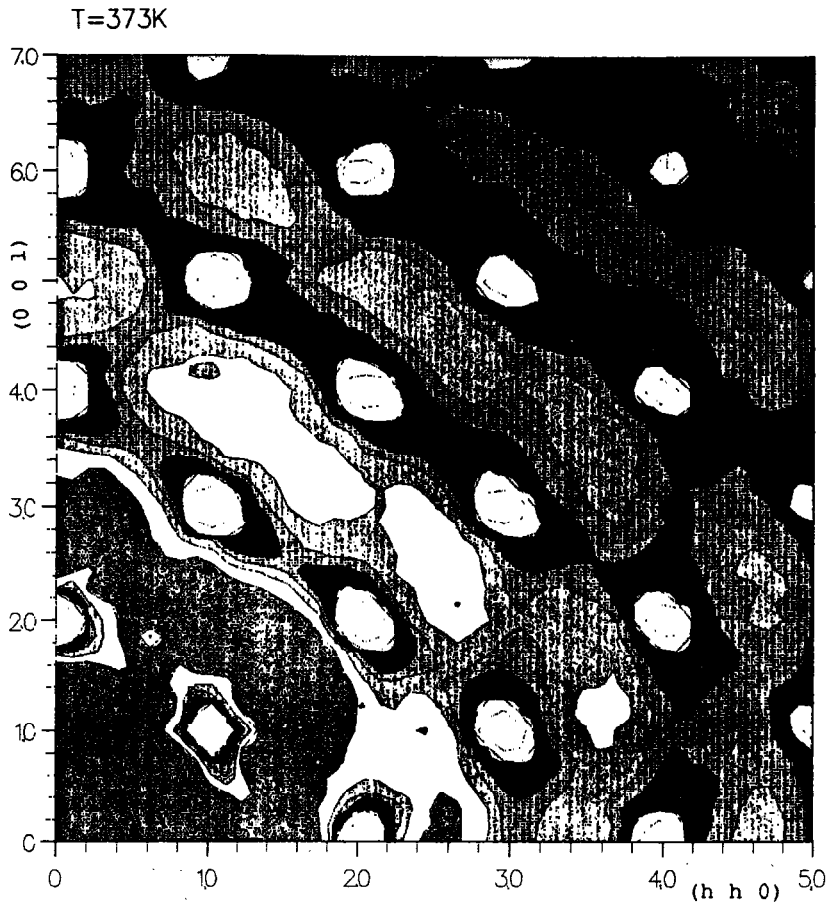
References

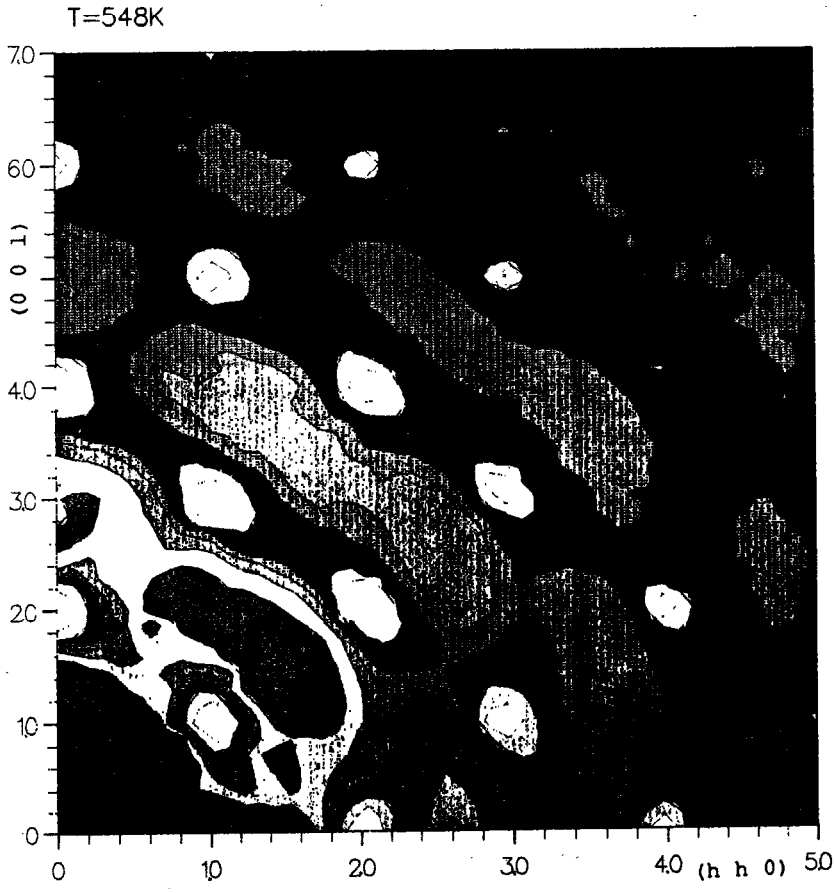
Hayes W, J. Phys. Coll. C6, 7 (1980)
Catlow C R A, Comins J D, Germano F A, Harley R T, Hayes W and I.B.Owen, J. Phys. C 14, 329 (1981)
Cheetham A K, Fender B E F and Cooper M J, J. Phys. C 4, 3107 (1971)
Keen D A, Hayes W and McGreevy R L J Phys Cond Matter 2, 2773 (1990)
Merisalo M, Lehmann M S and Larsen F K Acta Cryst. A40, 127 (1984)

Figure 4 – Scattering in the (hhl) plane of lead, measured on SXD at 5K, 293K, 373K and 548K. The increasing degree of diffuse scattering between the Bragg peaks as the temperature increases is obvious from these plots. Modelling of the whole pattern in a case such as this obviously has significant benefits over merely refining on Bragg intensities.






T=373K
7.0
6.0
(0 0 1)
4.0
3.0
2.0
1.0
0
0
1.0
2.0
3.0
4.0
(h h 0)
5.0


T=548K
7.0
6.0
(0 0 1)
4.0
3.0
2.0
1.0
0
0
1.0
2.0
3.0
4.0
(h h 0)
5.0