

## 21-Crystallography at Non-Ambient Temperatures and/or Pressures; Phase Transitions

the effects of deuteration on the transition temperature; and the structure of ammonia at ~5 GPa where the neutron data reveal a lower symmetry than expected. Examples of this work will be presented.

**PS-21.01.09 DATA COLLECTION AND ANALYSIS TECHNIQUES FOR ACCURATE NEUTRON POWDER-DIFFRACTION STUDIES ABOVE 10 GPa.** By J.S.Loveday\*, R.M.Wilson and R.J.Nelmes, Department of Physics, The University of Edinburgh, UK; J.M.Besson, S.Klotz and G.Hamel, Physique des Milieux Condensés (CNRS), Université Paris VI, France; and S.Hull, ISIS Facility, Rutherford Appleton Laboratory, UK.

The use of a pressure cell in a neutron powder diffraction experiment creates a number of problems for accurate data collection. The development of the Paris-Edinburgh opposed-anvil cell at the UK pulsed-neutron source, ISIS, for powder-diffraction studies to 10 GPa and above, has thus required careful attention to the neutron-scattering aspects of the experimental techniques.

The anvil design, the shielding geometry and the materials used have been optimised to give the best possible signal-to-background taking into account the sources of the background scattering and the energy of the neutrons involved. Finite-element calculations have been developed, and tested, to correct for the effects of attenuation by the pressure-cell materials. In the case of the sintered-diamond anvils, used to achieve the highest pressures, the attenuation corrections also have to include the effects of Bragg edges due to diffraction by the (polycrystalline) anvils. And it is frequently necessary to apply corrections for preferred-orientation effects in the samples.

Residual non-sample scattering and/or inadequate corrections for attenuation and preferred-orientation effects can bias refined structural parameters in all types of high-pressure set-up. Examples of these problems will be shown, and the current procedures for accurate structure refinement will be presented.

**PS-21.01.10 SYNCHROTRON DIFFRACTION ON Fe AND Au IN THE RANGE UP TO 1.1 Mbar IN NOVEL MODULAR HYDRAULIC DIAMOND SQUEEZER.** By G. Will and Chr. Höffner, Mineralogical Institute, University Bonn, Poppelsdorfer Schloß, 5300 Bonn 1, Germany.

We report measurements on gold and iron measured with synchrotron radiation at DORIS/HASYLAB, Hamburg, in a diamond anvil squeezer at pressures up to 1.1 Mbar. By the method of profile analysis and profile fitting with a new program HFIT developed in this laboratory we could separate overlapping peaks yielding very reliable data for the  $d$ -values. These were then used to

calculate lattice constants and volumes as a function of pressure. This technique of profile fitting will be reported. It is mandatory when doing synchrotron experiments at extended pressures where many overlapping peaks are present, most of them not even coming from the sample in question. In addition the background is non-monotonous in general and requires additional care.

In total we have performed about 100 experiments. The experimental data have been fitted by the Birch-equation as well as by the Murnaghan-equation. The results are used to calculate the compressibility parameters  $K_0$  and  $K'_0$ .

Further on we have developed a new diamond squeezer driven by a hydraulic oil pressure system. The cell is a modular system and the diamond setting can be used in an anvil lever system as well. The oil driven pressure cell allows us to vary the pressure in synchrotron experiments without entering the radiation area. This is very important for synchrotron experiments, because of the radiation hazards and the time consuming access to the experiments.

**PS-21.01.11 THE STRUCTURAL BEHAVIOUR OF COPPER IODIDE AT ELEVATED TEMPERATURES AND PRESSURES.** S. Hull\* and D.A.Keen, ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon., OX11 0QX, United Kingdom.

In common with the other group Ib halides, copper(I) iodide (CuI) has been widely investigated owing to the superionic behaviour it displays at elevated temperatures (1). Despite its simple zincblende structure, several aspects of the structural modifications associated with the onset of thermally induced disorder are still the subject of debate in the literature. We have recently addressed these topics, using powder neutron diffraction techniques.

The structure of  $\beta$ -CuI, stable between ~640K and ~670K has been determined in  $P\bar{3}m1$ , with  $Cu^+$  disordered over tetrahedral interstices in an essentially close-packed hexagonal anion sublattice. We find no evidence for cation occupancy of the octahedral voids as reported previously (2). Detailed investigations as a function of temperature through the  $\gamma \rightarrow \beta \rightarrow \alpha$  transitions demonstrate the gradual evolution of  $Cu^+$  disorder on the available tetrahedral sites in each phase. The preference for tetrahedral co-ordination of the cations is supported by measurements made at ambient temperature and elevated pressures. At  $p=16.3$ kbar CuI transforms to a rhombohedral structure which possesses  $R\bar{3}m$  symmetry and at  $p=42$ kbar to a tetragonal phase. The latter appears isostructural with the 'intermediate' phase of AgI, stable between 2.8kbar and 3.8kbar. This has the anti-litharge structure,  $P4/nmm$  (3), so that both high pressure forms can be considered as different geometrical arrangements of tetrahedrally co-ordinated  $Cu^+$  within slightly distorted cubic close-packed anion sublattices.