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

MS-21.01.04 STRUCTURAL EVOLUTION OF α-QUARTZ UNDER HIGH PRESSURES AND TEMPERATURES : A MOLECULAR DYNAMICS STUDY. By Surinder M Sharma, M S Somayazulu, S K Sikka, S L Chaplot and R Chidambaram, Bhabha Atomic Research Centre, Bombay 400 085, INDIA.

Pressure induced amorphization in α-quartz has been studied by molecular dynamics. Anisotropic amorphization occurs at about 20 GPa at 300 K. The structure is observed to contain two dimensional amorphous layers along the original ab plane, with different layers sheared along the c axis. This shearing is found to reduce with increase in the initial temperatures and completely vanishes for temperatures in excess of 750 K. The α-quartz structure close to the amorphization contains oxygens that are almost in a close packed configuration as suggested by Hazen et al (Sol. St. Comm. 72, 502, 1989). However, the oxygen sublattice is still far away from an ideal b.c.c. packing arrangement postulated by Bingelli and Chelikowski (Nature, 353, 344, 1991). Simulations carried out up to 80 GPa at 300 K reveal that the coordination number of Si saturates at a value of 6 beyond 60 GPa. The retrieved phase is observed to be permanently densified and continues to be anisotropic, with a coordination number of 4.3. On increasing the temperature of this phase beyond 1100 K, the coordination number of Si returns to a value of 4 and the resultant amorphous phase is found to be isotropic, accompanied by the formation of six membered ring structure which is different from that of the crystalline phase of α-quartz.

MS-21.01.05 HIGH PRESSURE DIFFRACTION STUDIES AT BSRL. By Y.C.Zhao, Beijing Synchrotron Radiation Lab., China

PS-21.01.06 CRYSTAL-STRUCTURE STUDIES OF II-VI, III-V AND GROUP IV SEMICONDUCTORS AT HIGH-PRESSURE USING ANGLE-DISPERSIVE POWDER-DIFFRACTION TECHNIQUES. By R.J. Nelmes, M.I. McMahon*, N.G. Wright and D.R. Allan, Department of Physics, University of Edinburgh, U.K.

Angle-dispersive powder-diffraction techniques, coupled with an image-plate area detector, have been developed at SRS Daresbury for crystal-structure studies at high pressure. The combination of high sensitivity and high resolution obtainable with these techniques has revealed new phases and unsuspected structural relationships in II-VI, III-V and group IV semiconductors. For example, silicon has been found to have an intermediate phase between the well-known β-tin and primitive hexagonal phases, reminiscent of the structural sequence found in InSb, while CdTe has been found to have a cinnabar phase between the well-known zincblende and NaCl phases, as previously found only in HgTe and HgSe. Details of this work, along with other recent results from InSb, InP, Ge and HgTe will be presented.

PS-21.01.07 HIGH-PRESSURE STRUCTURAL STUDIES USING SINGLE-CRYSTAL X-RAY DIFFRACTION TECHNIQUES. By D.R. Allan*, J.S. Loveday and R.J. Nelmes, Department of Physics, The University of Edinburgh, U.K.

We are applying single-crystal x-ray diffraction techniques to studies of the relationship between crystal structure and physical properties as they vary under pressure. For example, the superconducting transition temperature (T_c) in copper-oxide superconductors is believed to be strongly linked to a particular Cu-O bondlength. We are making a detailed comparison of $YBa_2Cu_4O_8$ and $La_{1.85}Sr_{0.15}CuO_4$, which both show a large rate of change of T_c with pressure. But initial results reveal quite different behaviour for the crucial Cu-O bondlength in the two materials. This is important, as it suggests that there is not a single, common mechanism for T_c variation. We are now extending this work to higher pressures where the difference may be expected to become even more definite and significant.

We are also studying the icosahedral boron-rich materials α-boron and B_4C in relation to recent work on their electrical conductivity. Models have been developed which are based on bipolaron hopping, and require the icosahedral units to be more compressible than the structural unit-cell to account for the anomalous P-dependence of the conductivity. We have started work to test whether these models are well founded.

The recent results from both of these programmes will be presented.

PS-21.01.08 CRYSTAL-STRUCTURE STUDIES TO 10 GPa USING NEUTRON POWDER DIFFRACTION TECHNIQUES. By R.J.Nelmes*, J.S.Loveday and R.M.Wilson, 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.

We have been developing an opposed-anvil pressure cell, able to compress samples of sufficient size for accurate crystal-structure studies to above 10 GPa. This cell is in use at the UK pulsed-neutron source, ISIS. After completing improvements to the signal-to-background and to attenuation corrections, we have been able to carry out successful structural studies in which good data to d-spacings of ~0.5 Å have been obtained. Rietveld profile refinement of these data yield interatomic distances with a precision of ~0.003 Å or better at all pressures.

Completed studies to date include the P-dependence of the O-D distance in D_2O ice VIII up to 10 GPa, which shows that the O-D distance varies significantly less than has been widely supposed on the basis of spectroscopic studies and assumptions about the interatomic potential; the compressibility of the icosahedra relative to the unit-cell volume in boron carbides B_4C and B_9C, which is a crucial variable in models of the transport properties of these materials; the H(D)-ordering transition in deuterated squaric acid ($D_2C_4O_4$) at 3.5 GPa, in relation to 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.

Furtheron 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 β–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 γ→β→α 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=16.3kbar CuI transforms to a rhombohedral structure which possesses $R\bar{3}m$ symmetry and at p~42kbar 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.