

## High Pressure I Elements and Simple Compounds

**MS18.01.01 AMORPHIZATION AND MOLECULAR DISSOCIATION OF  $\text{SnI}_4$  AT HIGH PRESSURES** N. Hamaya, K. Sato, K. Usui, (Department of Physics, Ochanomizu University, Tokyo 112, Japan), K. Fuchizaki (Department of Physics, Kyushu University, Fukuoka 812, Japan); Y. Fujii (Neutron Facility, ISSP, The University of Tokyo, Tokai, Ibaraki 319-11, Japan); Y. Ohishi (Tsukuba Research Laboratory, Sumitomo Chemical Co. Ltd., Tsukuba, Ibaraki 305, Japan)

Structural disordering induced by hydrostatic pressure has been observed in a wide variety of materials. Stannic iodide,  $\text{SnI}_4$ , is a molecular crystal which is known to exhibit pressure-induced amorphization and metallization. Previous works including x-ray diffraction, Raman and Mössbauer measurements led to a structural model of the amorphous phase that consisted of randomly oriented chains of  $\text{SnI}_4$  tetrahedral molecules. The primary purpose of this study is to clarify the structural disordering process upon the crystal-amorphous transformation and to search for a new crystal structure beyond the amorphous state at high pressures.

We have carried out a high-pressure, synchrotron powder x-ray diffraction measurement. The present study has revealed that the initial cubic structure of  $\text{SnI}_4$  transforms to a new crystalline phase at 7 GPa before the amorphization begins. This second phase gradually loses its crystalline character exhibited in the diffraction pattern with increasing pressure. Diffraction patterns characteristic of the amorphous state were observed between 20 GPa and 55 GPa. At about 60 GPa, a phase transition to the third crystalline phase takes place discontinuously. A diffraction pattern of the third phase consists of very low background and only diffraction peaks assigned to the fcc structure. This fact leads to a model of the third phase in which iodine ions are located at the ideal fcc-sites and tin ions randomly occupy, for instance, the tetrahedral sites in the fcc lattice. A very small value of its lattice constant indicates that this crystal structure results from the dissociation of  $\text{SnI}_4$  molecules.

**MS18.01.02 HIGH PRESSURE X-RAY STUDY OF  $\text{AlH}_3$  AND  $\text{AlD}_3$ : ANOMALOUS ISOTOPE EFFECT.** Stanislav P. Besedin and Andrew P. Jephcoat, Department of Earth Sciences, University of Oxford, Parks Road, Oxford, OX1 3PR, UK

The metal hydrides are of interest owing to a number of phenomena in which the quantum character of a light hydrogen atom in a metallic matrix is exhibited. We report synchrotron powder x-ray diffraction measurements at room temperature for the predominantly ionic (partly covalent) hydrogen-rich metal hydrides  $\text{AlH}_3$  and  $\text{AlD}_3$  in a diamond-anvil cell to maximum pressures near 53 GPa. Aluminium hydride has a rhombohedral unit cell (R-3c space group) with  $a=4.4493$  Å and  $c=11.8037$  Å in hexagonal axes. It can be regarded as "a three-dimensional polymer" all atoms of which are linked by Al-H-Al bonds. The structure can also be described in terms of a distorted hcp matrix of hydrogen atoms, in which one third of the octahedral interstices are occupied by aluminium atoms. The pressure-volume data obtained show an unexpected difference in the compressibility between isotopes, with  $\text{AlD}_3$  more compressible at all pressures. No structural phase transition from the rhombohedral aluminium lattice is observed in either isotope, which could be associated with the previous prediction of an insulator-to-metal transition at 46 GPa. On the basis of our data for  $\text{AlH}_3$ , we expect that the pressure for which the atomic hydrogen volume equals the 2.8-2.9  $\text{Å}^3/\text{H}$  atom characteristic of the transition metal hydrides, is near 80 GPa, higher than suggested by previous data. The difference between the compressibilities of the isotopic modifications is interpreted in terms of zero point dynamics.

**MS18.01.03 HIGH PRESSURE - HIGH TEMPERATURE STUDIES OF SUPERIONIC CONDUCTORS.** S. Hull, D. A. Keen, N. J. G. Gardner and W. Hayes<sup>‡</sup>. ISIS Science Division, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX. U.K. <sup>‡</sup>Clarendon Laboratory, Parks Road, Oxford, OX1 3PU. U.K.

The results of recent neutron diffraction investigations of the structural behaviour of model superionic compounds at elevated pressures and temperatures are presented.  $\text{CuCl}$ ,  $\text{CuBr}$ ,  $\text{CuI}$  and  $\text{AgI}$  form a family of tetrahedrally co-ordinated compounds which transform under hydrostatic pressure to octahedrally co-ordinated phases (rocksalt or distorted rocksalt structures) and have been widely studied at elevated temperatures because (with the exception of  $\text{CuCl}$ ) they undergo structural transitions to superionic phases characterised by exceptionally high cation conductivity. The pressure induced transition from 4-fold to 6-fold co-ordination occurs via intermediate phases of lower symmetry. Indirect evidence exists in the literature suggesting that some of the high pressure phases also exhibit superionic behaviour. This paper describes the first structural investigations of these effects, using neutron diffraction studies of powder samples to  $\sim 1.2$  GPa and  $\sim 800$  K.

Specifically, the following results are presented.

A superionic phase is observed at 0.8 GPa and 700 K in  $\text{CuCl}$ , which has no superionic phase at ambient pressure.

The onset of disorder in the high pressure rocksalt structured phase of  $\text{AgI}$  is observed.

The high pressure rhombohedral phase of  $\text{CuI}$  shows highly anisotropic lattice expansion on increasing temperature, but little cation disorder.

Finally, a brief description is given of the high pressure high temperature cell which is capable of taking some 2 cm<sup>3</sup> of sample to 1.2 GPa and 1000 K and is optimised for fixed geometry, energy dispersive neutron diffraction.

**MS18.01.04 FIRST PRINCIPLES CALCULATIONS OF CRYSTAL STRUCTURES AND TRANSITIONS UNDER HIGH PRESSURE.** Andres Mujica(1), Richard J. Needs(2), and Alfonso Munoz(1), (1)Dpto. de Fisica Fundamental y Experimental, Universidad de La Laguna, La Laguna E-38205, Tenerife, Spain, (2) Theory of Condensed Matter Group, Cavendish Laboratory, Cambridge CB3 0HE, United Kingdom

In this talk we review the current state-of-the-art in the theoretical study of crystal structures, based on the Density Functional Theory (DFT). The detail and precision now achievable will be illustrated with recent results from a DFT study of the structural stability of several III-V and II-VI binary compounds under high pressure, with an emphasis on the recently discovered Cmcm phase. Experimental results and our ab initio calculations are in excellent agreement, and establish the stability of a Cmcm structure in a variety of compounds. We have investigated the mechanism leading to the Cmcm phase and the evolution of its structural parameters with increasing pressure. We also show how Cmcm can be related to previously suggested structures, and thus how previous experimental observations can be reconciled within the present status of knowledge.