

**PS18.01.14 NEW STRUCTURAL SYSTEMATICS IN THE II-VI, III-V AND GROUP IV SEMICONDUCTORS AT HIGH PRESSURE.** R.J. Nelmes, M.I. McMahon, H. Liu and S.A. Belmonte, Department of Physics and Astronomy, The University of Edinburgh, Edinburgh, EH9 3JZ, U.K.

Diffraction studies of the core II-VI, III-V and group IV semiconductors have remained at the forefront of experimental high-pressure research since the introduction of the diamond anvil cell in the early 1960's. Recently, using angle-dispersive (AD) diffraction techniques with an image-plate area detector and synchrotron radiation, we have made a detailed re-examination of the high-pressure behaviour of most of these semiconductors. This work has yielded many new results which show that the structural systematics compiled over the last 30 years must be modified quite substantially. The supposed structures of many high-pressure phases have been found to be incorrect; new high-pressure phases and structural relationships have been found; and, contrary to the accepted picture, many of the high-pressure phases have been shown to have relatively low-symmetry structures, with variable atomic coordinates. The emerging systematics will be summarised. And the most recent new results of this programme will be presented, including: an apparently classic soft-mode transition in ZnSe, with implications for GaAs; a new and unexpected high-to-low cristobalite-type transition in HgSe and HgTe; a radical revision of the P-T phase diagram of InSb, and the phenomenon of intermediate phases as a feature of all its transitions; and the apparent fact that only the group IV elements have phases with true tetragonal or hexagonal symmetry.

**PS18.01.15 HIGH-PRESSURE SINGLE-CRYSTAL X-RAY DIFFRACTION STUDY OF  $\epsilon$ -FeSi.** Ross, N. L. Department of Geological Sciences, University College London, Gower St, London WC1E 6BT, UK

The crystal structure of cubic iron monosilicide,  $\epsilon$ -FeSi, has been determined between 0 and 7 GPa using single-crystal X-ray diffraction. At all pressures studied, the material has space group  $P2_13$ , with  $Z = 4$  and both atoms on sites  $4a$ ,  $(x,x,x)$ . The unusual seven-fold coordination of both Si and Fe is retained at high pressure, and the positional coordinates of Fe,  $x_{Fe} = 0.137$ , and Si,  $x_{Si} = -0.158$ , do not vary significantly with pressure. The interatomic distances show an approximate linear decrease with pressure due to the reduction of the cell parameter. The bulk modulus,  $K_0$ , determined from fitting a third-order Birch-Murnaghan EOS to the pressure-volume data is 176(3) GPa (with  $K_0' = 4.0$ ). The results from this study will be compared with recent high-pressure time-of-flight neutron powder diffraction experiments of  $\epsilon$ -FeSi using the POLARIS diffractometer at the ISIS spallation neutron source (Wood et al., *J. Phys.: Condens. Matter* 7, L475-L479, 1995).

**PS18.01.16 EQUATION OF STATE OF  $I4/mcm$   $KHF_2$  AND STABILITY TO 50 GPa: IMPLICATIONS FOR STRUCTURAL SYSTEMATICS IN  $AX_2$  SYSTEMS** Andrew G. Christy<sup>1</sup> and Simon M. Clark<sup>2</sup> <sup>1</sup>Research School of Chemistry, The Australian National University, Canberra, ACT 0200, Australia <sup>2</sup>Daresbury Laboratory, Warrington WA4 4AD, England.

Potassium Hydrogen Fluoride ( $KHF_2$ ) crystallises in the tetragonal system under ambient conditions, space group  $I4/mcm$ ,  $Z=4$ ,  $a=5.668(2)\text{\AA}$ ,  $c=6.801(7)\text{\AA}$ . Energy-dispersive X-ray diffraction was used to obtain cell parameters on a sample contained in a diamond anvil cell up to 12.3 GPa. The calculated cell parameters fit a third-order Birch-Murnaghan equation of state with  $K_0=25.1(15)$  GPa and  $K_0'=10.0(19)$ . The compressibility is greater by a factor of two along  $z$  despite short K-K distances in this direction ( $< 3.40\text{\AA}$ ), implying that F-F repulsion dominates the compressibility behaviour.

A reconnaissance study to higher pressure showed that the sample remained in this structure even when compressed to 67.6% of its volume at ambient. Extrapolation of the EOS gave the corresponding pressure as 50 GPa.

Estimation of the volume of an ordered  $P\bar{a}3$  pyrite structure for this compound suggests that, unusually, there is no contraction of the cell on orientation ordering of [FHF] groups from the high-temperature disordered phase. The pyrite structure is therefore unstable at positive pressure, and no transition into it is expected.

High-pressure stability of the tetragonal phase seems reasonable since if the H atoms are neglected, the structure is the same as that of the highly coordinated  $CuAl_2/Fe_2B$  type intermetallics. Nevertheless, H-bonding may play a role in stabilising this structure relative to the cotunnite/ $Ni_2In$  type structures found for alkaline earth difluorides at high pressure.

**PS18.01.17 STRUCTURE OF THE PEROVSKITES ALONG THE  $SrTiO_3$ - $SrGeO_3$  JOIN.** Andrzej Grzechnik, Herve Hubert, William Petuskey, and Paul McMillan, Arizona State University, Materials Research Group in High-Pressure Synthesis, Department of Chemistry and Biochemistry, Box 871604, Tempe, AZ 85287-1604

In this study, we report a new, high-pressure synthesis route to obtain mixed compounds along the perovskite join with non-transition (metastable phase) and transition metal B cations in the cubic  $ABO_3$  structure.  $SrGeO_3$  perovskite is stable above 6 GPa and 1273 K. When it is externally heated to 673 K, it completely decomposes into a mixture of amorphous and low-pressure phases. The onset of decomposition is observed as low as 398 K. The large temperature range (about 300 K) where decaying metastable  $SrGeO_3$  perovskite coexists with other phases suggests that the decomposition occurs locally in nucleation sites with different stress fields. The  $SrGeO_3$ - $SrTiO_3$  phases were synthesized from mixtures of  $SrTiO_3$  and  $SrGeO_3$  (an ambient pressure pseudowollastonite polymorph) at 7 GPa and 1373 K with a multiple anvil high-pressure and high-temperature device. Recovered material was analyzed with X-ray diffraction. The analysis of the X-ray patterns reveals that all the synthesized compounds are disordered with the  $Pm\bar{3}m$  space group, indicating that there is a complete  $SrGeO_3$ - $SrTiO_3$  solid solution at the synthesis conditions. Future analysis of the Raman spectra will allow examination of possible ordering on the nanometer scale and the degree of metastability of the obtained phases.