MS18.03.04 NEUTRON DIFFRACTION STUDIES OF HYDROGEN BONDED ICES.

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High-pressure structural studies of molecular "ices" (e.g. H_2O, NH_3, CH_4, H_2S) provide fundamental information on the behaviour of their interatomic potentials over a wide range of density. Since ices are often components of the outer planets, their high-pressure properties are also important for planetary modelling. The development of the Paris-Edinburgh cell, which has now raised the maximum pressure for neutron diffraction by a full order of magnitude to ~25 GPa, has made possible the first accurate structural studies of ices at pressures above 3 GPa.

Studies of ammonia phase IV have enabled the structure of this phase to be solved and reveal it to be orthorhombic with orientationally ordered molecules, as opposed to the rotationally disordered hexagonal-close-packed structure proposed on the basis of earlier x-ray work. Subsequent studies of D_2S and methane up to ~10 GPa suggest such structural complexity is a common feature of ices under pressure. Detailed structural measurements of ices VII and VIII provide the first direct evidence of oxygen site disorder in ice VII and lead to a more detailed understanding of the precise structural relationship between these two phases. Measurements of the structural pressure dependence of ice VIII to 25 GPa reveal unexpected behaviour of the interatomic potentials as a function of increasing density and show large changes in the atomic thermal motion under pressure.

MS18.03.05 COMPRESSIBILITY OF HYDROGEN BONDS.

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Compressibility, one of the fundamental properties of any substance, with reference to hydrogen bonded compounds, abundant in nature and industrial or pharmaceutical products, has received a relatively little coverage in literature. General features of the pressure dependence of hydrogen bonded structures - ionic or molecular crystals (e.g. ices) - will be discussed. Despite considerable differences in the composition and structure between such crystals, compressibility of the OH—O bonds is remarkably similar. A simple model can be applied to understand the mechanism of the hydrogen-bond transformations in the microscopic scale. High pressures change the balance between the hydrogen bonds and other cohesion forces, leading to phase transitions. The thermodynamic character of the phase transitions and the transformation of the hydrogen bond are interdependent: the first-order phase transitions are connected with breaking/formation of hydrogen bonds or proton transfer between the hydrogen bonded groups, while the second order phase transitions often involve proton disordering. Characteristic changes in the hydrogen bond dimensions accompanying these phase transitions will be systematized [A.Katrusiak, J.Mol.Struct. 269(1992)329; Phys.Rev. B48(1993) 2992, Phys. Rev. B51(1995)589; Cryst.Rev. - in press], and a series of physical phenomena resulting from these changes will be presented: for example, the structural origin of the tricritical point in the KDP-type ferroelectrics (KDP denotes the potassium dihydrogen phosphate) will be shown to be combined with the hydrogen-bond features, which allows one to evaluate the critical pressure or the Curie temperature from structural data.

MS18.03.06 HIGH PRESSURE PHASE TRANSITIONS OF FeS.

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In-situ observation of FeS by an energy-dispersive type X-ray method shows that a high pressure phase at 10.30GPa and 27°C has a monoclinic cell, and that the high pressure phase still has a framework of the NiAs type structure.

Troilite type FeS was synthesized in a sealed glass tube at 690°C for two weeks and then 100°C for two weeks. From the *d*-spacing of the *102* diffraction line of the NiAs type structure, the atomic ratio in troilite was calculated to be Fe:S=49.95:50.05. High pressure and high temperature experiments up to 16GPa and 800°C were carried out using a DIA type cubic anvil apparatus 'MAX80' installed at AR-NE5C in KEK. Diffraction lines with *d*-spacings larger than 3Å were carefully observed for a phase determination.

The phase boundary between a high pressure phase with the MnP type structure or a hexagonal structure (Fei *et al.* 1995) and simple NiAs type phases was determined by a simple straight line with a positive slope in the present P-T conditions. The phase boundary between the troilite and the high pressure phase has a negative slope.

A complex diffraction pattern was observed at 27°C and above 7GPa. From twenty-six diffraction lines of the high pressure phase at 10.30GPa and 27°C, an automatic indexing computer code 'DICVOL' showed that there was no possible crystal system higher than orthorhombic symmetry, and that there were only two possibilities of a monoclinic system. Comparing these two possibilities, a reasonable unitcell for the high pressure phase can be proposed to be $a = 8.044(4)$Å, $b = 5.611(2)$Å, $c = 6.433(3)$Å, $\beta = 93.11(4)°$ and $Z = 12$. The volume of the high pressure phase is calculated to be 2.8% smaller than that of the Fei's phase at 11.17GPa and 300°C.

MS18.03.07 HIGH-PRESSURE BEHAVIOR OF SILICA AND ITS ANALOGS

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The response of silica to high pressure has been studied extensively. Diamondcell experiments have revealed that SiO_2 quartz exhibits a rich and complicated polymorphism, involving an amorphous phase, a quartzlike phase, and a stishovitelike crystalline phase that persists to above 200 GPa. Pressurization of SiO_2 cristobalite indicates several crystallinecrystalline phase transformations which occur below 40 GPa, and amorphization has been reported near 30 GPa. We have recently prepared phosphorous oxynitride (PON), a material isoelectronic with SiO_2, having acristobalite-like P4 structure. Diamond-cell compression to 70 GPa without a medium shows gradual transformation of the P4 phase to a cristobalite I42d structure by 20 GPa. Under continued nonhydrostatic compression, the I42d phase persists to 70 GPa. Unlike the corresponding SiO_2 framework structures, there is no evidence for pressure-induced amorphization.