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Like water, ammonia is a major member of the group of simple hydrogen-bonded molecular ices. The study of its high-pressure properties is first of natural interest due to its abundance in the solar system, like in the Jovian planets. Ammonia also presents a fundamental interest in condensed-matter physics as an H-bonded solid. Hydrogen bonds are weaker in ammonia than in water since 3 H atoms share a single lone pair. Whereas the symmetric state of water ice has been observed experimentally, the symmetrization path in ammonia appears more complicated. Actually, the phase diagram is barely known above 10 GPa. The solid transforms to the orthorhombic phase IV above 4 GPa; the presence of new phases has been suggested by Raman [1], Brillouin [2] and IR [3] experiments. But these results are confusing — what are the transition pressures ?, and incomplete — what is the nature of these new phases ?

We have conducted X-ray diffraction experiments up to 120 GPa and polarized Raman scattering on single crystals up to 70 GPa at low temperature. The use of single crystals allowed us to observe for the first time both very weak diffraction peaks and Raman modes and follow their evolution with pressure. Comparison between NH_3 and ND_3 showed significant isotopic effects.

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Keywords: ammonia, high-pressure XRD, raman spectroscopy

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Phase Transitions in Transition Metal Monooxides: Interplay Between Structural, Magnetic, and Electronic Properties

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The iron monoxide $Fe_{1-x}O$ (wüstite) is an important member of the highly correlated transition metal monoxide group which includes NiO, CoO, and MnO, and is also an end-member component of the (Mg,Fe)O solid solution, the most abundant non-silicate oxide in the Earth. At ambient conditions wüstite exists in a cubic fcc-based rock-salt structure with a nonstoichiometric formula $Fe_{1-x}O$. At low temperatures a rhombohedral distortion of the cubic cell is known to occur as believed to be driven by antiferromagnetic ordering. A strong C_{44} elastic constant softening is also observed in the same temperature range. At high pressures the cubic-to-rhombohedral phase transformation occurs in FeO, and C_{44} mode softening also exists at high pressures. Elastic mode softening was assigned to a strong magneto-elastic coupling in FeO. We conducted combined high-pressure and low- and high-temperature X-ray and neutron diffraction, Mössbauer spectroscopy, and ultrasonic interferometry study of FeO, FeO-MgO solid solutions, and MnO. We revealed decoupling of magnetic ordering and structural distortion in nonstoichiometric FeO in a wide temperature (up to 1100 K) and pressure (over 100 GPa) range. For MnO we observed strong correlation between magnetic ordering and structural transition at ambient pressure and could not distinguish Neel (TN) and structural transition (TS) temperatures within experimental uncertainties. The pressure dependence of TN and TS in MnO, however, is different at elevated pressures, like in the case of FeO. Cubic-to-rhombohedral phase transition was observed for ferropericlase Mg0.8Fe0.2O at about 40 GPa and no transformation was observed in Mg0.95Fe0.05O at pressures up to 80 GPa. The existence of a rhombohedral distortion in ferropericlase with mantle composition at high pressures coupled with the absence of magnetic ordering has important implications for the interpretation of seismological data with respect to Earth lower mantle inhomogeneity.

Keywords: high-pressure, magnesiowüstite, phase transitions

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Successive Alternation of the Propagation Direction of the Inner Shell ordering by Pressure in a Cd-Yb 1/1 Approximant Crystal

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Cd_6Yb crystal, an approximant crystal of a binary quasicrystal of a Cd-Yb alloy, consists of a new type of atomic clusters that lack a partial icosahedral symmetry [1, 2]. The first inner shell of Cd_4, which has a tetrahedral shape instead of the typical icosahedral symmetry, is orientationally disordered at ambient pressure and temperature [2]. Single crystal synchrotron X-ray diffraction measurements revealed that the Cd tetrahedron exhibits various types of structural ordering sensitive to pressure and temperature. Four ordered phases appear in a *P-T* span up to 5.2 GPa and down to 10 K. The propagation direction of ordering alternates from [110] to [111] near 1.0 GPa and again to [110] at 3.5-4.0 GPa. The primarily ordered structures that appear between 210-250 K over a pressure span of 1-5.2 GPa further transform to finely ordered ones by cooling to 120-155 K. Super lattice reflection intensity measurements show that the structural transitions to primarily and finely ordered phases are driven by long and short-range interactions, respectively.

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Keywords: high-pressure phase transformations, quasicrystals, synchrotron X-ray diffraction

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Combining Laue Diffraction with White-beam Single-crystal EXAFS

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Polychromatic radiation has been used in high pressure x-ray diffraction studies for almost two decades, but has never been demonstrated to be competitive with monochromatic experiments in terms of applicability of its results in full structure determination. This presentation will summarize the outcomes of new development efforts located at the HPCAT 16BMB beamline of APS. It will be shown that by combining the experience and ideas from such fields as high-pressure crystallography, protein Laue crystallography, microdiffraction, and EXAFS, new crystallographic methods, offering unique advantages and optimized for high pressure applications, can be developed.

Transition elements control the oxidation-reduction process and magnetism of the Earth. The theoretically predicted and observed magnetic collapse in Fe_2O_3 and other Fe-containing oxides are usually associated with distortive structural transitions that can be definitively understood only by high-pressure SXD. Moreover, since conventional XRD techniques are not sensitive enough to detect continuous electronic transformations, such as spin crossover, complementary information from techniques such as conventional and synchrotron Mossbauer spectroscopy, X-ray emission spectroscopy or EXAFS, is needed. In our white beam SDX experiments diffraction data are obtained at the same time as x-ray absorption near-edge information, providing additional information about the local environment of individual ions as well as their spin state. As examples, data obtained for Cr_2O_3 and (Fe,Mg)O will be demonstrated.

Keywords: phase transitions, spin crossover, polychromatic diffraction