

temperatures and energies in dynamic fluctuations. This duality points to the fundamental issue of how mean-field behavior can describe so successfully important aspects of highly correlated electron systems.

Keywords: quantum phase transition, magnetic X-ray diffraction, high pressure diamond anvil cells

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High pressure induced charge ordering in lithium vanadate spinel

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The spinel oxide LiV_2O_4 has been attracting considerable interest as the first heavy fermion oxide [1]. Although the low temperature properties of LiV_2O_4 are in striking parallel with those of intermetallic heavy fermions, it is not clear whether their similar properties have similar origins. LiV_2O_4 has a face-centered-cubic (FCC), spinel structure, and the formal oxidation of V ion is 3.5+. Previous studies showed that LiV_2O_4 remains cubic down to low temperature and that no magnetic ordering occurs down to 20 mK, indicating that all V sites are crystallographically equivalent even at low temperatures. We found that this system shows a metal-insulator transition under pressure. The metal-insulator transition can be attributed to charge ordering of V ions, similar to one observed in AlV_2O_4 [2]. EXAFS measurements under high pressure for LiV_2O_4 (vanadium K edge at SLS, up to 22 GPa) indicated that a phase transition occurs probably associated with a charge ordered state[3]. It is probable that the phase transition we observed is of the same type as that of vanadium clusters, an interesting model proposed recently[4]. Experiments performed at the ESRF synchrotron (powder diffraction function of temperature and pressure) showed also a structural transition but at lower temperatures than that inferred from EXAFS measurements, and similar to the work reported earlier by Takeda et al[5].

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Keywords: high pressure, charge order, spinel

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Pressure-induced hydration and order-disorder transition in a synthetic gismondine zeolite

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Two high pressure phases of a potassium gallosilicate with a gismondine framework (K-GaSi-GIS) were characterized using Rietveld refinements of in-situ high-pressure, high-resolution synchrotron X-ray powder diffraction data. The observed response of the K-GaSi-GIS framework under hydrostatic pressure is a gradual flattening of the so-called 'double crankshaft' structural chain units. At pressures below 1.0(1) GPa, additional water molecules from the hydrostatic pressure-transmitting medium are inserted into the potassium-water guest network ('pressure-induced hydration') resulting in a 'super-hydrated' high pressure phase I. As the flattening of the 'double crankshaft' structural units in the GIS-framework continues above 1.6 GPa, the ellipticity of the cross-linking 8-ring windows is reduced below a certain threshold and a disordering of the potassium-water guest structure along the 8-ring channel, characteristic of a disordered high pressure phase II, is observed. The concerted framework distortion and guest network disordering accommodates the increased hydration level while maintaining the seven-fold coordination environment of the potassium cations to framework oxygen atoms and water molecules. We have thus established the atomistic details of a guest-host order-disorder transition under pressure-induced hydration conditions in a zeolite with GIS-framework and compared it to other zeolites during pressure-induced hydration. We find that the structural changes mediated by the extra framework cations and their coordination environment under PIH conditions are at the core of these different mechanisms and are driving the changes in the ellipticity of pore openings, order-disorder and disorder-order transitions and framework distortions.

Keywords: zeolite crystal chemistry, high-pressure chemistry, synchrotron powder diffraction

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Lattice dynamics in incommensurate elemental crystals at high pressure

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In recent years, surprisingly complex crystal structures have been discovered in the elements at high pressures. Incommensurately modulated structures and incommensurate host-guest composite structures have been observed in various elements across the periodic table, e.g., Rb, Ba, Sc, Te, P, and I. While considerable progress has been made in determining the detailed crystal structures of these complex phases, the mechanisms of their formation and stability are not yet fully understood. Experimental data on the lattice dynamics of the complex phases will be a key ingredient to address this question, and inelastic x-ray scattering (IXS) spectroscopy is the technique of choice to study phonons throughout the Brillouin zone on samples in diamond anvil high-pressure cells. IXS experiments were performed on single crystals of the incommensurate-composite phases Rb-IV and Ba-IV as well as the incommensurately modulated phase Te-III. As a unique feature of incommensurate composite systems, two LA-like phonon branches are observed in both Rb and Ba along the direction of incommensurability, which are attributed to separate LA-type lattice vibrations in the host and guest subsystems. The host and guest sound velocities have been determined as a function of

pressure, and it will be demonstrated that the guest-atom chains in the composite Rb-IV structure represent a realisation of the classic monatomic linear chain model. In modulated Te-III, a pronounced phonon anomaly is observed that will be discussed in the context of Fermi-surface nesting, Kohn anomalies and charge-density waves.

This work was performed in collaboration with M. I. McMahon, L. F. Lundegaard, S. R. Evans (University of Edinburgh) and A. Bossak, M. Krisch (ESRF, Grenoble).

Keywords: incommensurate crystals, lattice dynamics, inelastic X-ray scattering

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Phase transformations in silane — Hydrogen-dominant material

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The metallization of hydrogen directly would require pressure of 400 GPa, out of the reach of present experimental techniques. The dense group IVa hydrides attract considerable attention because hydrogen in these compounds is chemically precompressed and a metallic state is expected to be achievable at experimentally accessible pressures(1). We report the transformation of insulating molecular silane to a metal at 50 GPa, becoming superconducting at a transition temperature of $T_c = 17$ K at 96 and 120 GPa(2). The metallic phase has a hexagonal close-packed structure with a high density of atomic hydrogen, creating a three-dimensional conducting network. These experimental findings support the idea of modeling metallic hydrogen with hydrogen-rich alloy. The metallic $P6_3$ phase is apparently stable in the 50 to 110 GPa range. However it partly transforms into a transparent insulating phase at pressures ≥ 120 GPa. Concurrent with the onset of transparency, a pronounced Raman signal appears. Two distinct phases coexist to the highest experimental pressure of 192 GPa. We determined the transparent phase structure to be a $I4_1/a$ structure. The structure and its lattice parameters are in exact agreement with the $I4_1/a$ phase predicted to be thermodynamically stable in the pressure range 50 to 250 GPa(3). The observed transformations in stoichiometric silane with pressure are unusual. Molecular SiH_4 at a pressure of ~ 50 GPa does not transform to the predicted thermodynamically stable $I4_1/a$ phase(3) but instead collapses to a significantly denser $P6_3$ phase.

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Keywords: metallic hydrogen, high pressure, hydride

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Structure of drug-target proteins determined by both X-ray and neutron diffraction

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Crystallography enables us to obtain accurate atomic positions within proteins. High resolution X-ray crystallography provides

information for most of the atoms comprising a protein, with the exception of hydrogens. Neutron diffraction data can provide information of the location of hydrogen atoms to the structural information determined by X-ray crystallography. Here, we show the recent result of the structural determination of drug-target proteins, porcine pancreatic elastase (PPE) and human immunodeficiency virus type-1 protease (HIV-PR) by both X-ray and neutron diffraction. The structure of porcine pancreatic elastase with its potent inhibitor (FR13080) was determined to 0.94 Å resolution by X-ray diffraction and 1.75 Å resolution by neutron diffraction. It was found that there are two characteristic hydrogen bonding interactions in which hydrogen atoms were confirmed. One is located between a catalytic aspartate and histidine, another is involved in the inhibitor recognition site. The structure of HIV-PR with its potent inhibitor (KNI-272) was also determined to 0.93 Å resolution by X-ray diffraction and 2.3 Å resolution by neutron diffraction. The ionization state of the catalytic residues were clarified to show that Asp125 is protonated and Asp25 is deprotonated. The ionization state and the location of hydrogen atoms of the catalytic residue in HIV-PR were firstly determined by neutron diffraction. Furthermore, collaborative use of both X-ray and neutron to identify the location of ambiguous hydrogen atoms will be shown.

Keywords: neutron diffraction, protein, structure

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Neutron crystallographic analysis of deuterated and selectively CH_3 -protonated deuterated rubredoxin

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Neutron crystallography is used to locate hydrogen atoms in biological materials and can distinguish between negatively scattering hydrogen and positively scattering deuterium substituted positions in isomorphous neutron structures. Recently, Hauptman and Lang (2003) have shown that neutron diffraction data can be used to solve macromolecular structures by direct methods and that solution is aided by the presence of negatively scattering hydrogen atoms in the structure. Selective labeling protocols allow the design and production of group or residue specific H/D-labeled macromolecular structures in which the ratio of hydrogen to deuterium atoms can be precisely controlled. We have applied labeling protocols to selectively introduce protonated methyl groups into deuterated rubredoxin from *Pyrococcus furiosus* (PfRd). Perdeuterated and selectively CH_3 -protonated, deuterated rubredoxin were crystallized. High quality neutron data sets extending to 1.75 Å resolution were collected on the new LADI-III instrument at the Institut Laue-Langevin. Of special importance, the 1.75 Å data from the perdeuterated crystal required just 14 hours of beam time, a record which heralds a new era in neutron protein crystallography. We will present the production, crystallization, and neutron analysis of the perdeuterated and selectively CH_3 -protonated PfRd.

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