MS19.P13

High pressure compounds in xenon-hydrogen mixtures

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The study of binary mixtures of atomic (He, Ar, Xe, etc.) and diatomic (N_2, O_2, H_2, etc.) molecular solids is relevant for a better understanding of the interior of the giant planets. It has lead to the discovery of a new type of compound – the van der Waals (vdW) compound – and provides essential information on the interactions among simple molecules.

It was long believed that group 18 elements were inert and un-reactive and could not form compounds. A new chemistry field started in 1962, when the first noble gas compound, xenon hexafluoroplatinate, was synthesised [1]. Since then, many compounds have been created combining noble gases with other chemical elements [2].

Here we present a study of vdW compound formation in the xenon-hydrogen system under high pressure. We have studied several compositions (between 7% and 15% vol Xe) to map the binary phase diagram. Complex phase behaviour as a function of composition and pressure was observed with the formation of different stoichiometric phases.

These novel Xe-H_2 compounds have been characterized by single-crystal and powder x-ray diffraction at beamline I15 of Diamond Light Source. We find three separate phases with orthorhombic, hexagonal and rhombohedral structures as function of pressure and composition. These novel structures will be presented in relation to other rare gas-hydrogen compounds, in particular $Ar(H_2)_2$ [3], $Kr(H_2)_4$ [4], and the previously reported $Xe(H_2)_8$ [5].

A rare gas hydrogen system not only offers the possibility of the discovery of unusual stoichiometric compounds, but also allows the study of the hydrogen molecule in a modified environment compared to pure H_2 solid. The study of the detailed intra-molecular response of H_2 to compression can give insight into new pathways to hydrogen metallization. This has been suggested for the $Ar(H_2)_2$ compound [3]. In the Ar-H system the H_2 vibron is seen to increase continuously under pressure. In contrast our Raman spectroscopic measurements on rhombohedral $Xe(H_2)_8$ show shifted vibron frequencies relative to the pure (bulk) H-H stretching mode which soften with pressure and appear to cross the pressure-frequency trajectory of the pure H_2 vibron around 50 GPa.

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MS19.P14

Neutron diffraction study on the pressure-induced cubic-tetragonal structural distortion in LaD_2 using total scattering spectrometer NOVA

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Rare-earth metals absorb large amount of hydrogen to form di and trihydrides. For a dihydride LaH_2, in which hydrogen atoms are accomodated in the tetrahedral interstitial sites of the host fcc metal lattice alone and the octahedral sites remain empty, we found a pressure-induced phase separation by synchrotron radiation X-ray diffraction [1]. We also found a lattice distortion from the cubic to a tetragonal one before the phase separation. X-ray diffraction measurements, however, provided no information on the hydrogen positions and occupancies in the metal lattice. They are crutial for undestanding the origin of the lattice distortion and hence the mechanism of the phase separation.

High-pressure neutron diffraction experiments were performed for LaD_2 with a total scattering spectrometer NOVA constracted at J-PARC [2]. Rietveld analysis of an ambient pressure profile of a powder sample yielded a lattice constant a=5.652 (2) Å and hydrogen occupancies 0.94(4) at T-site and 0.09(6) at O-site. In the high pressure experiments, we used a Paris-Edinburgh cell [3]. High pressures up to 10 GPa and above were genarated with single toroid anvils made of tungsten carbide and double toroid anvils of sintered diamond, respectively. LaD_2 powder was encapsulated in a gasket made of TiZr null alloy together with a pressure medium of deuterated methanol-ethanol 4:1 mixture. We obtained diffraction profiles at ten pressure conditions from 0.1 to 17GPa.

The fcc lattice of LaD_2 began distortion to a tetragonal lattice around 7GPa. The peak splitting arising from the tetragonal distortion increased in magnitude on further compression to the phase separation pressure of 11 GPa. A similar lattice distortion has been reported for superstoichiometric $LaH_{2+\delta}$, in which excess hydrogen atoms occupy the O-sites to make the cubic lattice distorted [4]. Partial transfer of the T-site D atoms into the O-sites in LaD_2 is one possible cause for the distortion. Refinement of the diffraction profiles measured for the tetragonal phase at several pressure points are carrying out now. The microscopic mechanism of the cubic-tetragonal structural trasition and the following phase separation will be discussed on the basis of the refined structural parameters.

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MS19.P15

High pressure structure and magnetism of one 1-D molecular magnetic material

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Molecular magnetic materials(MMM) have been attracted much attention for increasing demands on smaller size magnetic memory devices and interest in the interpretation of the mechanism for complicated magnetic interactions. Many studies focus on investigating the magnetic coupling mechanism and the magneto -structural correlation. Many methods can be used to control magnetic property.

P.MS.19

The external perturbations can be temperature, light irradiation, pressure, and pulsed magnetic fields all may change the magnetic coupling interaction in transition metal systems. Here, we use pressure as external force to study magneto -structural correlation.

We report here the structure and magnetic behavior of one 1-D helical chain iron complex [FeII(μ-bpt)(μ- COOC$_5$H$_4$N)·1/2 H$_2$O]$_n$ (bpt=3,5-bis (pyrid-2-yl)-1,2,4-triazole), [**1**], in ambient conditions and under hydrostatic pressure. The complex was crystallized in a tetragonal space group I4$_1$/a at ambient pressure, each iron atoms linked by one bpt and one isonicotinic acid legend, which form an infinite helical chain along the screw axis 4$_1$ at c-axis direction. The iron atoms are iron (2+) high spin state with distorted N4O2 coordinated shell.

High-pressure powder X-ray diffraction experiments from 0.03GPa to 2.79GPa pressure were carried out to understand precisely the correlation between the structure and magnetic behavior. The careful analysis of a series high pressure structures showing a pressure-induced shrinking more than 10% along the chain direction, which can describe as spring compressed 10%. This make the iron-iron distance from 4.445(2) Å at ambient pressure change significantly to 4.083(6) Å at around 2GPa. Magneto -structural correlation will be discussed .The coordinated shells of Iron (N4O2) also decrease 0.11 Å about averagely. The spin state of iron and magnetic property of title compound also will be shown in this report

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Keywords: high pressure XRD, molecular magnetic materials, high pressure magnetism

MS20.P01

Structure and OD character of 5M_3 ferriphlogopite from Ruiz Peak

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The first finding of a non-MDO mica polytype where two types of layers coexist is here reported. The sample is a 5-layer ferriphlogopite from Ruiz Peak, New Mexico, crystallizing in *C*2, *a* = 5.3146(2) Å, *b* = 9.2063(3) Å, *c* = 49.730(2) Å, β = 92.031(4)°. Data collection was performed on a Mar345 equipped with image plate detector, with completeness of 99.4 % up to resolution 0.8 Å, 5049 unique reflections of which 3195 observed, and redundancy 13.6. The homo-octahedral stacking sequence was determined by PID analysis [1] and corresponds to the 5M_3 polytype [2]. The structure model was obtained from the atomic coordinates of the 1M polytype by applying the stacking vectors, and refined with Jana2006 [3], to R$_{(obs)}$ = 7.03%. A reliable model for the distribution of the octahedral cations (Mg^{2+}, Al^{3+}, Fe^{3+}, Ti^{4+}) in the 9 independent sites cannot be obtained by structure refinement; the occupation of these sites has instead been estimated by exploiting the OD nature of mica polytypes [4]. An iterative computation of the Fourier map from an hybrid data set including computed family diffractions (*k* = 3*n*), which correspond to the family structure in which all octahedral site have the same content, and observed non-family diffractions, followed by adjustment of the model to reproduce the computed map, has been performed; this unambiguously resulted in two layers out of three having a prominent peak in a *cis* site, all the layers being meso-octahedral. The OD symbol for this polytype is |1.5 5.3 5.5 1.1 3.1|.

The 5M_3 polytype with all layer of type M1 (origin of the octahedral sheet in the *trans* site) belongs to the 3T structural series. In this case, however, the presence of M2 layers testifies the occurrence of structural adjustments at the polytype formations stage [5]. The original components could have been a two equal basic structures (1M or 2M_1) differently oriented, or two different basic structures (1M or 2M_1 or 3T). The possible formation mechanism is currently under investigation.

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Keywords: mica, OD, polytypism

MS20.P02

Euclidean groups in spaces of arbitrary dimensions

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Different categories of Euclidean groups are established according to an analysis of the Fundamental theorem on Euclidean groups which is formulated and proved. The first division is into the *space, subperiodic* and *site point groups*. According to the character of the translation subgroup, the groups with the *discrete, continuous* and *semicontinuous* lattice are distinguished. The groups are classified as the *crystallographic, noncrystallographic* and *partially crystallographic* groups. In this connection, the concepts of crystallographic and space groups are amended.

Geometric classes and their splitting into arithmetic classes are defined as usual. Arithmetic classes are the natural classification units and the groups of such a class are distinguished by systems of nonprimitive translations in Seitz symbols for Euclidean operators. If the geometric class is reducible (irreducible) then the arithmetic class is either reducible or decomposable (irreducible). The factorization of the groups of decomposable or reducible classes by partial translation subgroups leads to groups of lower dimensions of the translation subgroup.

The class of the systems of nonprimitive translations which differ only by shift functions define an ***extension class*** within which the groups differ only by their location. Groups of the extension class have the same Hermann-Mauguin symbol and the same symmetry diagram. It is shown how to take the group location into consideration which is not done in Vol. A of IT. As a result, the data about subgroups are incomplete. The location of groups has been first considered in Vol. E of IT and in a software attachment GI * KoBo-1 to Vol. D of IT.

Diagrams of the Young type are suggested for a rough classification of groups in arbitrary dimensions. The groups up to three dimensions are considered in detail as the groups of material physics and a unique system of Hermann-Mauguin symbols for them is developed.

Keywords: seitz symbols, extension class, group location

MS20.P03

3D space groups 2D hyperbolic orbifolds and "sponge" groups

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