

Structural Studies of Metal-Hydrogen Interactions in Solid-State Metal Hydrides

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Metal-hydrogen interactions lead to a variety of interesting phenomena such as metal-semiconductor transitions ($\text{LaMg}_2\text{NiH}_7$), directional metal-hydrogen bonding ($\text{ErNi}_3\text{-H}$, $\text{LaNi}_3\text{B-H}$), hydrogen induced valence transitions ($\text{CeMn}_{1.8}\text{Al}_{0.2}\text{-H}$), unexpected H-site energies (ZrTi_2H_x), frequency dependence of B-H modes on metal atom size (MBH_4 ; $M=\text{Na,K,Rb,Cs}$, and metal atom relaxations by $\sim 0.6 \text{ \AA}$ around vacancies on H sites (RH_{3-x} , $R=\text{La,Nd}$).

The project studies the influence of metal-hydrogen interactions on physical and chemical properties of various metallic, covalent and ionic metal-hydrogen systems.

Hydrogenation of metallic $\text{Ce}(\text{Mn}_{1-x}\text{Al}_x)_2$ leads to a volume expansion of $\Delta V/V=42\%$ that is the largest known among metal hydrides, and a metal atom site exchange driven by repulsive Al-H interactions. Magnetic susceptibility data confirm a H-induced valence transition from Ce^{IV} to Ce^{III} .

The occupancies of adjacent deuterium sites in metallic $\text{ZrTi}_2\text{D}_{4.3}$ have been studied at high temperature in-situ measurements (DMC). The site energy of the smaller ZrTi_3 -type interstices is higher by $\sim 127\text{meV}$ than that of the bigger Zr_2Ti_2 -type interstices. This value is of the same order of magnitude as the energy difference between the vibrational ground state and the first excited state of hydrogen in ZrTi_3 -type interstices as found in a previous INS study, but different in sign from that derived from model calculations.

A hydrogen induced metal-semiconductor transition without major changes in the metal substructure has been discovered in the $\text{LaMg}_2\text{Ni-H}$ system. High-resolution data on D2B (ILL) reveal tetrahedral 18-electron $[\text{NiH}_4]^{4-}$ complexes and “interstitial” hydride anions H^- surrounded by La and Mg only suggesting the limiting ionic formula $\text{LaMg}_2\text{NiH}_7=\text{La}^{3+} \cdot 2\text{Mg}^{+2} \cdot [\text{NiH}_4]^{4-} \cdot 3\text{H}^-$. Similar studies on related systems are under way on HRPT (SINQ).

Directional metal-hydrogen bonding was found in the metallic $\text{ErNi}_3\text{-H}$ and $\text{LaNi}_3\text{B-H}$ systems (HRPT). As shown in Fig. 1 hydrogen in $\beta_1\text{-ErNi}_3\text{H}_x$ occupies two sites in the AB_2 -type building block. One (D1) corresponds to

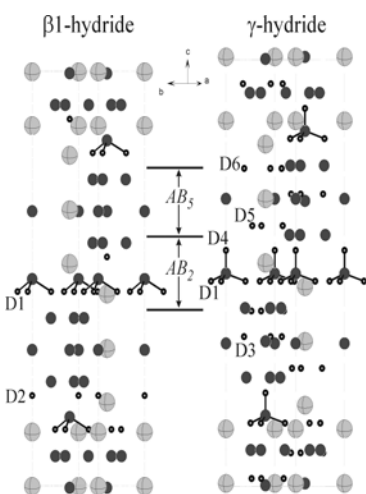


Figure 1: Ni-D bonds (solid lines) in rhombohedral ErNi_3D_x

three ligands of a Ni centered NiH_4 tetrahedron, and the other (D2) bridges a Ni triangle. In $\gamma\text{-ErNi}_3\text{H}_x$ D2 becomes nearly empty while four other D sites become occupied.

One (D4) completes the fourth ligand of the NiH_4 tetrahedron, and three (D3,D5,D6) are located in the AB_5 building block. The formation of tetrahedral NiH_4 units suggests directional bonding effects and a possible metal-semiconductor transition such as in $\text{LaMg}_2\text{NiH}_7$.

The structure and dynamics of $[\text{BH}_4]^-$ complexes in covalent alkali borohydrides MBH_4 ($M=\text{Na,K,Rb,Cs}$) have been investigated by diffraction (DMC) and IR spectroscopy (Dr. Hagemann, University of Geneva) on deuterides. As shown in figure 2 the frequency of the stretching mode, $\nu(\text{A}_{1g})^{-2/3}$, for the $[\text{BD}_4]^-$ units scales with the B-D distances.

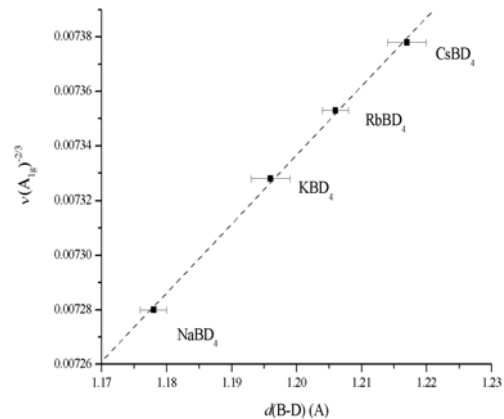


Figure 2 : Frequency of stretching mode $\nu(\text{A}_{1g})^{-2/3}$ versus B-D bond distances of $[\text{BD}_4]^-$ units in MBD_4 ($M=\text{Na,K,Rb,Cs}$)

In the ionic hydrides RH_3 ($R=\text{rare-earth}$) atom relaxations around hydrogen vacancies were studied experimentally (HRPT) and theoretically (P. Herzig, University of Vienna). *Ab-initio* calculations by VASP on nearly stoichiometric LaH_3 ($\text{La}_{32}\text{H}_{95}$) confirm energetically favored atom relaxations around empty hydrogen sites. The metal octahedra around empty octahedral sites tend to expand (by $\sim 0.02 \text{ \AA}$), while the hydrogen atoms on tetrahedral sites shift by up to $\sim 0.10 \text{ \AA}$ towards the faces of empty metal octahedra. These findings are of interest for the study of metal-insulator transitions in these systems.

The work has so far lead to a dozen publications. For downloadable reprints and preprints see <http://www.unige.ch/sciences/crystal/yvonk/pub.html>

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