Solid-State Structures and Properties of Europium and Samarium Hydrides

Why metal hydrides are fascinating in inorganic chemistry?

- Extremely versatile chemical bonding
- Chrystal structures
- Physical properties
- hydrogen storage materials

Synthesis and Structural Characterization

$Eu + H_2 \rightarrow EuH_2$

$2\ SmMg_2 + 7\ H_2 \rightarrow 2\ SmMg_2H_7$

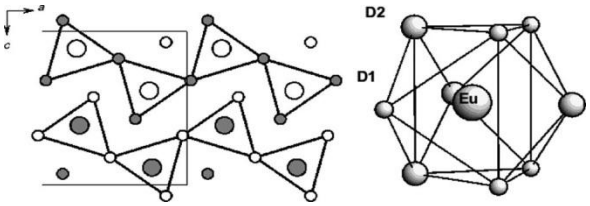
$4\ EuH_2 + 2\ Ir + H_2 \rightarrow 2\ Eu_2IrH_5$

$EuH_2 + LiH \rightarrow EuLiH_3$.

$6\ EuH_2 + 7\ MgH_2 \rightarrow Eu_6Mg7H_{26}$ at 3.5 G Pa.

Solid – State Structure of Europium Hydrides

Binary europium dihydride (deuteride) has got the highest neutron absorption of all known (investigated) europium hydrides. Its crystal structure, proposed to belong to the ortho rhombic $PbCl_2$ type structure



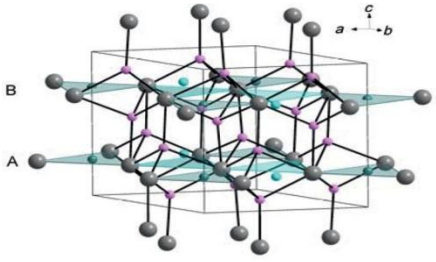
Crystal structure of EuD_2 in a projection along crystallographic b axis [Eu (large), D (small), y = 1/4 (empty symbols),y = 3/4 (filled symbols)] (left) and coordination polyhedron of europium in EuD_2 (right).

The $PbCl_2$-type arrangement shows trigonal EuD_6 prisms linked by common tri- angular faces along b to form columns. Further linking by common edges results in zigzag chains of interconnected prisms running along a. The complete coordination polyhedron around europium is a tricapped trigonal prism of deuterium atoms with nine Eu–D distances .

Why often used deuterides? Lower incoherent scattering relative to ^1H

Solid-State Structures of Samarium Hydrides

From neutron diffraction data, SmD_3 could be shown to belong to the fully ordered trigonal LaF_3 type. Deuterium fills tetrahedral and trigonal-planar voids in a hexagonal closest packing of samarium atoms.(Sm as large gray spheres, D1 small pink spheres in nearly tetrahedral coordination,D2 small turquoise spheres in nearly tri- angular coordination, D3 small dark green spheres in trigonal planar coordination.



Optical and Electrical Properties

Most of the europium and samarium hydrides assumed to be ionic or complex hydrides for the reasons of

- crystal chemical
- colored reasons

This indicates semiconducting behavior in accordance with structural properties.

- Optical absorption measurements are rare. In EuH_2 the optical band gap was shown to be 1.85 eV, confirming its semiconducting behavior.

- In other cases, temperature- dependent electrical resistivity measurements allowed $EuLiH_3$, Eu_2RuH_6, and Eu_2IrH_5 to be classified as semiconductors with band gaps of 1.5, 0.08, and 0.15 eV, respectively
- To characterize the electronic structure and to predict physical properties of europium and samarium hydrides quantum mechanical calculations are performed .

Magnetic Properties

All europium hydrides studied so far show ferromagnetism with Curie temperature in the range of $7K \leq T_c \leq 38K$ and effective magnetic moment of $7.3\ \mu_B \leq \mu_{eff} \leq 8.4\ \mu_B$. This indicates europium to be divalent in all these hydride. Trivalent europium could not be established in a hydride matrix so far, probably due to the medium oxidizing power on hydrogen.

References:

- Eur.J.Inorg.Chem.2010,2582-2593/ Solid-State Structures and Properties of Europium and Samarium Hydrides /H.Kohlman