



NordForsk

**FunHy**  
NEUTRONS FOR MULTI-FUNCTIONAL HYDRIDES

## FunHy Newsletter

### Who and where?

Gustav Ek, Martin Sahlberg and Ulrich Häussermann from FunHy have along with other collaborators recently published the article *Hydrogen induced structure and property changes in  $\text{Eu}_3\text{Si}_4$*  in the Journal of Solid State Chemistry (DOI: 1016/j.jssc.2019.05.033).

### Why?

Zintl phases, which are composed of an active metal (i.e. alkali, alkaline earth, or rare earth) and a more electronegative p-block metal or semimetal, represent a large family of inorganic compound. As their characteristic feature, atoms of the electronegative component appear reduced and may form polyanionic structures to achieve an octet. Like many intermetallic compounds Zintl phases can react with hydrogen to form hydrides. However, the rather high ionicity of Zintl phases makes such hydrides peculiar. Hydrogen takes an ambivalent role and can be incorporated in two principal ways: either hydridic, where H is exclusively coordinated by active metals (interstitial hydrides), or as part of the polyanion where it acts as a covalently bonded ligand (polyanionic hydrides). Chemical structures and physical properties of Zintl phases can change profoundly upon H incorporation. This provides interesting prospects for fundamental inorganic chemistry and materials science.

### How?

Hydrides  $\text{Eu}_3\text{Si}_4\text{H}_{2+x}$  were obtained by exposing the Zintl phase  $\text{Eu}_3\text{Si}_4$  to a hydrogen atmosphere at a pressure of 30 bar and temperatures from 25 to 300 °C. Structural analysis using powder X-ray diffraction (PXRD) data suggested that hydrogenations in a temperature range 25 – 200 °C afford a uniform hydride phase with an orthorhombic structure (*Immm*,  $a \approx 4.40 \text{ \AA}$ ,  $b \approx 3.97 \text{ \AA}$ ,  $c \approx 19.8 \text{ \AA}$ ), whereas at 300 °C mixtures of two orthorhombic phases with  $c \approx 19.86$  and  $\approx 19.58 \text{ \AA}$  were obtained.

The assignment of a composition  $\text{Eu}_3\text{Si}_4\text{H}_{2+x}$  is based on first principles DFT calculations, which indicated a distinct crystallographic site for H to be occupied in the  $\text{Eu}_3\text{Si}_4$  structure. In this position, H atoms are coordinated in a tetrahedral fashion by Eu atoms. The resulting hydride  $\text{Eu}_3\text{Si}_4\text{H}_2$  is stable by -0.46 eV/H atom with respect to  $\text{Eu}_3\text{Si}_4$  and gaseous  $\text{H}_2$ . Deviations between the lattice parameters of the DFT optimized  $\text{Eu}_3\text{Si}_4\text{H}_2$  structure and the ones extracted from PXRD patterns point to the presence of additional H in interstitials also involving Si atoms. Subsequent DFT modeling of compositions  $\text{Eu}_3\text{Si}_4\text{H}_3$  and  $\text{Eu}_3\text{Si}_4\text{H}_4$  showed

considerably better agreement to the experimental unit cell volumes. However, the ordered monoclinic model structures do not provide a good match to the experimental, orthorhombic, PXRD patterns. It was then concluded that the hydrides of  $\text{Eu}_3\text{Si}_4$  have a composition  $\text{Eu}_3\text{Si}_4\text{H}_{2+x}$  ( $x < 2$ ) and are disordered with respect to H in  $\text{Si}_2\text{Eu}_3$  interstitials. Hydrides  $\text{Eu}_3\text{Si}_4\text{H}_{2+x}$  decompose at temperatures above  $300\text{ }^\circ\text{C}$  in a dynamic vacuum into unidentified products. Thus the hydrogenation of  $\text{Eu}_3\text{Si}_4\text{H}_{2+x}$  is not reversible. From magnetic measurements the Curie-Weiss constant and effective magnetic moment of  $\text{Eu}_3\text{Si}_4\text{H}_{2+x}$  were obtained. The former indicates antiferromagnetic interactions, the latter attains a value of  $\sim 8\ \mu_B$  which is typical for compounds containing  $\text{Eu}^{2+} 4f^7$  ions.

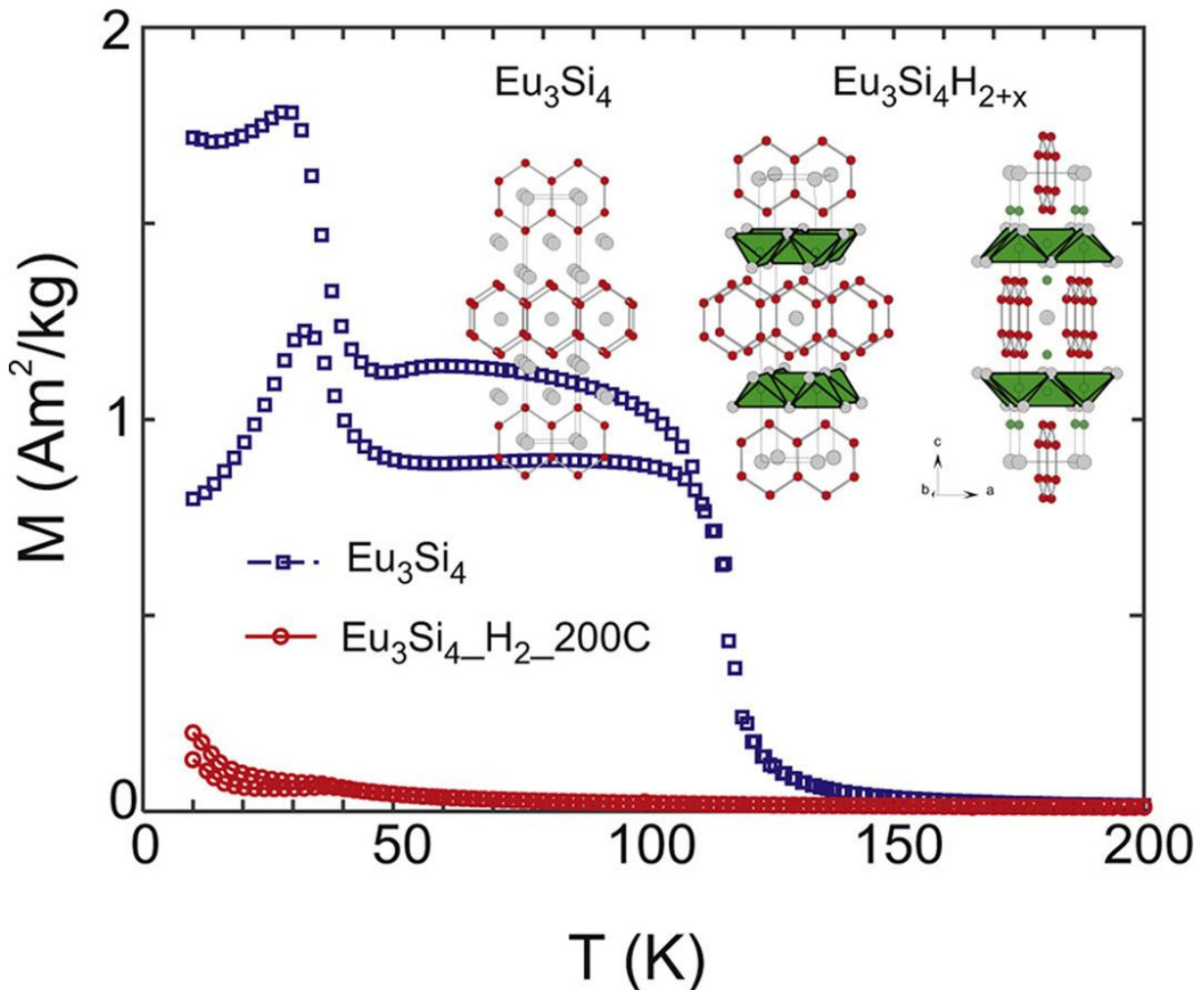


Figure 1: Ferromagnetic  $\text{Eu}_3\text{Si}_4$  absorbs hydrogen to yield hydrides  $\text{Eu}_3\text{Si}_4\text{H}_{2+x}$  with quenched ferromagnetism.

FunHy webpage: <http://inano.au.dk/en/about/research-groups/nano-energy-materials/projects/neutrons-for-multi-functional-hydrides-funhy/>