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Variations of structure and magnetic properties in UTGe hydrides (T = late transition metal)

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ABSTRACT

Hydrogenation of UTGe compounds results in formation of stable α- and β-hydrides, and modification of the crystal structure and magnetic properties. T_C (3 K) of UCoGe increases up to 50 K in β-hydrides and T_C (9.5 K) of URhGe up to 17 K in α-hydrides. The type of magnetic order is changed in UNiGe-H and UIrGe-H. The observed effects are attributed to the increased U–U spacing in the hydrides.

1. Introduction

Magnetic properties of uranium-based intermetallics are intimately related to the character of the 5*f* electronic states, ranging between a localized character, similar to lanthanides, and itinerancy, which is reminiscent of magnetism emerging in transition metals. For purely band systems, the actinide–actinide spacing is a crucial parameter, which determines the magnetic properties. However, for uranium compounds with the U–U spacing (d_{U-U}) large enough the principal controlling parameter is the 5*f*-ligand hybridization.

Hydrogenation in general leads to changes/modifications of both crystal and electronic structure of intermetallic compounds. It brings a relatively small perturbation to the system, namely a lattice expansion and the hydrogen bonding with other atoms in the lattice. New formed hydrides represent autonomous compounds, often exhibiting new and very interesting physical properties. Besides, studies of their properties can provide additional information on the specific features of interatomic interactions in the initial compounds. Hydrogen absorption in actinide compounds strongly supports the tendency to form local 5*f* magnetic moments and gives rise to magnetic order. This can be partially attributed to 5*f*-band narrowing due to enhanced inter-actinide spacing.

This type of development has already been indicated for selected members of UTX (T = transition metal, X = *p*-element) family. Hexagonal structure (ZrNiAl-type) of UNiAl-H [1], UCoSn-H and URuSn-H [2,3] significantly expands, even up to 12.4% for $UNiAlH_{2.0-2.3}$. The antiferromagnetic (AF) ordering of UNiAl (T_N = 19 K) is lost in $UNiAlH_{0.06-0.58}$, changed into ferromagnetic (F) one in $UNiAlH_{0.7}$ (T_C = 87 K), and then turns back to AF in $UNiAlH_{2.0-2.3}$ (with higher T_N of 94–117 K). Hydrogen absorption in UCoSn and URuSn causes only the shift of T_C from 82 K up to 102 K in $UCoSnH_{1.4}$ and from 54 K weakly down to 51 K in $URuSnH_{1.4}$. In the case of silicides, such as UCoSi-H, UPdSi-H, UNiSi-H [4,5], the orthorhombic crystal structure (TiNiSi-type) transforms into the hexagonal one (ZrBeSi-type) and expands even by about 8% in $UNiSiH_{1.0}$. The latter is a ferromagnet with $T_C \approx 98$ K, whereas UNiSi is an antiferromagnet with $T_N \approx 85$ K. T_N ($\approx$31 K) of UPdSi increases up to 46 K in $UPdSiH_{1.0}$. The volume expansion is not sufficient to induce a magnetic order in UCoSi-H. Other UTSi

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compounds did not exhibit any noticeable H absorption. Replacing Si by larger Ge provides larger interstitials, and the hydrogenation conditions may be more favorable due to purely geometrical conditions as the expanded interstitials can allocate hydrogen atoms more easily.

This work presents results of studies of the U magnetism tuned by hydrogen absorption and concomitant lattice expansion in UTGe compounds (stoichiometry 1:1:1), in our case involving T from the end of the 3*d*- (Fe, Co, Ni), 4*d*- (Rh, Pd) and 5*d*- (Ir, Pt) series. In this kind of compounds, the hybridization between the 5*f* and *d*-states is gradually reduced with increasing population of the transition metal *d*-electron states. UTGe compounds crystallize mainly in the orthorhombic TiNiSi-type of structure (an exception is UFeGe, which undergoes a structural phase transition at $T = 500$ K, with the room temperature (RT) phase being monoclinically distorted) [6]. These compounds show, depending mostly on the strength of the 5*f*-ligand hybridization, diverse types of ground state, from Pauli paramagnetism (P) to AF and/or F order. The extremely strong magnetocrystalline anisotropy, with the *a* direction as the general hard anisotropy direction [7] can be related to the *a*-axis alignment of the U chains, whereas the shortest d_{U-U} between the chains is larger than the value within the chain.

Knowing the effects of hydrogen absorption in selected UTX compounds and the structural and magnetic properties of UTGe compounds, it is interesting to investigate hydrogen-induced changes in this particular group of compounds.

2. Experimental details

2.1. Sample preparation

Polycrystalline samples of UTGe (T = Fe, Co, Ni, Rh, Pd, Ir and Pt) were prepared by arc melting of stoichiometric amounts of the constituent metals in a mono-arc furnace under protection of an Ar atmosphere. A heat treatment was only necessary for UCoGe in order to improve the quality of the sample. The as-cast pieces were wrapped in Ta foil and annealed in quartz tubes under a high vacuum, for 24 h at 1200 °C and 20 days at 950 °C. The phase composition was checked by means of XRD-3003 Seifert or Bruker D8 Advance diffractometers with Cu-K$_{\alpha}$ radiation in a step regime (step of 0.02° for 2θ). The Rietveld analysis of the X-ray diffraction (XRD) data was performed using the FullProf program.

2.2. Hydrogenation and decomposition

The bulk materials were crushed into submillimeter particles and loaded in a reactor for hydrogenation. After so-called activation of the surface by the thermal cycling of sample up to $T = 523$ K in a dynamic vacuum ($p \approx 2 \times 10^{-6}$ mbar), pure hydrogen gas was introduced into the reactor. Depending on its pressure ($p_{H_2} = 0.5$–156 bar), various H stoichiometries could be achieved. Last step of hydrogenation process was the thermal cycling (twice) of the sample up to $T = 773$ K under the given H_2 pressure in order to promote the hydrogen absorption. The crystal structures of the synthesized products were checked by XRD.

The absolute amount of absorbed hydrogen in UTGe hydrides was determined by thermally induced desorption (heating of the sample up to $T \approx 773/673$ K in an evacuated calibrated volume). The crystal structures of the decomposed products were checked by XRD.

2.3. Magnetic and specific-heat measurements

Magnetic measurements on fine powders with particles fixed by a glue in random orientation were performed in Quantum Design Physical Properties Measuring System (PPMS) in the temperature range 2–300 K and external magnetic fields up to 9 T. The *ac* susceptibility ($\chi_{ac}(T)$) was measured in zero *dc* field and *ac* field of 1 mT with frequency 80 Hz. The Magnetic Property Measurement System (MPMS) with Superconducting Quantum Interference Device (SQUID) detection system equipped with a 7 T magnet was used is few cases.

The high-field magnetization curves for UNiGe and its β-hydrides were measured at $T = 1.5$ K on random powders fixed by cyanoacrylate glue, in pulsed magnetic fields up to 60 T (pulse duration 20 ms) at High-field Laboratory in Dresden, Germany. The magnetization was measured by the induction method using a coaxial pick-up coil system. Detailed description of high-field installation is given in Ref. [8].

Temperature dependence of specific heat was studied on pellets pressed in a die with tungsten carbide faces also by means of the PPMS system.

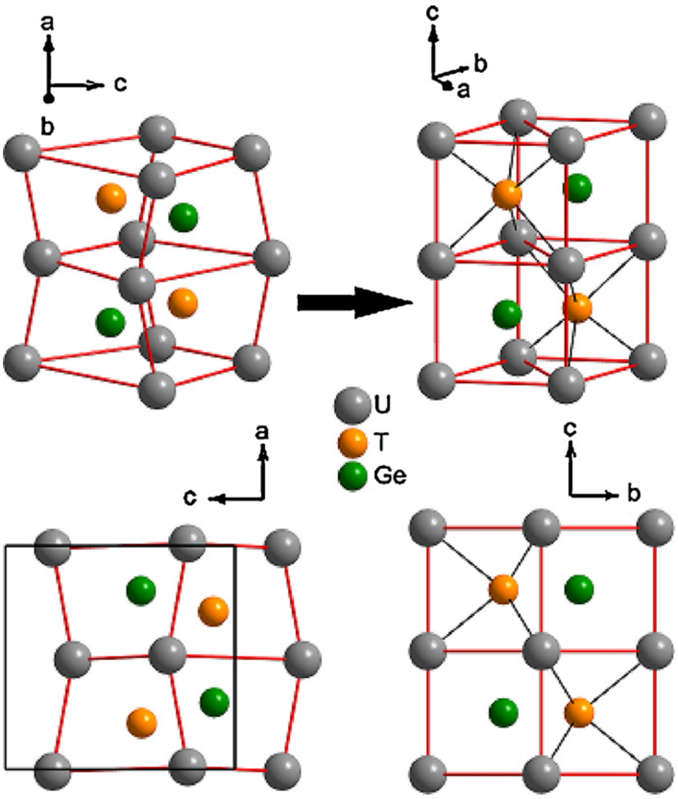

Fig. 1. The relationship between the unit cells of TiNiSi (left) and ZrBeSi (right) structure types and their projections. Hydrogen atoms locate inside the U_3T tetrahedra (max. 2 H/f.u.)..

3. Results and discussion

3.1. Crystal structure

The orthorhombic TiNiSi-type of structure (space group *Pnma*), the most common one reported for UTGe compounds, is built of distorted trigonal prisms U_6 centred either by X or by T atoms (atomic positions U – 4*c* (x_U; 0.25; z_U); T – 4*c* (x_T; 0.25; z_T); X – 4*c* (x_{Ge}; 0.25; z_{Ge})). It is an ordered variant of the $CeCu_2$ structure considered as a distortion of the hexagonal AlB_2 structure.

UTGe compounds were found to absorb hydrogen, forming stable α- or/and β-hydrides. The exception is UPtGe. This compound does not absorb any noticeable amount of hydrogen up to $p_{H_2} = 156$ bar and $T = 773$ K. Lattice parameters of UTGe and their hydrides are presented in Table 1. The label of an α-hydride is used to describe a solid solution of a small amount of hydrogen randomly distributed in the lattice. Such hydride adopts the TiNiSi-type of structure, slightly expanded. A β-hydride is the H-rich phase significantly expanded, adopting in our case the ZrBeSi-type of structure.

The ZrBeSi-type of structure (space group *P*6$_3$/*mmc*) is closely related to the TiNiSi-type, which can be also considered as orthorhombically deformed hexagonal ZrBeSi-type of structure (superstructure to AlB_2-type). Due to formal reasons, the crystal axes are interchanged between the hexagonal and orthorhombic structures. The simple relation between the lattice parameters of these two structure types is: $c_{hex} = a_{orth}$ and $a_{hex} = b_{orth} = c_{orth}/\sqrt{3}$. The relationship between the TiNiSi and ZrBeSi structure types is illustrated in Fig. 1.

Based on the rare-earth (R) ternary compound as $LaNiSnD_2$ [9,10] with a similar structure transformation upon hydrogenation as reported for UTSi and UTGe compounds, it was found that