Magnetism of UTGe compounds tuned by hydrogen absorption

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Abstract. UTGe compounds absorb hydrogen up to 2 H atoms/f.u., which has a dramatic impact on the 5f magnetism. The $T_C$ value of UCoGe increases to 50 K. Magnetic susceptibility of spin fluctuator UFeGe markedly increases. For ferromagnetic URhGe only $\alpha$-hydride could be obtained, which moderate increase of $T_C$ and spontaneous moment. The $\alpha$-hydride of UCoGe is surprisingly paramagnetic despite of a small volume expansion (0.25 %).

1. Introduction
Hydrogenation of UTGe intermetallic compounds is a capable tool used for investigation of their magnetic properties. The basic thermodynamic properties of metal-hydride systems can be assessed from the phase diagrams, which show the formation of the solid solution of hydrogen in intermetallic compounds. The solid solution of a small amount of hydrogen ($\leq 0.1$ H/f.u. in our case) is called $\alpha$-phase ($\alpha$-hydride) and characterized by the same type of crystal structure as a pure compound, with no negligible volume expansion. For higher concentration of hydrogen we can obtain a $\beta$-phase ($\beta$-hydride) with the crystal structure modified from the orthorhombic TiNiSi-type for the pure compound to the hexagonal ZrBeSi-type for the hydride. Applied pressure of hydrogen and temperature play a crucial role in hydrogenation process. In some cases the maximum available pressure (150 bar in our setup) is not sufficient to reach pure $\beta$-phase and the system ends up in a pure $\alpha$-phase or in the region where the two phases coexist. Our investigation of UTGe compounds hydrides involved all such cases.

Hydrogenation, besides a notable lattice expansion for $\beta$-hydrides, leads to the modification of magnetic properties. This fact was already shown in some hydrogenated UTSi compounds (UCoSi-H, UPdSi-H, UNiSi-H) [1,2]. The saturated hydrides of UTSi compounds contain about 2 H atoms/f.u.. This work inspired us to study respective germanides, which can provide larger interstitials and give more favourable hydrogen storage conditions. UTGe compounds crystallize mostly in the orthorhombic TiNiSi-type of structure, space group $Pnma$. UFeGe undergoes a distortion at 500 K into the monoclinic low-temperature structure. UCoGe originally supposed to be non-magnetic spin fluctuator [3], was recently identified as possible weak ferromagnet, in analogy to URhGe. The values of Curie temperatures were reported as $T_C = 3$ K and 9 K for UCoGe [4] and URhGe [5,6], respectively. Magnetic susceptibility data for UFeGe indicate paramagnetic behaviour with characteristic features of spin fluctuations [6].
2. Experimental details
The parent compounds UTGe were prepared by arc melting of stoichiometric amounts of the pure components. The crystal structure was checked by powder X-ray diffraction (XRD-3003 Seifert diffractometer, Cu-Kα radiation). For the hydrogenation the sample was crushed into sub-millimeter pieces and placed into a reactor. Next step is the surface activation by annealing up to $T = 523 \text{ K}$ under high-vacuum conditions (pressure of $10^{-6} \text{ mbar}$). The reactor is subsequently filled by pure hydrogen gas and thermally cycled (twice) to $T = 773 \text{ K}$ at a given H pressure to promote hydrogen absorption. The main indication of H absorption is a variation of crystal structure parameters detected by XRD. The hydrogen content can be determined by the thermally induced decomposition of the hydride in a closed volume. Magnetic properties were studied both for the UTGe compounds and its hydrides by means of an extraction magnetometer in the Quantum Design Physical Properties Measuring System (PPMS) and in the Magnetic Property Measurement System (MPMS). For magnetization measurement, powder of the hydrides with randomly oriented particles was fixed by a glue to avoid orientation of the grains by external magnetic field and uncontrollable preferential orientation.

3. Results and discussion

3.1. Crystal structure
Initially we applied a high-pressure synthesis procedure for the UTGe compounds with temperature cycling up to $T = 773 \text{ K}$. In the case of UCoGe we found that a single-phase hydride of UCoGe with high occupancy (1.7 H atoms per formula unit) can be synthesized at much lower pressure (5 bar), relative to silicides giving an effect of the crystal structure transformation from the orthorhombic TiNiSi-type to hexagonal one (ZrBeSi-type), with 10 % of unit cell expansion. A pure $\alpha$-hydride, which preserves the orthorhombic structure, was also successfully prepared at $p_{\text{H}_2} = 2 \text{ bar}$ with the H concentration of 0.1 H/f.u. and volume expansion about 0.25 %. The coexistence was not detected for UGoGe hydrides.

The crystal structure refinement of UFeGe provided the monoclinic crystal structure with room-temperature lattice parameters $a = 6.987(1) \text{ Å}$, $b = 4.304(1) \text{ Å}$, $c = 6.983(1) \text{ Å}$, $\beta = 93.9^\circ$, space group $P2_1/m$ (in good agreement with [7]). Applied pressure of H$_2$ (96 bar) caused that 80 % of the monoclinic phase was transformed to the hexagonal one (ZrBeSi-type), the rest remaining as the high temperature phase of UFeGe, probably due to temperature cycling during hydrogenation process (estimate of the hydrogen content gives a value 1.7 H atoms/f.u.). Another eventual hydrogenation attempt under the highest pressure (156 bar) resulted in pure $\beta$-hydride of UFeGe (1.8 H atoms per formula unit). The monoclinic symmetry was lifted to hexagonal reaching 5.5 % of volume expansion and lattice parameters $a = 4.176(1) \text{ Å}$ and $c = 7.337(2) \text{ Å}$.

In the case of URhGe we obtained only the $\alpha$-phase with less than 0.1 H/ f.u. despite applying the pressure of 150 bar. The crystal structure remains orthorhombic, but with a distinct shift of peaks in the diffraction pattern due to hydrogen absorption.

For the U(Co,Fe,Rh)Ge compounds and their hydrides a small amount of the impurity phases U(Co,Fe,Rh)$_2$Ge$_2$, was detected by XRD.
Table 1. Lattice parameters and unit cell volume of UTGe and the hydrides. Notice the change in notation between the two structure types: For UCoGe and UFeGe, $a$ corresponds to $c_{\text{hex}}$, $c$ to $a_{\text{hex}}$.

| Compound       | Structure type | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) | $\Delta V/V$ (%) | $d_{\text{U-U}}$ (Å) |
|----------------|----------------|---------|---------|---------|------------|------------------|---------------------|
| UCoGe         | Orthorhombic   | 6.847(2)| 4.207(1)| 7.228(2)| 52.06      | -                | 3.48                |
| UCoGeH$_{0.1}$| Orthorhombic   | 6.852(1)| 4.198(1)| 7.259(1)| 52.19      | 0.25             | 3.48                |
| UCoGeH$_{1.7}$| Hexagonal      | 4.093(2)| -       | 7.934(4)| 57.54      | 10.5             | 3.97                |
| UFeGe         | Monoclinic ($\beta = 93.7^\circ$) | 6.977(1)| 4.305(1)| 6.983(1)| 52.33      | -                | 3.45                |
| UFeGe$_{1.8}$ | Hexagonal      | 4.176(1)| -       | 7.337(2)| 55.41      | 5.5              | 3.67                |
| URhGe         | Orthorhombic   | 6.876(2)| 4.333(1)| 7.507(2)| 55.91      | -                | 3.49                |
| URhGeH$_{x<0.1}$ | Orthorhombic | 6.898(2)| 4.318(1)| 7.583(3)| 56.47      | 1.0              | 3.51                |

3.2. Magnetic properties
For UTGe series, the hydrogenation is not as straightforward as found in the silicides [1,2]. In the case of paramagnetic UFeGe, the hydrogenation does not induce magnetic order, but the susceptibility increases markedly and becomes monotonously increasing with decreasing $T$. Some kind of ferromagnetic impurity for the hydride was detected by $ac$ susceptibility measurement. The $dc$ susceptibility shown in figure 2 was therefore corrected using the standard procedure.

As to UCoGe, we started from the polycrystal, which exhibited a weak ferromagnetism with $T_C = 3$ K. Besides the increase of magnetic susceptibility, the Curie temperature for UCoGeH$_{1.7}$ exhibits a larger change - it increases to $\approx 50$ K. The temperature dependence of magnetization below this temperature as well as $ac$ susceptibility data indicate that the system is inhomogeneous and in reality we observe a distribution of $T_C$ values. This can be related to the fact that the H sublattice is not occupied completely, to the full occupancy of 2 H atoms/f.u..The spontaneous magnetization, seen from magnetization curves at $T = 2$ K (figure 1) is not dramatically enhanced. The moment was estimated to be about 0.05 $\mu_B$/f.u. (0.03 $\mu_B$/f.u. for UCoGe), but suggest that ferromagnetic ordering for the hydride is intrinsic.

Surprisingly the $\alpha$-hydride of UCoGe loses the ferromagnetism despite a weak volume expansion. This variation was found to be fully reversible.

As magnetic properties of U compounds are critically dependent on the inter-uranium spacing $d_{\text{U-U}}$, it is interesting to monitor variations if this parameter with hydrogenation. The values for UTGe compounds and their hydrides are listed in the table 1, where we can see that $d_{\text{U-U}}$ is much higher for the $\beta$-hydride of UCoGe than for UCoGeH$_{0.1}$ and it exceeds the Hill limit 3.4-3.6 Å, considered as a minimum spacing needed for onset of magnetism. The difference in $d_{\text{U-U}}$ between $\alpha$ and $\beta$ hydrides of UCoGe may explain the appearance of ferromagnetism in the $\beta$ hydride.
Figure 1. Magnetization curves of U(Fe,Co,Rh)Ge compounds and their hydrides measured at \( T = 2 \) K.

Figure 2. Temperature dependence of magnetic susceptibility for URhGe and its hydride measured in \( \mu_0 H = 3 \) T, \( \chi_{corr}(T) \) for UFeGe and its hydride. The insert shows \( \chi(T) \) for UCoGe and its hydrides measured in \( \mu_0 H = 1 \) T.

For the URhGe hydride, a broad well-pronounced peak is observed on the \( \chi_{AC}(T) \) plot with maximum between 9 K and 20 K. The value of \( T_C \) suggests that URhGeH\(_{0.1}\) is magnetically inhomogeneous. In the high-temperature range, i.e. for \( T > 100 \) K, the \( dc \) magnetic susceptibility \( \chi(T) \) of the \( \alpha \)-hydride follows a modified Curie–Weiss (MCW) behaviour with an effective moment \( \mu_{\text{eff}} = 2.0 \mu_B/\text{f.u.} \) for URhGeH\(_{0.1}\) and a negative paramagnetic Curie temperature \( \Theta_p \approx -2 \) K (with a temperature-independent term \( \chi_0 = 0.9 \times 10^{-8} \text{ m}^3\text{mol}^{-1} \)). We should compare the values for the hydride with the values for the pure URhGe, which has \( \mu_{\text{eff}} = 1.8 \mu_B/\text{f.u.} \), \( \Theta_p \approx -1 \) K, \( \chi_0 = 1.6 \times 10^{-8} \text{ m}^3\text{mol}^{-1} \). The hydrogenation of URhGe increases the spontaneous magnetization from 0.14 \( \mu_B/\text{U-atom} \) for the parent compound to 0.24 \( \mu_B/\text{U-atom} \) for the hydride (both fixed powder data) at \( T = 2 \) K (figure 1).

4. Conclusion

We have shown that the structure of the UTGe compounds tend to follow the same pattern as the UTSi compounds, with an increase of symmetry upon hydrogenation. The H-induced variations of magnetism are quite strong for UTGe series. The \( \beta \)-hydride of UCoGe exhibits a stronger ferromagnetism than UCoGe. The increase of \( T_C \) up to 50 K in the hydride can be attributed to a significant volume expansion, exceeding 10 %. The \( \alpha \)-hydride, with a small volume expansion of 0.25 % is non-magnetic. A closer inspection of the structure data reveals that only two out of the three lattice parameters expand in UCoGeH\(_{0.1}\). The parameter \( b \) shrinks by a small amount in the \( \alpha \)-hydride, so it is legitimate to speculate that it is the \( b \)-parameter, which critically modulates the magnetic
properties. Hydrogen absorption in UFeGe causes the volume expansion and leads to enhancement of magnetic interaction, but it is not sufficient enough to induce magnetic order. The hydride remains paramagnetic. The lattice volume of URhGeH\(_{0.1}\) increases by about 1%. The hydrogenation for this compound increases the spontaneous magnetic moment as well as the magnetic susceptibility values. These indications allow to conclude that the increase of interatomic distances between the uranium atoms is a primary parameter, which determines magnetic properties.

A possible influence of H bonding, which would substantially modify charge balance, can be excluded e.g. by \(^{57}\)Fe Mössbauer spectroscopy experiment, performed on UFeGe and UFeSi and their hydrides, which exhibit a negligible variation of the isomer shift due to the hydrogenation [8].

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