

Structure and magnetism of a new series of UTSn hydrides

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Received 7 June 2004; received in revised form 29 December 2004; accepted 1 January 2005

Available online 20 July 2005

Abstract

We studied crystal structure and magnetic properties of UCoSnH_{1.4} and URuSnH_{1.4} hydrides. They adopt the same hexagonal structure as the parent compounds. Both compounds remain ferromagnets after hydrogenation, but the tendencies of the magnetic properties differ: UCoSn exhibits a more typical behaviour expected for intermetallics of uranium upon hydrogenation (T_C increases from 82 to 102.5 K, the spontaneous magnetic moment increases from 0.64 to 0.70 μ_B /f.u.), but the influence of hydrogen absorption on URuSn is surprisingly opposite (T_C decreases from 54 to 51 K, its magnetic moment gets reduced to 0.48 μ_B /f.u. in URuSnH_{1.4} from 0.53 μ_B /f.u. in URuSn).

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Keywords: Hydrogen storage materials; X-ray diffraction; Magnetic measurements

1. Introduction

An interesting trait of uranium intermetallics is their varying ability to absorb hydrogen. Due to the modifications in the electronic density distribution and in the interatomic spacing, hydrogenation leads to changes in the physical properties of the intermetallics, namely their magnetic properties. Unlike typical lanthanide compounds, which are characterised by a small impact of hydrogenation on the size of magnetic moments, the uranium compounds demonstrate a large influence of hydrogenation both on the size and stability of the magnetic moments, and on their interactions.

Although the hydrides and deuterides of RENiAl compounds have been widely studied [1], so far the absorption of hydrogen was found only for UNiAl among equiatomic uranium ternaries crystallising with the hexagonal ZrNiAl structure type. UNiAl orders antiferromagnetically at $T_N = 19.3$ K [2]. Several UNiAl-based hydrides with different hydrogen content have been found [3–7]. The range of hydrides with orthorhombic structure (space group *Pnma*) with a hydrogen content up to 0.58 H atom per formula unit (f.u.) does

not show magnetic ordering down to 2 K. The hydride with a higher hydrogen content, hexagonal UNiAlH_{0.7}, shows ferromagnetic ordering below 87 K. Further hydrogenation results in the recovering of antiferromagnetic ordering, the Néel temperature for UNiAlH_{2.3} is 99 K.

To find more compounds absorbing hydrogen with the same type of structure, we inspected the UTSn group and found considerable absorption of hydrogen for UCoSn and URuSn.

2. Experimental

UCoSn and URuSn intermetallic compounds were used as starting materials for hydrogenation. The samples were crushed into submillimeter particles, the surface of which was activated by annealing at $T = 473$ K for 2 h in a dynamic vacuum (10^{-5} mbar). The reactor was subsequently filled with pressurised hydrogen (120 bar), and then subjected to thermal cycling up to $T = 923$ K. The hydrogen absorption was registered by a drop of the total pressure.

The hydrogen content in the hydrides was more precisely estimated by the decomposition of the hydrides heating the sample in a closed volume up to $T = 923$ K. At the end of the process, the reactor was cooled down and the pressure

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increase was recalibrated to ambient temperature. The released hydrogen was pumped out and the whole process was repeated. The pressure change allowed quantifying the amount of hydrogen released. For both compounds the hydrogen content was estimated to be (1.4 ± 0.1) H at./f.u.

The crystal structure of the parent compounds, as well as of all hydrides, was studied by means of X-ray diffraction. The powder patterns were obtained with a Siemens D500 powder diffractometer using Co $K\alpha$ radiation. The crystal structure analysis was performed using a full profile Rietveld refinement.

The magnetic susceptibility of UCoSn and URuSn and their hydrides was studied in various magnetic fields, using a Quantum Design PPMS extraction magnetometer. The grains of the samples were fixed in random orientation by acetone-soluble glue, which prevents rotation of individual grains under the influence of a magnetic field.

3. Results

We have been inspecting the UTSn group (T is a late 3d, 4d or 5d metal) and found a significant H absorption for UCoSn and URuSn. Hydrides with the composition UCoSnH_{1.4} and URuSnH_{1.4} are formed. The decomposition curves of the hydrides point to a single-stage decomposition process at $T \approx 500$ °C.

Both UCoSnH_{1.4} and URuSnH_{1.4} hydrides crystallise in the hexagonal ZrNiAl-type of structure similar to the initial compounds. Hydrogenation leads to a unit cell expansion in both cases, which prevails in the basal plane and is significantly larger for UCoSn: the volume expansion reaches 3.2% for UCoSn, while it is 1.2% for URuSn. The findings on the crystal structure of UCoSn and URuSn compounds and their hydrides are summarised in Table 1. Hydrogen positions could not be specified.

UCoSn and URuSn are known to be ferromagnets with ordering temperatures $T_C = 80$ – 88 K and $T_C = 51$ – 55 K, respectively [8]. Hydrogenation does not change the type of magnetic ordering for either compound, but modifies magnetic moments and ordering temperature (Fig. 1).

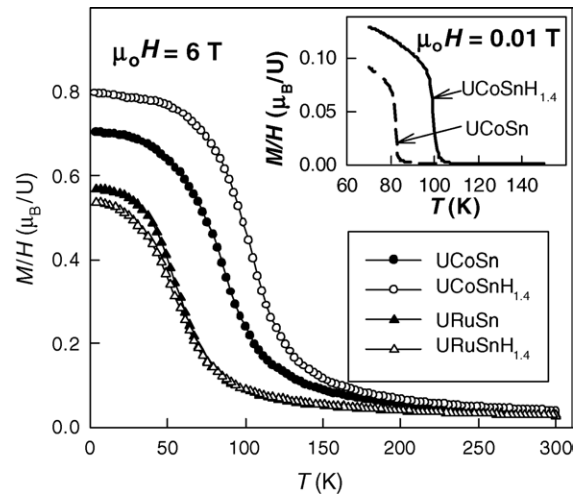


Fig. 1. Temperature dependence of the magnetic susceptibility $\chi(T)$ for UCoSn, URuSn and their hydrides, measured in $\mu_0 H = 6$ T. The inset shows the temperature dependence of the magnetic susceptibility for UCoSn and UCoSnH_{1.4} in $\mu_0 H = 0.01$ T.

However, the change of magnetic properties upon hydrogenation has different character for the two compounds. According to the magnetic susceptibility measurements, the ordering temperature grows in the case of UCoSn from 82 K in the parent compound to 102.5 K in the hydride. The ordering temperature for the UCoSnH_{1.4} hydride, determined from the Arrott plot, appears to be the highest Curie temperature found for the equiatomic uranium ternaries so far. The spontaneous magnetic moment of uranium atoms, measured on fixed randomly oriented powder, increases from $0.64\mu_B/\text{U-atom}$ in UCoSn to $0.75\mu_B/\text{U-atom}$ in UCoSnH_{1.4} (Fig. 2).

Surprisingly, an opposite impact of hydrogenation on the magnetism is observed for URuSn. The ordering temperature decreases from 54 K in the initial compound to 51 K in the hydride. Unlike the majority of the uranium intermetallics studied upon hydrogenation, the hydrogenation weakens the ferromagnetic interactions, and the magnetic moment of the uranium atoms decreases from $0.53\mu_B/\text{U-atom}$ in the parent compound to $0.48\mu_B/\text{U-atom}$ in hydride (Fig. 2).

Table 1

Comparison of crystal structure and magnetic susceptibility parameters of UCoSn, URuSn and their hydrides

	UCoSn	UCoSnH _{1.4}	URuSn	URuSnH _{1.4}
a (Å)	7.1459(7)	7.2386(6)	7.3509(8)	7.3932(14)
c (Å)	3.9943(6)	4.0189(5)	3.9496(7)	3.9492(19)
Volume per unit cell (Å ³)	176.6	182.4	184.8	186.9
$\Delta V/V$ (%)	–	3.3	–	1.1
$d_{\text{U-U}}$ (Å)	3.74	3.78	3.84	3.87
μ_{eff} ($\mu_B/\text{f.u.}$)	2.0	2.0	1.7	1.9
Θ_p (K)	77	97	49	42
χ_0 (10^{-8} m ³ /mol)	1.3	1.1	1.5	1.2
T_C (K)	82	102	54	51

Lattice parameters a and c , volume per formula unit, relative increase of volume with respect to the parent compounds, inter-uranium spacing $d_{\text{U-U}}$, parameters of the fit of the susceptibility in the modified Curie–Weiss regime (high T): effective moments μ_{eff} , paramagnetic Curie temperature Θ_p , the T -independent term χ_0 and the ordering Curie temperature T_C are given.

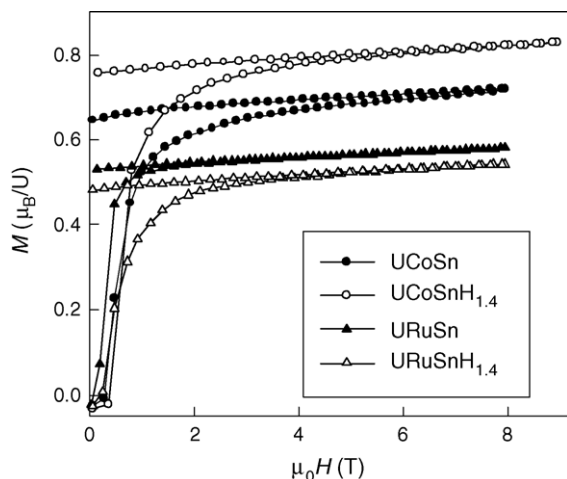


Fig. 2. Magnetisation curves of UCoSn, URuSn and their hydrides measured at $T = 2$ K.

The results of the analysis of in the paramagnetic region of the magnetic susceptibility of UCoSn and URuSn and the corresponding hydrides, described by modified Curie–Weiss law, are also summarised in Table 1.

Magnetisation curves and susceptibility behaviour have a character, which does not change qualitatively between the parent compounds and their hydrides, and the lattice expansion preserves the basic geometry of the lattice with the shortest inter-U spacing within the basal plane. This geometry leads generally (for U intermetallics) to a strong uniaxial anisotropy with the magnetic moments aligned along the c -axis. Consequently, the spontaneous magnetisation obtained on randomly oriented powders corresponds to 50% of intrinsic U moments, and we can estimate the μ_U values as $1.50\mu_B$ for UCoSnH_{1.4} and $0.96\mu_B$ for URuSnH_{1.4}.

4. Discussion

The values of T_C (102.5 K) and μ_U ($1.50\mu_B/\text{f.u.}$) found in UCoSnH_{1.4} are record values among all UTX ferromagnets. Similar ordering temperature was only found for the anti-ferromagnet UNiAlH_{2.3} ($T_N = 99$ K, μ_U could not be determined) [6]. The theory of hybridisation-mediated exchange interaction in light actinides assumes that magnetic moments are gradually reduced by the strengthening of the 5f–ligand hybridisation, which, though, mediates the exchange interaction. This model seems appropriate for narrow band systems with moderate hybridisation. For magnetic systems with broader 5f bands we may assume the situation of a typical band magnetism, for which the ordering temperature and the size of magnetic moments are proportional to each other.

Hydrogen absorption can be expected as increasing the localisation of the 5f states due to the reduction of the 5f–5f overlap (consequence of the lattice expansion). Comparing the properties of UCoSnH_{1.4} with other ZrNiAl-structure compounds of the UCoX series one can see the gradual de-

velopment of magnetism with a unit cell expansion (i.e. the U–U distance increases): while UCoAl exhibits no magnetic ordering, T_C and μ_U increase with the volume in the sequence UCoGa–UCoSn–UCoSnH_{1.4}.

If hydrogen occupies positions close to the transition metal T, one can also speculate that the bonding of the d-states of the transition metal with the hydrogen states withdraws partly the d-states from the 5f–d hybridisation, leaving the 5f states less hybridised. The two strong reasons are the most plausible source of strengthening of the magnetism in light actinide hydride systems due to hydrogen absorption. They can be taken responsible for the variations of the UCoSn magnetism, which points to rather an itinerant character of its magnetism, resulting from a rather strong 3d–5f hybridisation.

The case of URuSn seems to be rather curious, not fitting into the context mentioned above. In fact, authors are not aware of any analogous cases of a reduction of T_C and μ_s due to hydrogen absorption in U intermetallics. The degree of the 5f delocalisation in URuSn should not differ dramatically from the UCoSn situation. The 4d states hybridise even less with the 5f's than the corresponding 3d states, while the d-states of the Fe subgroup are closer to the Fermi level than for the Co subgroup, and thus overlap more in energy with the 5f states, contributing to a stronger delocalisation. Consequently, the anomalous tendency in the URuSn hydride looks incompatible with the two general mechanisms. The key may be the smaller lattice expansion for a comparable H content, pointing to different interstitial positions occupied in this case. We may also speculate then about a predominant effect of a reduction of the density of states at the Fermi level, $N(E_F)$, which may tend to suppress the magnetism. To elucidate this issue, a specific heat study may be important. Also the hydrogen positions should be specified using neutron diffraction technique on deuterides. The real volume effect can be also separated by magnetisation studies under external pressure. In addition we plan to investigate hydrogenation in the pseudoternary system U(Co, Ru)Sn and its impact on magnetism.

Acknowledgments

The authors acknowledge the financial support of the Grant Agency of the Czech Republic (project # 202/04/1103). This work is a part of the research plan MSM 0021620834 financed by the Ministry of Education of the Czech Republic.

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