

5f Magnetism studied in complex intermetallic U-based hydrides

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Abstract

Hydrogen absorption in uranium ternary intermetallic compounds typically increases ordering temperatures and magnetic moments. The case of URuSn hydride, which does not behave accordingly, can be related to specific H positions revealed by neutron diffraction on deuterides. Tuning through the onset of magnetic ordering by means of H absorption was found for the U₂T₂X compounds as U₂Co₂Sn. For U₂Ni₂SnD_{1.8}, we demonstrated that the anisotropic lattice expansion leads to U moments reorientation, as a result of hybridisation-induced two-ion anisotropy, with respect to U₂Ni₂Sn, in which the U–U coordination is poised between two regimes.

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1. Introduction

Specific features of actinide magnetism originate in the large variability of the 5f localization and strong spin–orbit interaction. For pure elements, the real cross-over from itinerant to localized behaviour takes place between Pu and Am. The 5f states in U metallic systems remain with few exceptions on the itinerant side of the Mott transition. The incipient 5f localization reflects in 5f band narrowing, which leads eventually to the fulfilment of the Stoner criterion in analogy to 3d magnetism, if the density of states at the Fermi level, $N(E_F)$, reaches a sufficiently high value. The prominent role of the inter-uranium spacing d_{U-U} , tuning the 5f bandwidth by varying 5f–5f overlap, is reflected in the so called Hill criterion, stating that magnetism is likely to appear over $d_{U-U} > 340$ pm, while for lower values the ground state should be non-magnetic, most likely superconducting (see Ref. [1] and references therein).

For $d_{U-U} \gg 340$ pm, another delocalising mechanism, the 5f-ligand hybridisation, starts to dominate. A different regime of

magnetism is related here to the dual role of the hybridisation: besides delocalization and suppressing U magnetic moments it contributes to the inter-site exchange interactions. Therefore, one band model is not sufficient to describe variations of magnetism. Highest ordering temperatures are achieved at intermediate strength of hybridisation. Stronger hybridisation facilitates a stronger effective inter-site coupling, but suppresses U magnetic moments.

Understanding the occurrence of U magnetism and its basic features was enabled by the exploration of large isostructural families of U ternary intermetallics, which allowed to study the impact of the 5f-ligand hybridisation in a systematic way, eliminating the influence of various crystal structures [1]. In this direction, involving hydrides of known compounds, with expanded crystal structures, which preserve the structure type (i.e. also the coordination of U atoms) or modify it only slightly, can bring additional vital information and serve as a probe for the system. Studies of the situation around the verge of magnetism with interesting regions characterized by quantum criticality can be particularly intriguing, compensating the drawbacks as certain structure imperfections and powder character of samples. The aim of this contribution is to review recent results of structure

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and magnetic studies of hydrides of U ternary intermetallics including studies of hydrogenation of UTX and U_2T_2X compounds.

2. UTX–H compounds

Two extended groups of ternary equiatomic ternaries have been used for hydrogenation studies. The group exhibiting the hexagonal structure (ZrNiAl structure type) is shared by numerous rare-earth isotopes, as RENiAl, which absorb hydrogen readily [2]. Unfortunately, the structure modifications related to hydrogenation cannot be used as analogy to uranium counterparts, as the hydrogen positions are different from UNiAl. For example, TbNiAlD_{1.28} (the highest deuteride of TbNiAl prepared) has two hydrogen positions, one in the trigonal bipyramid Tb₃Ni₂ (hydrogen in the Tb–Ni plane) and one in Tb₃NiAl (hydrogen between two Tb–Ni planes), reaching a volume increment relative to TbNiAl about 7%. On the other hand, deuterium in UNiAlD_{2.2} occupies besides the trigonal bipyramid Al₃Ni₂ position also two positions out of the high symmetry planes, namely, in the U₃Al and U₃Ni tetrahedra (the last with a variable partial occupancy), yielding the enormous volume increase of about 12% [3]. This volume expansion has a dramatic consequence for UNiAl. Its antiferromagnetic transition increases from 19 to 94 K in UNiAlD_{2.1} and in another sample with a nominal composition UNiAlH_{2.3} $T_N = 99$ K was registered. The impact of hydrogenation of RENiAl hydrides is just opposite. Ordering temperatures are severely suppressed, presumably due to the loss of metallicity, leading to suppression of the RKKY interaction [2]. Unfortunately, other ternaries of the UTAI type could not be prepared despite a significant effort, and the hydrogen absorption capability vanishes fast when substituting Co or Fe for Ni. The hydride of UCoAl prepared by a special procedure using several kbar pressures does not belong to structural isotypes any more [4].

Besides UTAI compounds, the ZrNiAl structure type is shared also by extended UTGa, UTSn and UTIn series. For further studies we selected the UTSn one, which is more abundant

than UTIn and larger Sn atoms should lead to a larger interstitial positions than in those with Al or Ga. Here, the hydrogen absorption was also limited, but two pure compounds forming hydrides were identified, namely UCoSn and URuSn [5,6]. It is interesting to note that also here the hydrides are formed for T elements from the upper right corner of the transition metal series (UNiSn has another structure). The stoichiometry UCoSnH_{1.4} and URuSnH_{1.4}, achieved under standard hydrogenation conditions, suggests that the hydrides should have the same structure details including occupied hydrogen positions. Later, we will see that it is not the case. Both UCoSn and URuSn are ferromagnets and ferromagnetism is preserved also in the hydrides. As seen in Table 1, the Curie temperature T_C increases in UCoSn (from 82 to 102 K in the hydride), but the increase is relatively smaller than in UNiAl. Also the volume expansion is much smaller, reaching 3.3%. The ferromagnetic type of order allows to estimate ordered U moments (only small induced moments occur in such types of compounds). The magnetization is somewhat higher in the UCoSnH_{1.4} than in UCoSn. Assuming the uniaxial anisotropy is preserved, respective ordered moments $\mu = 1.5$ and $1.3 \mu_B/U$ can be estimated for the hydride and pure UCoSn, respectively [6].

Surprisingly, URuSn, despite small but non-negligible volume expansion (1.1%) does not exhibit stronger magnetism when hydrogenated. Both T_C (54 K) and μ ($0.5 \mu_B$) stay constant or even perhaps slightly decrease [6]. To elucidate reasons for such aberration, neutron diffraction studies on UCoSn and URuSn deuterides were undertaken.

The deuterides were synthesized using URuSn and UCoSn precursors (about 10 g each), which were crushed into submillimeter particles, activated for 2 h at $T = 423$ K in high vacuum (10^{-7} mbar). For the deuteration process we used a high pressure (120 bar) deuterium gas (purity 99.96%). Temperature was cycled up to $T = 923$ K. The thermal desorption in vacuum (up to 1023 K) indicated a release of deuterium corresponding to the stoichiometry URuSnD_{0.6} and UCoSnD_{0.6}. This low D content is rather surprising, as both volume increments in the deuterides correspond to that of the hydrides studied previously [6]

Table 1
Comparison of crystal structure and basic magnetic characteristics of UCoSn and URuSn and their hydrides and deuterides

	UCoSn	UCoSnH _{1.4}	UCoSnD _{0.6}	URuSn	URuSnH _{1.4}	URuSnD _{0.6}
a (pm)	714.59(7)	723.86(6)	723.45(6)	735.09(8)	739.32(14)	745.30(22)
c (pm)	399.43(6)	401.89(5)	402.33(5)	394.96(7)	394.92(19)	395.04(15)
V (10^8 pm ³)	1.766	1.824	1.824	1.848	1.869	1.900
$\Delta a/a$ (%)	–	1.3	1.2	–	0.6	1.4
$\Delta c/c$ (%)	–	0.6	0.7	–	0.0	0.0
$\Delta V/V$ (%)	–	3.3	3.3	–	1.1	2.8
x_U	0.589(1)	0.600(1)	0.601(1)	0.591(2)	0.591(2)	0.595(1)
x_{Sn}	0.250(2)	0.257(2)	0.251(3)	0.249(3)	0.261(3)	0.254(3)
d_{U-U} (pm)	374	383	383	384	387	393
μ_{eff} ($\mu_B/f.u.$)	2.0	2.0	2.1	1.7	1.9	1.6
Θ_p (K)	77	97	102	49	42	58
χ_0 (10^{-8} m ³ /mol)	1.3	1.1	1.1	1.5	1.2	1.6
T_C (K)	82	102	104	54	51	54

Lattice parameters a and c , unit cell volume V , their respective increments due to hydrogenation; internal structure parameters of U and Sn atomic sites x_U and x_{Sn} ; shortest inter-uranium spacing d_{U-U} ; effective moments μ_{eff} ; paramagnetic Curie temperatures Θ_p ; T independent susceptibility terms χ_0 , all obtained from fitting to the modified Curie–Weiss law; Curie temperatures T_C .

Table 2

Rietveld refined atomic parameters for $\text{UCoSnD}_{0.6}$ and $\text{URuSnD}_{0.6}$: internal parameters x , y and z and the coefficients of the site occupancy n , obtained from neutron diffraction at $T = 300$ K

Atom site		x	y	z	n
$\text{UCoSnD}_{0.6}$					
U	3g	0.596(1)	0	0.5	1
Co1	1b	0	0	0.5	1
Co2	2c	1/3	2/3	0	1
Sn	3f	0.259(1)	0	0	1
D	4h	1/3	2/3	0.445(9)	0.44(2)
$\text{URuSnD}_{0.6}$					
U	3g	0.598(3)	0	0.5	1
Ru1	1b	0	0	0.5	1
Ru2	2c	1/3	2/3	0	1
Sn	3f	0.259(1)	0	0	1
D1	2d	1/3	2/3	0.5	0.68(3)
D2	3g	0.215(35)	0	0.5	0.14(2)

with much higher H concentration of 1.4 H atom per formula unit (f.u.) determined volumetrically. A good overall agreement was found for the T_C values (see Table 1) The neutron diffraction study was performed at HMI Berlin using the E2 diffractometer at $T = 300$ K. The results given in Table 2 indicate different deuterium lattice sites for the two compounds. While in UCoSn the D atoms occupy randomly one of the two U_3Co tetrahedra and are therefore located out of the U planes, in URuSn the main D position is within the U planes, coordinated in the trigonal bipyramid U_3Ru_2 (one of the sites occupied e.g. in $\text{UNiAlD}_{2.2}$). This situation explains why unlike UCoSn , URuSn expands only within the a direction upon hydrogenation.

The exact reasons for the lack of variations of magnetism in URuSn hydrides has still to be explored. Also the reason for a double occupancy in the case of hydrides comparing to the deuterides remains unclear. The occupancy of both adjacent U_3Co tetrahedra would yield $\text{UCoSnH}_{1.33}$, which is close to the stoichiometry observed indeed for the hydride. This would then need the H atoms displaced somewhat far apart, such that $z_H < 0.3$. Such anomalous structures were observed already for $\text{RE}_3\text{Ni}_3\text{In}_3\text{D}_4$ systems, characterized by anomalously short D–D spacing of 160 pm [7]. But such differences of H and D positions in UCoSn remain so far on the level of speculations.

3. $\text{U}_2\text{T}_2\text{X–H}$ compounds

The research in the group of UTX compounds has shown that because the hydrides cannot be synthesized for all members, these compounds cannot be used to study details of the onset of magnetism. Similar to compounds with the ZrNiAl structure are also those which crystallize in the orthorhombic TiNiSi structure type [6,8]. Another family of intermetallics, which covers the onset of magnetism, is based on the U_3Si_2 tetragonal structure. Its ordered variant, the Mo_2FeB_2 structure type, is found for numerous U compounds with X being typically In or Sn [1]. For those with non-magnetic ground state but close to the onset of magnetism, as $\text{U}_2\text{Co}_2\text{Sn}$ and $\text{U}_2\text{Co}_2\text{In}$, the hydrogenation

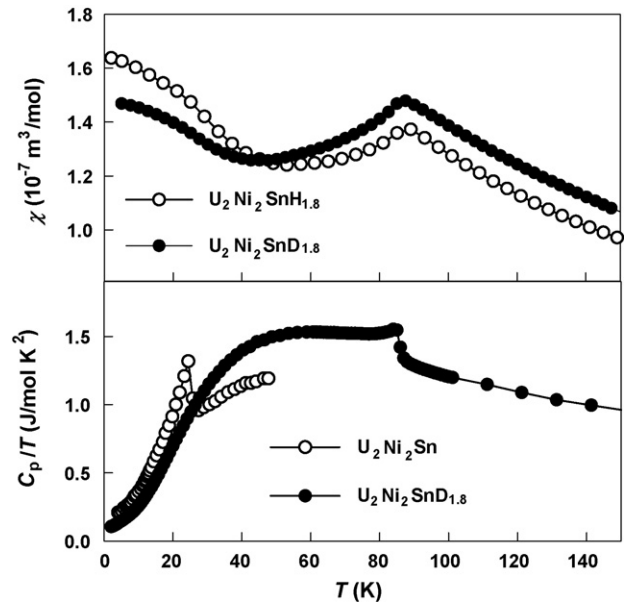


Fig. 1. Temperature dependence of magnetic susceptibility for $\text{U}_2\text{Ni}_2\text{SnH}_{1.8}$ ($\mu_0 H = 3$ T) and $\text{U}_2\text{Ni}_2\text{SnD}_{1.8}$ ($\mu_0 H = 4$ T) – upper panel; specific heat C_p of $\text{U}_2\text{Ni}_2\text{Sn}$ and $\text{U}_2\text{Ni}_2\text{SnD}_{1.8}$ – lower panel.

induces a magnetic order, and the hydrogen content in α - and β -hydride is a convenient variable to tune the system across the cross-over line [9]. So as to specify hydrogen positions in this type of compounds, we undertook the synthesis and investigation of $\text{U}_2\text{Ni}_2\text{Sn}$ deuteride.

The deuteration of $\text{U}_2\text{Ni}_2\text{Sn}$ was performed using the D_2 pressure of 92 bar. The decomposition of a part of the sample in vacuum gave the stoichiometry 1.8 ± 0.1 D atom per f.u., similar to the related hydride. It agrees very well with the stoichiometry obtained by means of the Rietveld refinement of neutron diffraction data, (1.79 ± 0.02) D atom per f.u. Also the lattice parameters for the deuteride, $a = 743.5(1)$ pm, $c = 376.2(1)$ pm, which were determined by X-ray diffraction, agree well with those obtained for the hydride, $a = 744.5(1)$ pm, $c = 376.4(1)$ pm [6], both being substantially larger than the parameters of the $\text{U}_2\text{Ni}_2\text{Sn}$ precursor, $a = 726.3(1)$ pm, $c = 369.5(1)$ pm. Also magnetic susceptibility (Fig. 1) exhibits the cusp attributed to the Néel temperature $T_N = 87$ K for the hydride and 85 K for the deuteride. Such a small isotope effect can be attributed e.g. to a different character of lattice vibrations.

The neutron diffraction on the deuteride revealed that the D atoms occupy the 8k sites inside the U_3Ni tetrahedra close to

Table 3

Rietveld refined atomic parameters for $\text{U}_2\text{Ni}_2\text{SnD}_{1.8}$: internal parameters x , y and z and the coefficients of the site occupancy n , obtained from neutron diffraction at $T = 120$ K

Atom Site		x	y	z	n
$\text{U}_2\text{Ni}_2\text{SnD}_{1.8}$					
U	4h	0.1788(6)	0.6788(6)	0.5	1
Ni	4g	0.3747(5)	0.8747(5)	0	1
Sn	2a	0	0	0	1
D	8k	0.3859(10)	0.8859(10)	0.5338(63)	0.448(6)

the U plane, choosing randomly one of the two adjacent ones (see Table 3). Such position can qualitatively explain that the expansion due to deuteration is larger along the basal plane than along the tetragonal axis c ($\Delta a/a = 2.4\%$, $\Delta c/c = 1.8\%$). As we see later, this small difference can have in a special case quite dramatic consequence.

As illustrated by numerous examples, U intermetallics exhibit a generally strong magnetic anisotropy, which determines directions of U magnetic moments in the ground state. It is based on a semi-qualitative model of hybridisation-induced two-ion anisotropy, which tends to orient magnetic moments perpendicular to the shortest U–U links (see Ref. [1] for overview). In compounds with the shortest U–U spacing within a plane, an easy axis anisotropy appears with U moments perpendicular to the plane. For structures characterized by chains of U atoms, the anisotropy is close to an easy plane type. These surprisingly general principles were found to hold also for the U_2T_2X compounds, for which the U–U spacing along c , is somewhat shorter than along a , U magnetic moments tend to orient within the basal plane. The exception is U_2Ni_2Sn , for which the c axis spacing is marginally (by about 3%) larger than that along a . Indeed, U moments orient along c , forming antiferromagnetic structure by alternating U-moment orientation in adjacent U planes [1].

In the case of $U_2Ni_2SnD_{1.8}$, the anisotropic lattice expansion brings the respective U–U spacings to a practical equality (within the error bars), it is therefore intriguing to see if its magnetic structure changes. The neutron diffraction experiment performed at $T = 1.8$ K reveals no additional magnetic reflection comparing to the diffraction pattern taken in the paramagnetic state ($T = 120$ K), in particular the peak $(1/2, 1/2, 1/2)$ well distinguished in U_2Ni_2Sn [10] is missing here. We have to conclude that despite unambiguous antiferromagnetic order the magnetic unit cell is identical with the crystallographic one. The only possibility is that there is antiferromagnetic coupling between the 4 U moments within one unit cell. The best fit was found for the magnetic structure with non-collinear U moments within the basal plane, aligned along equivalent $(1, 1, 0)$ diagonals in the way found for the magnetic structure of U_2Pd_2In (see Ref. [1] and references therein). The size of moments $(0.8 \pm 0.3) \mu_B/U$ remains about the same as in U_2Ni_2Sn , i.e. corresponds to the strongly itinerant magnetism.

Indispensable information on magnetism and electronic structure of metallic systems can be obtained from the temperature dependence of specific heat. Unfortunately, the fine hydride powders are not suitable for the most common microcalorimetry technique. We have developed a technique of production of composite samples, in which hydride grains are bound together by a pure metal (Cu or Ag) mixed together in well-defined ratio in a fine powder form and pressed into a pellet [11]. Using a new type of die with WC faces allows to form thin pellets even without the metallic bond, if pressure of several kbar is applied. This method was tested on $U_2Ni_2SnD_{1.8}$, the specific heat of which is plotted together with that for U_2Ni_2Sn in Fig. 1. Specific heat (in the C_p/T versus T representation) clearly indicates the magnetic phase transitions. The lattice contribution to C_p for

the hydride is strongly non-Debye like, which prohibits to quantify the magnetic entropy related to the transition (equal to the excessive area below the C_p/T curve), but an estimate indicates that it remains about the same as in U_2Ni_2Sn [1], i.e. only a small fraction of R ln 2. This again corroborates the band character of the 5f magnetism in this compound.

4. Conclusions

The key to the understanding of the variations of the U magnetism in hydrides, the hydrogen positions, were determined for several compounds representing the UTX and U_2T_2X families. We proved that the reason for different behaviour of UCoSn and URuSn upon hydrogenation dwells in difference of H sites. For $U_2Ni_2SnD_{1.8}$, we demonstrated that the anisotropic lattice expansion can lead to U moments reorientation with respect to U_2Ni_2Sn , in which the U–U coordination is poised between two regimes.

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