Hydrogenation affecting the 5f magnetism

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Abstract. In the case of 5f magnetism, the net increase of \( T_c \) due to the interstitial doping by hydrogen is generally understood as due to the increase of the density of states at the Fermi level, resulting from 5f band narrowing. The record value of \( T_c \) among UTX compound can be achieved in hydrides of U(Co,Fe)Sn series (\( T_c = 108 \) K for 15% of Fe). This concept, based on the 5f band formed by periodic array of U sites, does not work for Th doped compounds. In the case of U sublattice diluted by a non-magnetic element the expansion cannot have dominant effect, partly because already doping by non-magnetic Th leads to an expansion.

1. Introduction
Magnetic properties of 5f intermetallics are strongly dependent on peculiarities of the crystal structure (inter-uranium distances, atomic environment) and the electronic structure, mostly on the degree of the f-ligand hybridization and the tendency for localization or itinerancy. The degree of the 5f localization in uranium compounds is primarily dependent on the inter-uranium spacing. The critical spacing for Stoner criterion being fulfilled is \( d_{U,U} = 3.4 - 3.6 \) Å. This value is called the Hill limit. The ground state of compounds with inter-uranium distance smaller than the Hill limit is typically non-magnetic (often superconducting). For \( d_{U,U} \) larger than the Hill limit they incline to a magnetic ground state. Development of magnetic properties can be studied by e.g. choosing various ligands in isostructural compounds. In addition, interstitial doping by hydrogen (deuterium) can provide a new variable, giving additional information on the peculiarities of interatomic interactions in the initial compound. Unlike variable ligands, the hydrogenation can often tune properties over a small critical range.

2. Materials synthesis and experimental details
A possible way to synthesize intermetallic hydrides is to expose the parent compound to the hydrogen atmosphere. Subsequent thermal cycling helps to establish thermodynamic equilibrium. Controlled temperature-induced desorption in a calibrated volume is used to find out the amount of absorbed hydrogen. Not all compounds are able to absorb hydrogen. There are criteria, which have to be fulfilled, to form a hydride. The Westlake’s criterion states that available interstitial sites must have a spherical volume with radius \( \geq 40 \) pm to be occupied by hydrogen. The Shoemaker’s exclusion rule
states that two tetrahedra, sharing the same face, cannot be occupied simultaneously. Moreover the minimum H-H spacing should be about 210 pm. However one should keep in mind that there are always some exceptions from these rules. In order to predict whether the material would form hydride it is also necessary to take into account geometry of the unit cell, surface properties, etc. In practical life, the best way to test the hydrogen absorption capacity is a trial.

Here we describe the results of hydrogenation studies of selected UTX (T - late transition metal, X - p-metal) compounds on the basis of UCoSn. This type of compounds crystallizes in the ZrNiAl structure type (atomic positions: U – 3g (x0;0;0.5), T1 – 1b (0;0;0.5), T2 – 2c (1/3;2/3;0), X – 3f (x0;0;0). It is a hexagonal structure with two types of basal planes, one with U and T atoms, and the other with T and X atoms. Each uranium atom has four nearest uranium neighbours within the U–T layer and U–T layers are separated by the lattice parameter c. Inter-uranium distances in a direction are in the range of the Hill limit, while they are somewhat larger in the direction c. There is strong hybridization along the nearest U direction. Magnetic moments are almost universally perpendicular to that direction (along the c-axis), leading to the giant easy-axis anisotropy [1].

In our case, hydrides of U(Co,Fe)Sn and (U,Th)CoSn were synthesized using the procedure described above. In order to facilitate the absorption, the activation of the surface was performed by annealing at T = 473 K for 2 hours in a dynamic vacuum (10⁻⁶ mbar). The reactor was subsequently filled with pressurized hydrogen (120 bar), and then exposed to thermal cycling up to T = 923 K.

The crystal structure of both parent compounds and hydrides was studied by X-ray diffraction by means of XRD-3003 (Seifert) diffractometer using Cu Kα radiation (2θmin = 20°, 2θmax = 120°, Δ2θ = 0.02°). Magnetic susceptibility was studied in various magnetic fields up to 9 T using Quantum Design PPMS extraction magnetometer on powders with grains fixed in random orientation.

3. Results and discussion

In the case of UCoSn, the hydride with composition UCoSnH1.4 is formed [2]. It crystallizes in the hexagonal ZrNiAl type of structure similar to the initial compound. Hydrogenation leads to a unit cell expansion, prevailing in the basal plane. The expansion reaches 3.2 %. The ordering temperature grows from TC = 82 K in the parent compound to 102 K in the hydride. The spontaneous magnetic moment, measured on randomly oriented fixed powder, increases from 0.64 μB/U in UCoSn to 0.75 μB/U in the hydride.

The U(Co,Fe)Sn compounds with 3, 10, 15 and 20 % of Fe were synthesized and hydrogenated. The hydrogenation of this series leads to unit-cell expansion reaching approximately 3.3 %. The Curie temperature, determined from AC-susceptibility curve, increases with increasing Fe concentration to 98 K for UC0.80Fe0.20Sn. Increasing tendency continues up to 15 % Fe where the solubility limit apparently comes into action. There was shown that only limited substitution of Co by Fe (20 % limit) is possible in this series [3]. The Curie temperature is higher for the hydrides than for their precursors. The increment is decreasing with increasing Fe concentration from ΔT = 19 K (TC = 83 K for UCoSn and 102 K for UCoSn-H) to ΔT = 6 K (TC = 98 K for UCo0.80Fe0.20Sn and 104 K for UCo0.80Fe0.20Sn-H) (figure 1). The desorption experiment showed that the amount of absorbed hydrogen has a decreasing tendency with increasing Fe concentration. Neutron diffraction performed on UCoSn-D detected that H (D) atoms occupy U3Co tetrahedral sites, which allow to accommodate 1.33 H/f.u.
If the U-sublattice is diluted by a non-magnetic element, as in the case of the (U,Th)CoSn series, the 5f magnetism is gradually suppressed [4]. The long-range magnetic order disappears at approx. 60 % Th. ThCoSn was found to be a Pauli paramagnet down to 4.2 K. The hydrogenation leads to a unit-cell expansion ranging between 3.0 % and 3.6 %. As seen in figure 2, the desorption experiment showed that the amount of hydrogen has a decreasing tendency with increasing Th concentration from 1.4 H/f.u. in UCoSn to 0.8 H/f.u. in ThCoSn. Studies of temperature dependence of magnetic susceptibility indicate a certain increase of $T_C$ in the hydrides, but the Th concentration at which the ferromagnetism vanishes remains practically unchanged. The comparison of the susceptibility data measured on parent compounds and their hydrides shows a somewhat higher susceptibility for the hydrides (figure 3). The obtained data were fitted to a modified Curie-Weiss law. Values of the effective magnetic moments are decreasing with increasing Th concentration (2.3 \(\mu_B/U\) for $U_{0.8}Th_{0.2}CoSn$, 2.0 \(\mu_B/U\) for $U_{0.6}Th_{0.4}CoSn$). The effective moments for hydrides were found to be higher (3.3 \(\mu_B/U\) for $U_{0.8}Th_{0.2}CoSn-H$, 2.2 \(\mu_B/U\) for $U_{0.6}Th_{0.4}CoSn-H$). The field dependence of the magnetization was measured at 5 K (figure 4, 5). As seen in the table 1, the spontaneous magnetization decreases with increasing Th content even if it is normalized per U atoms.
4. Conclusions

In the case of 5f magnetism, the net increase of $T_C$ is generally understood as due to the increase of the density of states at the Fermi level, resulting from the 5f band narrowing. This concept, based on the 5f band formed by periodic array of U sites, does not work for Th doped compounds. In the case of diluted U sublattice the expansion cannot have dominant effect, partly because already doping by non-magnetic Th leads to an expansion. Interaction with other types of states starts to be important in such case. The hydrogenation of the U(Co,Fe)Sn series leads to a slight increase of respective Curie temperatures, and the maximum value 108 K is achieved for UCo$_{0.85}$Fe$_{0.15}$Sn-H. The increment is decreasing with increasing Fe content. Such relatively modest effect can be compared with a dramatic increase of the Neél temperature for UNiAl (formed in the same structure) from 19 K to 99 K in UNiAlD$_{2.1}$. The increment is much higher due to larger volume expansion (12 %) and considerable shift of U and Ni atoms, resulting in the increase of symmetry [5].

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