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Variations of magnetic properties of UH_3 with modified structure and composition

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UH_3 based hydrides with modified structure and composition can be prepared using high H_2 pressures from precursors in the form of rapidly cooled uranium alloys. While the alloys with α-U structure lead to the β-UH_3 type of hydrides, γ-U alloys (*bcc*) lead either to α-UH_3 hydride type or nanocrystalline β-UH_3. The nanocrystalline β-UH_3 structure, appearing for Mo alloying, can accommodate in addition numerous other *d*-metal components, as Ti, Zr, Fe, Nb. The pure Mo alloyed hydrides $(UH_3)_{1-x}Mo_x$ exhibit increasing Curie temperature T_C with maximum exceeding 200 K for $x = 0.12–0.15$. Other components added reduce the T_C increment with respect to pure UH_3 (170 K). Also alloying by Zr gives a weaker enhancement. Seen globally, the T_C variations are rather modest, which reflects the prominence of interaction of U with H. It is suggested that important ingredient is a charge transfer, depopulating the U-6*d* and 7*s* states, while the 5*f* band stays at the Fermi level.

1. Introduction

An important issue related to application of uranium and its alloys is interaction with hydrogen. Uranium form a trihydride existing in two structural modifications. Any contact of U metal (α-U) with H leads to formation of the stable form β-UH_3, a dark pyrophoric powder. The other allotropic variant, α-UH_3, is a transient form which was never prepared as a pure phase, as it converts fast into β-UH_3. The crystal structure of α-UH_3 is formed by the *bcc* lattice of U atoms, with the volume expanded by 60% with respect to γ-U, filled by H atoms. Also β-UH_3 is cubic, the unit cell is larger and contains two different U sites. Besides the *bcc*-type sites 2*a* there exist also 6*c* sites, which form linear chains with smaller U-U spacing [1]. The shortest U-U distances are 330 pm for β-UH_3 (between the 6*c* sites) and 360 pm for α-UH_3. β-UH_3 was the first 5*f* ferromagnet discovered (with the Curie temperature $T_C \approx 170$ K), and its magnetic order is undoubtedly connected with the volume expansion, as all the phases of U metal are Pauli paramagnets. There exist controversial reports about magnetic properties of α-UH_3. Earlier works, cited in [1] report almost the same T_C as for β-UH_3, which would be surprizing in the context of known sensitivity of the 5*f* magnetism to all kinds of variables. Later neutron diffraction study deduced a non-magnetic ground state [2].

We explored a possibility of retaining the α-UH_3 structure if the hydrogenation starts not from pure U metal, but an alloy. Uranium metal has three allotropic phases: α-phase with an orthorhombic structure (space group *Cmcm*), β-phase with a tetragonal structure (space group $P4_2/mmm$), and γ-phase with a body centered cubic A2-type structure ($Im\bar{3}m$). There exists an extended literature on possibility to retain the *bcc* structure, which is stable at high temperatures only (above 1049 K), by admixture of diverse transition metals. Such alloys represent important class of nuclear fuels [3], and we had been combining the alloying with rapid cooling to reduce the necessary concentration of dopants so as to investigate superconducting properties at concentration close to pure *bcc* U [4]. The α-UH_3 stabilization proved successful and we found that single phase hydrides of the type $(UH_3)_{1-x}Zr_x$ are formed at high hydrogen pressures for $x > 0.15$ [5]. We found that magnetic properties are indeed similar to β-UH_3 and T_C is even enhanced with Zr alloying reaching 185 K for 15 at.% Zr. Ordered moments remain close to 1.0 μ_B/U in all the cases. The alloying is accompanied by a dramatic increase of magnetic coercivity [5].

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We can expect Zr, which has marginally larger atomic diameter than U ($r_{Zr} = 160$ pm, $r_U = 156$ pm), to occupy the U position in α-UH_3. Another way of UH_3 alloying was identified several decades ago. Hydrogenation of U_6Fe and U_6Co led to β-UH_3 type hydrides, with T_C also enhanced to 173 and 185 K, respectively [6,7]. ^{57}Fe Mössbauer spectroscopy study of U_6FeH_{17}, which corresponds to $(UH_{\approx 2.8})_{0.86}Fe_{0.14}$ in our notation, suggests that much smaller Fe tends to enter the U-6*c* position in β-UH_3 [6]. The alloyed β-UH_3 hydrides can be naturally obtained from low-alloyed U precursor, in which *bcc* U is absent and the alloy adopts the orthorhombic α-U structure. This was tested e.g. for 4% Mo, and such hydrides are much easier to work with comparing the pure UH_3, as they lack the pyrophoricity.

Higher concentrations of Mo brought a third type of hydride. Pure *bcc* precursors could be prepared using Mo concentrations >11 at.%. Such materials did not yield the α-UH_3 type, but the X-ray diffraction patterns exhibited only several very broad lines, indicating an amorphous or nanocrystalline state, which can be probably associated with β-UH_3 [8,9]. Recent total scattering experiment and Pair Distribution Function analysis revealed that such hydrides are indeed primarily based on the β-UH_3 structure motif, but the grain size is merely 1–2 nm [10]. The increase of T_C up to 203 K for Mo concentrations 12–13% is contrasting with known suppression of the 5*f* magnetism observed for reduced crystallinity for other types of U systems [11]. Similar to Zr, higher concentrations of alloying metal lead to a reduction of T_C [9]. The general increase of T_C is striking fact from the point of view of dilution of the 5*f* sublattice by a weakly correlated metal as Mo or Zr. Similarly Fe in U_6Fe and the related hydride behaves as non-magnetic element [6].

Besides the unexpected increase of ordering temperatures, the variations of magnetic properties are relatively very modest. The character of hysteresis loop, which depends on grain size and other involved properties, is naturally rather different for the Mo and Zr alloyed hydrides, but the fundamental properties as the U moment and T_C vary so little that it induces an impression that the U-H interaction may have a dominant role instead of the U-U separation and related band effects.

The present work reviews how the composition affects the structure and magnetic properties in a broader context, dealing with several alloying elements applied in the same time. Facing a complex phase situation we have to analyze carefully not only the crystal structure of the hydride but also of its metallic precursor.

The diversity of structure variations for the two alloying elements opened a question what happens if we use two different alloying elements. Our experiments show that if sufficient concentration of Mo is used, it determines the crystal structure, which can accept also other alloying elements. We tested alloys with Mo and Ti, Fe, Zr, Nb as a second element. Such second alloying decreases slightly the Curie temperature in comparison with $(UH_3)_{1-x}Mo_x$ and broadens the transition.

2. Materials synthesis and experimental methods

U-based alloys were prepared by arc melting in Ar atmosphere. Each ingot was turned and remelted 3 times for better homogenization of constituents. Because the alloys are not in the range of thermodynamic stability of the *bcc* structure (γ-U), we subsequently used ultrafast (splat) cooling to ensure the phase homogeneity. Another advantage of samples produced by splat cooling, which are in fact foils about 100 μm thick, is that the shape allows taking X-ray diffraction pattern from the surface. The alloys are otherwise hard and cannot be crushed into powder. The XRD study, performed using the Bruker D8 Advance diffractometer with Cu-Kα radiation, indicated the *bcc* structure plus a small amount of impurities (UC and UO_2), residing mostly at the surface.

Additional phase purity analysis was done by means of X-ray energy dispersive microanalysis (EDX) using the scanning electron microscope (SEM) FEI Quanta 200 FEG (field emission gun). The surface was prepared by mechanical polishing, followed by Ar ion bombardment using the voltage 4 kV. The most discriminative method for phase analysis (as we see, the α-U structure has to be avoided in the splats if we should not end with regular β-UH_3 type of material) turned out to be Electron Back Scatter Diffraction, preformed using Scanning electron microscope (SEM) ZEISS Auriga Cross Beam with Field Emission Gun (FEG) and Focused Ion Beam (FIB) equipped with Electron Back Scattered Diffraction (EBSD) detector, X-ray energy dispersive analyzer (EDX) by EDAX-TSL. The system allows TEM lamellae preparation, simultaneous 3D EBSD and 3D EDX mapping. Fine details of microstructure were studied by transmission electron microscopy (TEM) using a JEOL JEM 2000 FX microscope equipped with a thin-window X-ray energy dispersive analyzer (EDX).

For the hydrogenation, the samples were placed in an alumina crucible into a reactor, which could be pressurized to 150 bar of H_2. The reactor was first evacuated down to 10^{-6} mbar and then H_2 gas was introduced. We found that minimum H_2 pressure for the hydride formation is, irrespective of composition, in the range 4–5 bar. Higher pressures (up to 100 bar) can only fasten the process, but the H amount absorbed remains the same. As lower pressures better allow to monitor the process (by recording pressure variations in a closed volume) and its completion, we used as a standard the H_2 pressure of 5 bar.

The desorption in a closed evacuated volume was performed to determine the total H concentration. The total amount of H_2 released corresponds to approximately 3 H atoms per 1 U atom. (There is some uncertainty, we obtained values in the range 2.7–3.0 H/U in different hydrides).

The hydride samples were subsequently crushed and subjected for further structure characterization by X-ray powder diffraction. The Physical Property Measurement System (PPMS) equipment was used for magnetization, performed in the temperature range 2–300 K and in magnetic fields up to 14 T, using powder samples with grains fixed by a glue in a random orientation.

3. Crystal structure

3.1. U alloys with Mo or Zr

Fig. 1 illustrates the structural variations of U splats with increasing concentration of alloying elements as seen in X-ray diffraction. Both Mo and Zr alloying leads to a rapid suppression of numerous α-U peaks and for 15% of Mo or Zr the structure corresponds to the *bcc* phase, with the lattice parameters close to that found in pure U at elevated temperatures. While the *a*-parameter of U metal at $T = 1050$ K is approx. 352 pm, extrapolation of the temperature dependence to the room temperature gives 348 pm. The alloying by smaller Mo atoms reduces *a* to 333 pm for 30% Mo [12].

Fig. 1 indicates that distinguishing α- and γ-U may be in reality bit tricky. Most of the lines of γ-U overlap with lines of α-U, and we have to specify those of γ-U which cannot be attributed to other phases. Those are, however, weak. It turns out useful to concentrate on the diffraction angles 35–40°, where the reflection γ(110) appears. Fig. 2 reveals that there is no sign of α-U for 12% Mo. In the same time, the splitting of the (110) reflection around this concentration exhibits a weak tetragonal distortion, characterizing the so-called γ^0 structure [12]. The splitting vanishes for 13% Mo, for which $a = 344$ pm was determined. Alloying with larger Zr atoms