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UH₃-based ferromagnets: new look at an old material

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Abstract

UH₃ is the first discovered material with ferromagnetism based purely on the 5*f* electronic states, known for more than half century. Although the U metal is Pauli paramagnet, the reduced 5*f*-5*f* overlap in compounds allows for moment formation and ordering, typically if the U-U spacing exceeds the Hill limit, i.e. about 340 pm. The stable form of UH₃, known as β-UH₃, has rather high $T_C \approx 170$ K. Such high value is rather unusual, considering $d_{U-U} = 331$ pm. Properties of metastable α-UH₃ with $d_{U-U} = 360$ pm could be never well established. Using the fact that α-UH₃ is in fact *bcc* U with interstitials filled by H, we attempted to synthesize α-UH₃ starting from the γ-U alloys, with the *bcc* structure retained to room temperature by doping combined with ultrafast cooling. While up to 15% Zr a contamination by β-UH₃ was obtained, 20% Zr yielded single phase α-UH₃. The T_C value remains high and very similar to β-UH₃. One can see an increase up to 187 K for 15% Zr, followed by a weak decrease. Magnetic moments remain close to 1 μ_B/U atom. An insight is provided by *ab-initio* calculations, revealing a charge transfer towards H-1*s* states, depopulating the U-6*d* and 7*s* states, leaving almost pure 5*f* character around the Fermi level. The 5*f* magnetism exhibits a high coercivity (μ₀*H_c* up to 5.5 T) and large spontaneous volume magnetostriction of 3.2·10⁻³. Even higher increase of T_C , reaching up to 203 K, can be achieved in analogous Mo stabilized hydrides, which yield an amorphous structure. The compounds represent, together with known hydrides of U₆Fe and U₆Co, a new group of robust 5*f* ferromagnets with small d_{U-U} but high T_C . Although common hydrides are fine powders, some of the new hydrides described as (UH₃)_(1-x)T_x (T = Zr or Mo) remain monolithic, which allows to study transport and thermodynamic properties.

1 Introduction

UH₃, which becomes ferromagnetic below $T_C \approx 170$ K, belongs to the first known 5*f* materials with magnetic ordering, discovered more than half century ago [1]. However, we

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cannot conclude that we well understand its electronic structure and low temperature properties. UH_3 is the only binary Uranium hydride, however it appears in two structure modifications. The common form is $\beta\text{-UH}_3$, which has a large cubic unit cell ($a = 664 \text{ pm}$) with 8 formula units, two different U sites and H positions depending on internal parameters. Besides this form, there is also $\alpha\text{-UH}_3$, which is thermodynamically unstable. The U positions represent a simple *bcc* lattice. It is formed during low temperature hydrogenation, but transforms fast into $\beta\text{-UH}_3$, and was therefore never studied in a pure form. Its magnetic properties confronted with those of $\beta\text{-UH}_3$ represent an important piece of evidence, but they were never well established. While earlier works, cited in ref. [1], assume ferromagnetic ground state and Curie temperature coinciding with that of $\beta\text{-UH}_3$, a later neutron diffraction work concluded that it is non-magnetic [2]. That would seriously contradict to the concept of U magnetism depending mainly on the $5f5f$ overlap. The density of $\alpha\text{-UH}_3$ (11.12 g/cm^3) is slightly higher than for $\beta\text{-UH}_3$ (10.92 g/cm^3), which means that the average U-U distances are somewhat higher in the latter case. However, the distance between the U atoms occupying the specific $6c$ position is only 331 pm in $\beta\text{-UH}_3$, i.e. much shorter comparing to 360 pm in $\alpha\text{-UH}_3$. The significance of the shortest distance suggests that properties of α - and $\beta\text{-UH}_3$ should be actually dramatically different and magnetic properties (U moments and ordering temperature) should be more pronounced in $\alpha\text{-UH}_3$.

Thus one of persisting issues are the properties of $\alpha\text{-UH}_3$, which remains, besides the stable $\beta\text{-UH}_3$ phase, as a metastable species never existing in a pure form. The other and more general issue is (in)adequacy of description by conventional *ab-initio* calculations (see e.g. [3]), which does not seem to reproduce well e.g. photoelectron spectra [4]. Here we have to look back a bit and ask how much we generally understand the $5f$ magnetism, with large orbital moments induced in itinerant states by strong spin-orbit interaction, what is the relation of the $5f$ bonding and magnetic anisotropy, affecting not only directions of ordered moments but also determining the type of magnetic fluctuations in the paramagnetic state. We have also to question what can be maximum achievable ordering temperatures. Although few anomalous U-based compounds are prominent characters in the drama of unconventional superconductivity and quantum criticality, it is also worth to turn to more regular materials, testing the relevance of our basic ideas in the field of actinides. Having this in mind as a main goal, we compare here magnetic properties of different UH_3 varieties, including $\alpha\text{-UH}_3$, which we succeeded to synthesize as a pure phase using the Zr alloying. Modifying the composition and inspecting how properties develop, which is the most conventional tool, is not easily available, as none of the two UH_3 modifications has any counterpart, which would give a simple solid solution. We have taken the route starting from metastable $\gamma\text{-U}$ alloys, which are actually alloys of U metal with selected d -elements, which prevent the phase transformation of U in the sequence $\gamma\text{-}\beta\text{-}\alpha$, retaining thus the *bcc* $\gamma\text{-U}$ phase to ambient temperatures and below. As we demonstrated, the necessary amount of the alloying elements can be reduced by ultrafast cooling (we employed the splat cooling technique [5]), so we have available relatively extended concentration ranges of various $(\text{U}_{1-x}\text{T}_x)\text{-H}$ systems ($\text{T} = \text{Zr}$ or Mo). Such hydrides do not turn into a fine pyrophoric powder as common UH_3 . In fact the $\gamma\text{-U}$ alloys are much more stable in air than pure U metal, their

hydrogenation needs elevated pressures, and in most of cases large monolithic (albeit brittle) of the hydrides could be obtained, which facilitates subsequent studies [6–9].

II Materials synthesis, structure, experimental methods

Starting $U_{1-x}Zr_x$ and $U_{1-x}Mo_x$ alloys were prepared by arc melting in Ar atmosphere. Each ingot was turned and remelted 3 times for better homogenization of constituents. As 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 μ m 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 K_α radiation, indicated the *bcc* structure plus a small amount of impurities (UC and UO_2), residing mostly at the surface. Pure U splats used for comparison exhibit the α -U structure.

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 gun 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, performed 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).

The phase analysis revealed that U alloys with Mo concentrations of 11 at.% or higher are of single phase, either *bcc* or with a weak orthorhombic distortion, which is called γ_0 phase. No α -U phase could be identified by EBSD. The alloy with 4 % Mo, on the other hand, exhibits a pure α -U phase, with no γ -U present. The situation is somewhat different for the Zr alloying. For 11% and 15% Zr, XRD still reveals traces of α -U phase (no EBSD study has been performed so far for Zr alloying), 20% Zr and more is of single *bcc* phase. 40% Zr exhibited inhomogeneities in Zr distribution, and was therefore excluded from further study.

The samples were hydrogenated using a standard procedure [6,8], exposing sample to high hydrogen gas pressure. We found that minimum H_2 pressure for the hydride formation in γ -U alloys is, irrespective of composition, in the range 4-5 bar. Higher pressures (up to 100 bar) can only speed up the process, but the H amount absorbed remains the same. As lower pressures allow better monitoring of 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 exception was the alloy with 4 % Mo, which had the α -U structure. In this case the hydrogenation

proceeded in the pressure range below 1 bar H_2 as in pure α -U. The product was, unlike for pure U metal, stable in air.

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). Therefore we adopted the formula $(UH_3)_{1-x}(Zr-Mo)_x$. The uncertainty as to the H concentration is affected by the fact that it has to be determined from the pressure increase in a closed system, which is not all at the same temperature. Cooling the reactor (i.e. the hot part of the system) to the room temperature leads to a re-absorption of the gas, presumably by the α -U phase.

Working with two systems, U-Zr and U-Mo, gave surprisingly two different structure modifications of the hydrides. The Mo alloyed hydrides exhibit only few broad diffraction lines, suggesting amorphization. As identified in [6] for $UH_3Mo_{0.18}$ (i.e. $(UH_3)_{0.85}Mo_{0.15}$), the structure is closely related to β - UH_3 , but with very small coherence length. Simulations indicate the grain size about 1 nm only. The same results were received for all other Mo concentrations, with the exception of $(UH_3)_{0.96}Mo_{0.04}$, which exhibits a standard crystalline β - UH_3 state. If the structure is amorphous, many other alloying elements (besides Mo) can be incorporated into the hydride maintaining its single phase character. Their description goes beyond the framework of the present contribution.

The XRD patterns for the Zr doped hydrides reveal a crystalline state, which is clearly different from β - UH_3 . A closer inspection indicated a *bcc* structure, which is very much expanded (by 75 % in volume) with respect to the *bcc* precursors [8]. The lattice parameters $a \approx 416$ pm are very close to the known α - UH_3 structure. Small amount of ZrC impurity was also observed from diffraction patterns for all hydrides. A small amount of ZrH_2 is not excluded. The hydride prepared from the pure U splat shows mixture of β - UH_3 and α - UH_3 phases, with β - UH_3 as the dominant phase. When adding Zr, the concentration of α - UH_3 phase increases while the concentration of β - UH_3 decreases. For $x = 0.15$ only tiny peaks of residual β - UH_3 could be recognized. For $x = 0.20$ no β - UH_3 can be observed. Analysis of the peak broadening indicates a grain size in the range 10-20 nm. Such grains, absent in the Mo alloying case, can be indeed recognized in TEM micrographs (Fig. 1).

The Physical Property Measurement System (PPMS) equipment was used for magnetization and specific heat measurements, performed in the temperature range 2-300 K and in magnetic fields up to 14 T. For the specific heat measurements, the samples were in the form of powder pressed to make a pellet. Magnetization was measured on powder samples with randomly oriented grains fixed by glue.

Some of the hydride samples allowed to attach electrical contacts by a silver paste and to measure the temperature dependence of electrical resistivity, also using the PPMS system.

III Results

3.1 Magnetic properties

All the hydrides studied were found ferromagnetic. The Curie temperatures can exceed substantially those of regular β -UH₃, which vary somewhat in literature but don't exceed ≈ 170 K. The alloyed hydrides tend to higher T_C values especially for lower alloying levels. The T_C -values, determined from low-field $M(T)$ dependences, Arrott plots, and temperature dependences of specific heat exhibit a higher uncertainty for higher concentrations of Mo or Zr, which is reflected by the error bars in Fig. 2. However, the values have a clearly decreasing tendency for higher concentrations of Mo or Zr. The maximum in both cases (quite remarkably) appears in the concentration range 12-15%; the decrease at still lower concentrations is close to the end of stability of the new types of hydrides. The α -U phase, even with few percent of alloying metal, yields normal β -UH₃ structure, with T_C approaching (from above) the values of pure β -UH₃. The dotted line indicates that we may expect increasing T_C already within the α -U phase. Up to now we have not studied hydrogenation of the mixed-phase (α - γ) alloys. At the present stage we can only speculate why the maximum T_C occurs for both systems for the same concentration of alloying elements. In the β -UH₃ structure type with 8 U atoms in unit cell, a periodic replacement of one of them by Mo would yield (U_{0.875}Mo_{0.125})H₃, which is just around the Mo concentration giving the maximum T_C . This game naturally does not work in the Zr system with different structure type, but there more substantial admixture of β -UH₃ on the account of α -UH₃ happens below this concentration. Uncertain in both cases is the role of possible H vacancies, the existence of which is suggested by the formula we use, derived from the fact that the real H concentration scales rather with concentration of U and not with all metal atoms. Details of atomic arrangements will have to be revealed by high-resolution TEM and pair distribution function studies, which are planned.

All the hydrides exhibit very wide hysteresis loops at low temperatures. In the Zr alloying case, the loops, the example of which was presented in [8], are rectangular. Below $T = 6$ K, the smooth magnetization changes into several apparently erratic steps. The width of the loop increases with the Zr concentrations and reaches ≈ 11 T. The hysteresis loops for the Mo-alloyed UH₃ differ by their very slow approach to saturation [6,9]. This may reflect the almost amorphous structure, with random orientation of local easy-magnetization directions, equivalent in fact to a non-collinear ferromagnet. Very strong magnetic anisotropy occurs as a rule in U intermetallics due to strong spin-orbit interaction and directionality of U-U bonding [10]. Only one large step appears at low temperatures in this case. This may indicate a long range exchange coupling between individual nanograins. The size of magnetic moments can be quite easily estimated for the Zr alloyed UH₃, amounting to 1.0 μ_B /U atom. We cannot, however, exclude that Zr atoms carry a non-negligible moment, too. Such possibility was indicated by *ab-initio* calculations mentioned below. If that is true the U moments would tend to a decrease with progressing alloying, which is more expected trend, in *5f*-band magnetism, than invariable U moments. Modeling the approach to saturation in Mo alloyed UH₃, we obtained U moments even higher, of approx. 1.1 μ_B /U.

Important information on magnetism is provided by spontaneous magnetostriction. We determined the magnetostriction by measuring the T dependence of the lattice parameter by means of XRD (see Fig.3). The results for $(\text{UH}_3)_{0.85}\text{Zr}_{0.15}$ representing the α - UH_3 structure [8] are compared with $(\text{UH}_3)_{0.96}\text{Mo}_{0.04}$ ($T_C \approx 180$ K), which has pure β - UH_3 structure, but lacks the pyrophoricity of pure UH_3 , and with literature data for UD_3 [11], from which we took for easier comparison also the Debye type of lattice expansion, serving as a background for estimation of pure magnetic effect. The hydrides exhibit a large magnetostriction leading to an invar effect. The lattice parameters for the β - UH_3 type lattice were rescaled to match the α - UH_3 unit cell. The latter exhibits the spontaneous volume magnetostriction $\omega_s = 3.2 \cdot 10^{-3}$, which is higher than that estimated for β - UH_3 , $2.7 \cdot 10^{-3}$ in [11] and represents a truly remarkable value among the $5f$ systems. Our value for $(\text{UH}_3)_{0.96}\text{Mo}_{0.04}$ is somewhat smaller than the literature data for UD_3 , $\omega_s = 2.2 \cdot 10^{-3}$. They show that when both types of structures are measured using the same equipment, the behavior in the paramagnetic state, i.e. even the thermal expansion at high temperatures, is practically identical. As deduced in [8], the temperature dependence of magnetostriction scales with square of spontaneous magnetization, M_s^2 , which is a finding corresponding to the band character of magnetism. A question is whether the lower magnetostriction in β - UH_3 can be related to internal parameters of the crystal structure, which in principle allows better accommodating the increase of the volume of U atoms. The thermal expansion coefficient $\alpha_v = 21 \cdot 10^{-6} \text{ K}^{-1}$ can be estimated from the linear part of $\alpha(T)$ in the range 220- 300 K.

3.2 Other electronic properties

The character of the alloyed hydrides, which are brittle but retain larger monolithic pieces, facilitates measurements of specific heat and enables studies of electrical resistivity. The resistivity of Mo alloyed UH_3 combines features of UH_3 , mainly very high (for a metal) absolute values ($600 \mu\Omega\text{cm}$ in the paramagnetic state) [6], with flat temperature dependence having a weakly negative slope. Such negative slope was observed, as a rule, for the precursor U-Mo alloys, affected by the weak localization phenomenon. Presence of such negative slope in the hydride corroborates the conclusion that Mo atoms do not try to segregate and remain randomly distributed in the U positions. It seems that random orientation of U magnetic moments in the ferromagnetic state contributes to the localization. This can be deduced from the field dependence of resistivity in the ordered state, which is characterized by a decrease by more than 20% in the field of 9 T, and has a hysteretic behavior reflecting the hysteretic behavior of magnetization (Fig. 4). Such decrease in field was not observed in the Zr-alloyed UH_3 [8], which exhibits regular decrease of $\rho(T)$ below T_C . As the resistivity in the paramagnetic state remains practically unaffected by such magnetic fields, it is evident that the field alignment of U moments below T_C in the amorphous type causes actually a decrease of $\rho(T)$ similar as in Zr-alloyed UH_3 .

Interesting findings obtained from the specific heat measurements include information on temperature shifts of magnetic phase transitions and the values of the Sommerfeld coefficient of electronic specific heat γ , which remains around 30 mJ/mol K^2 (up to 35 mJ/mol U K^2 normalized per U atom) irrespective of type of alloying and structure [6,8]. It is therefore about twice higher comparing to the precursor U-Mo and U-Zr alloys, being themselves enhanced with respect to α -U (9 mJ/mol K^2). The variations are affected by the

larger U-U spacing, leading typically to $5f$ band narrowing and increasing the density of states at the Fermi level $N(E_F)$, and also by the splitting of spin-up and spin-down sub-bands, at which $N(E_F)$ decreases.

3.3 Ab-initio electronic structure calculations

The fact that increasing the U-U spacing leads to appearance of U magnetic moments and their ordering seems compatible with our conventional view of magnetism in uranium intermetallics, in which the U-U spacing reaching a certain value (i.e. the Hill limit, approx. 340-360 pm) is considered to be the basic pre-requisite. Less understandable in this context is that a material at or even slightly below the Hill limit, where one expects very weak itinerant ferromagnetism, has ordering temperatures far exceeding 100 K. The other puzzling fact is that both hydrides have almost identical magnetic properties despite rather different crystal structures, and neither amorphization nor alloying by essentially non-magnetic metals make any qualitative change. The positive aspect is that we can simply deal with much simpler α -UH₃ structure with one U site and no internal parameters, and the calculations should be representative also for β -UH₃ with 4 times larger unit cell.

First theoretical analysis of electronic structure (using the APW method) was performed by Switendick [11], who noticed the properties of α - and β -UH₃ may be very similar despite different U-U distances. The suggestion that the U-U interaction is not as important as the U-H interaction seems to be right, although the work does not provide reliable details of the situation of $5f$ states. More recent scalar relativistic computations of UH₃ (both for the α - and β -form) using the VASP package [13,3] reveal a mixed ionic and covalent bonding, while the latter becomes more important at small volumes and for the U (II) sites in β -UH₃, which have some of the U neighbours at lower U-U distances.

We employed fully relativistic calculations including the spin-orbit interaction to assess to which extent basic magnetic properties (U ordered magnetic moments) can be reproduced assuming band magnetism [8]. The full potential local orbitals code (FPLO) applied on α -UH₃, solving the Dirac equation in the framework of local spin density approximation (LSDA), gives at the experimental volume of α -UH₃ almost complete compensation of large spin $M_S = 2.7 \mu_B$ and orbital $M_L = -2.72 \mu_B$ magnetic moments (Fig. 5). We assumed that the cancellation of both moments is accidental, the values of spin and orbital components in our calculations are considerably volume dependent (both components decrease with decreasing volume). The equilibrium volume α -UH₃ comes out by 9% higher ($a = 426$ pm) than the experimental one. At this volume, the orbital moment dominates over the spin moment already, while the total moment of $0.4 \mu_B/U$ is still too small comparing with experiment.

Occupancies of individual electronic states for α -UH₃ compared with hypothetical *bcc* U of the same lattice parameter $a = 414$ pm indicate that H in a compound with strongly electropositive elements like U behaves electronegatively and the $1s$ occupancy increases from 1.0 to 1.74. This leads to the depletion of the U- $7s$ states (0.42 electrons almost completely lost), while the U- $6d$ states lose about 50% of their occupancy, from 1.22 to 0.63. The $5f$ states are affected very little, in fact their occupancy slightly increased, from 2.62 to 2.71. The almost complete loss of U- $7s$ electrons and partial depopulation of U- $6d$ states can

be taken responsible for high values of electrical resistivity. H-1s states, although occupied by more than one electron, form typically states separated from the Fermi energy by several eV and cannot contribute to the charge transport. Such situation with the 6d states shifted up in energy reduces the 5f-6d hybridization and supports the formation of ordering of the 5f magnetic moments.

Studies of the volume dependence (Fig. 5) show that compressing below 90% of the experimental lattice parameter a_0 leads to a fast collapse of both spin and orbital moments of α -UH₃. Before reaching this limit, the orbital moments are reduced faster with pressure than the spin moments. The dramatic decrease starts at a -values corresponding to d_{U-U} lower than the Hill limit 340 pm, and the d_{U-U} values around 300 pm, corresponding to weakly paramagnetic γ -U, still allow for small magnetic moments. The same type of calculation for γ -U at its experimental volume (i.e. α -UH₃ without hydrogen) yields a non-magnetic state.

In addition, Disordered Local Moment [17] calculations were used to compare moments in the paramagnetic state, which allows to assess spontaneous magnetostriction effects, obtained as a difference between equilibrium volumes in ordered ($T = 0$ K) and disordered paramagnetic states. The same method was used to describe the effect of disorder imposed by random Zr substitution [8].

The calculation employed the tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic-sphere approximation (ASA) combined with the coherent-potential approximation (CPA) [14–16] for the treatment of random binary U_{1-x}Zr_x alloys with Zr concentrations $x < 0.5$ [8]. The alloy structure kept as *bcc* (no H atoms for simplicity) with the lattice parameter equal to that of *bcc* UH₃ ($a = 416$ pm).

The results show that the large negative orbital moment of U, $-2.5 \mu_B$, is very stable with respect to Zr alloying. The positive spin magnetic moment ($3.5 \mu_B$) in the ferromagnetic state depends slightly on the Zr concentration (decreases to $3.0 \mu_B$ for 50% Zr), but the spin moment in the DLM state is very stable again, staying at $2.2 \mu_B$ irrespective of Zr concentration. The comparison of U moments between the ferromagnetic and DLM state reveals that the moments are actually reversed. While the spin moment dominates in the ferromagnetic state (the correct value $\mu_U = 1.0 \mu_B$ is most likely fortuitous), the insensitivity of the orbital moment to the spin disorder state makes the orbital moment dominant in the paramagnetic state. As there is no systematic information on U orbital moments in the DLM state (the DLM approach was used for actinides in the context of phase stability studies [19]) we cannot be conclusive as to the relevance of the calculated orbital moments in the DLM state. It should be noted that the Zr atom in the ferromagnetic alloys exhibits a positive spin moment with values ranging between $1.20 \mu_B$ for $x = 0.1$ and $0.64 \mu_B$ for $x = 0.5$, in contrast to the DLM state where it is quenched completely, testifying that Zr moments are induced by the ferromagnetic order in the U subsystem. The stability of U moments in the binary U-Zr alloys is quite surprising having in mind the absence of magnetic order in pure metallic Zr. The stability of U-moments seems to be related to the observed weak concentration dependence of the Curie temperature of the ternary (UH₃)_{1-x}Zr_x system.

To confront the large observed spontaneous magnetostriction, we have employed the same approach as in the case of systems containing transition and rare-earth metals [19–21]. This approach is based on comparison of equilibrium lattice parameters of the magnetically ordered state (ground state) and of the DLM state (paramagnetic state), which yields the spontaneous volume magnetostriction. In the case of *bcc* UH₃ we applied the TB-LMTO-CPA method to a simplified model, containing one formula unit in the atomic basis on the *bcc* Bravais lattice: besides the sites of the *bcc* lattice occupied by U atom, six tetrahedral interstitial sites (per one U site) of the *bcc* lattice are randomly occupied by H atoms and vacancies (atoms with atomic number $Z = 0$) with probability 1/2, so that the total chemical composition of the model coincides with the real system. The calculations were confined to the scalar-relativistic approximation (neglecting the spin-orbit interaction). The volume dependence of the total energies of both types of states is displayed in Fig. 6. The DLM state has a slightly reduced equilibrium lattice parameter comparing to the ferromagnetic state. The equilibrium lattice parameter in the ferromagnetic state agrees reasonably well with the measured value and with the theoretical value calculated by the more accurate fully relativistic technique (see above). The relative difference of the lattice parameter in the two magnetic states can be (after multiplication by the factor of 3) identified with the spontaneous volume magnetostriction. Its calculated value amounts to $\omega_s = 7.5 \cdot 10^{-3}$, which represents a large effect, being of a similar magnitude as the measured value ($\omega_s = 3.2 \cdot 10^{-3}$). The origin of this large positive magnetostriction can be, in analogy to the transition-metal and rare-earth-metal systems, ascribed mainly to the reduction of the spin magnetic moment in the DLM state as compared to the ferromagnetic state. The obtained semi-quantitative agreement between the theoretical and measured spontaneous magnetostriction corroborates the itinerant nature of magnetism of the UH₃ system. The energy shift of the two parabolas (Fig. 6) can also be used for an estimation of the strength of exchange interactions between the U magnetic moments in the hydrides. This simple approach identifies the calculated difference between the ground-state energies of both states with a lattice sum of pair exchange interactions; this lattice sum is in turn proportional to the Curie temperature T_C in the mean-field approximation [22]. In the case of a classical isotropic Heisenberg Hamiltonian, the resulting T_C is given by $T_C = 2 E / (3k_B)$, where $E = E_{\text{DLM}} - E_{\text{FM}}$ denotes the energy separation of the DLM and FM states (per one U atom) and k_B is the Boltzmann constant. For the studied *bcc*-UH₃, we have obtained $E = 1.45$ mRy/f.u. which yields $T_C = 153$ K. This estimation indicates that the underlying electronic structure is compatible with the relatively high Curie temperatures (close to 200 K) observed in α - and β -UH₃. A more complete investigation of the exchange interactions, including anisotropic exchange interactions and employing more sophisticated methods of statistical physics, goes beyond the scope of this pilot study.

IV Discussion and concluding remarks

The findings on alloyed UH₃ materials demonstrate a somewhat surprising fact that uranium material with the U-U spacing in the Hill limit range can have very robust basic magnetic characteristics, which do not vary significantly with varying structure, composition, or even diluting the U sublattice. The fact that even amorphous uranium-based materials can be

strong ferromagnets is rather surprising, examples known so far indicate suppression of magnetic moments and ordering with increasing crystallographic disorder [23].

In fact there exist in literature other examples of alloyed UH_3 . Those were prepared by hydrogenation of U_6Fe or U_6Co , and were reported with the stoichiometry $\text{U}_6\text{FeH}_{17}$ and $\text{U}_6\text{CoH}_{18}$ [24,25] and $\beta\text{-UH}_3$ structure type and T_C possibly somewhat enhanced with respect to UH_3 . Reasons for the robustness of magnetic and other properties remain so far unclear, the suggested depopulation of $6d$ and $7s$ states is one of reasons. Besides further theoretical analyses more experimental data should be collected. The fact that the new hydrides can be prepared as monolithic opens an avenue for more systematic investigations of transport properties, as Hall effect and thermopower, which may give more insight into the situation of electrons at the Fermi level.

We can ask whether there are any U compounds in analogous situation, with a certain depopulation of $6d$ and $7s$ states, while still preserving metallicity, with the $5f$ band at the Fermi level, all possibly leading to strong exchange interactions and high ordering temperatures. Very interesting in this respect are uranium pnictides, i.e. compounds with N, P, As, Sb, or Bi, which have the bonding character between ionic and covalent. For uranium (and generally actinide) nitrides, certain ionicity is reflected in the shift of the U- $4f$ core-level lines in XPS towards higher binding energies, which is 0.4 eV between U and UN, but additional 1.3 eV for U_2N_3 [26,27]. Both materials are antiferromagnets, the Néel temperature of 53 K increases to 94 K for U_2N_3 , but it collapses fast for further excess of U, likely due to the loss of metallicity [28]. In UH_3 , there is the $4f$ -line shift, as well, albeit only 0.4 eV [29]. The shift, however, reflects sensitively also the occupancy of the $5f$ states, which, as suggested above, may slightly increase, so the two effects may partly compensate each other. Other U pnictides have even higher ordering temperatures, and probably the highest among U binary ferromagnets was found in U_3As_4 ($T_C = 198$ K) [30]. This record may be actually exceeded by several Kelvin by our alloyed UH_3 materials. There are however U-pnictogen ternaries with even higher Curie or Néel temperatures. As to ferromagnets, the record holder is probably UCu_2P_2 with $T_C = 216$ K, which has, in addition, similar $\rho(T)$ behaviour as UH_3 , with ρ reaching almost 1 m Ωcm in the paramagnetic state [31]. The fact that magnetooptical studies [32] show low concentration of free carriers in this compound may indeed indicate that this is the source of high ordering temperatures.

Finally, we would like to make a remark on practically coinciding basic magnetic characteristics of α - and $\beta\text{-UH}_3$. At first glance it may look as natural consequence of very similar density, meaning that the average U-U spacing is almost the same in both phases. More detailed look reveals that while all U atoms in $\alpha\text{-UH}_3$ have 8 U nearest neighbours at 360 pm, $\beta\text{-UH}_3$ has two types of U positions. 1/4 of U is in U_I positions, which have as neighbours 12 U_II atoms separated by 370 pm. 3/4 of U atoms lying in the U_II positions form linear chains with a small in-chain U-U separation ≈ 330 pm (i.e. 2 neighbours at such distance), while farther neighbours are the U_I atoms at 370 pm.

In reality, as shown in Ref. [33], the width of the $5f$ band W_f when expressed as power law of the interatomic distances R , $W_f = W_{f0}(R_0/R)^n$, has a very high exponent $n = 6\text{--}7$, which

means that the shortest distances should be more significant than those to the more remote atoms. The equivalence of magnetic properties of the two modifications serves therefore a good argument that the $5f$ - $5f$ overlap is not the main tuning parameter in the hydrides, but the U-H interaction is significant, if not dominant. This is underlined by the fact that the H atoms are equidistant from all U neighbours in β -UH₃ [34] and that both U moments (μ_I and μ_{II}) are magnetically equivalent [35].

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References

- [1]. Troc R, Suski W. J Alloys Comp. 1995; 219:1.
- [2]. Lawson AC, Goldstone JA, Huber JG, Giorgi AL, Conant JW, Severing A, Cort B, Robinson RA. J Appl Phys. 1991; 69:5112.
- [3]. Taylor, ChD. Phys Rev B. 2010; 82:224408.
- [4]. Gouder, T., Seibert, A., Rebizant, J., Huber, F., Havela, L. Actinides 2006-Basic Science, Applications and Technology. Materials Research Society Symp Proc. Blobaum, KJM.Chandler, EA.Havela, L.Maple, B., Neu, MP., editors. Vol. 986. 2007. p. 17-28.
- [5]. Tkach I, Kim-Ngan NTH, Warren A, Scott T, Gonçalves AP, Havela L. Physica C. 2014; 498:14.
- [6]. Tkach I, Mašková S, Mat j Z, Kim-Ngan N-TH, Andreev AV, Havela L. Phys Rev B. 2013; 88 060407(R).
- [7]. Havela L, Paukov M, Tkach I, Matej Z, Kim-Ngan N-TH, Andreev AV. MRS Proceedings. 2014; 1683 mrs14-1683-s03-02. doi: 10.1557/opl.2014.431
- [8]. Tkach I, Paukov M, Drozdenko D, Cieslar M, Vondráková B, Mat j Z, Kriegner D, Andreev AV, Kim-Ngan N-TH, Turek I, Diviš M, et al. Phys Rev B. 2015; 91 115116.
- [9]. Tkach I, Kim-Ngan NTH, Mašková S, Andreev AV, Mat j Z, Havela L. Acta Phys Polonica. 2014; 124:292–293.
- [10]. Havela L, Sechovský V, de Boer FR, Brück E, Nakotte H. Physica B. 1992; 177:159.
- [11]. Andreev AV, Zadvorkin SM, Bartashevich MI, Goto T, Kamarád J, Arnold Z, Drulis H. J Alloys Comp. 1998; 267:32.
- [12]. Switendick AC. J Less Common Met. 1982; 88:257.
- [13]. Taylor, ChD, Lookman, T., Lillard, RS. Acta Materialia. 2010; 58:1045.
- [14]. Turek I, Drchal V, Kudrnovský J, Šob, M., Weinberger, P. Electronic structure of disordered alloys, surfaces and interfaces. Kluwer; Boston: 1997.
- [15]. Shick AB, Drchal V, Kudrnovský J, Weinberger P. Phys Rev B. 1996; 54:1610.
- [16]. Turek I, Kudrnovský J, Carva K. Phys Rev B. 2012; 86:174430.
- [17]. Gyorffy BL, Pindor AJ, Staunton J, Stocks GM, Winter H. J Phys F: Met Phys. 1985; 15:1337.
- [18]. Jeffries JR, Söderlind P, Cynn H, Landa A, Evans WJ, Weir ST, Vohra YK, Lander GH. Phys Rev B. 2013; 87:214104.
- [19]. Khmelevskiy S, Turek I, Mohn P. Phys Rev Lett. 2003; 91:037201. [PubMed: 12906444]
- [20]. Khmelevskiy S, Turek I, Mohn P. Phys Rev B. 2004; 70:132401.
- [21]. Turek I, Rusz J, Diviš M. J Alloys Comp. 2007; 431:37.
- [22]. Turek I, Kudrnovský J, Bihlmayer G, Blügel S. J Phys: Condens Matter. 2003; 15:2771–2782.
- [23]. Havela L, Miliyanchuk K, Rafaja D, Gouder T, Wastin F. J Alloys Comp. 2006; 1320:408–412.
- [24]. Drulis H, Vagizov FG, Drulis M, Mydlarz T. Phys Rev B. 1995; 52:9500.

- [25]. Andreev AV, Bartashevich MI, Deryagin AV, Havela L, Sechovsky V. *Phys Stat Sol A*. 1986; 98:K47.
- [26]. Black L, Miserque F, Gouder T, Havela L, Rebizant J, Wastin F. *J Alloys Comp*. 2001; 315:36–41.
- [27]. Havela L, Wastin F, Rebizant J, Gouder T. *Phys Rev B*. 2003; 68:085101.
- [28]. Troc R. *Solid State Commun*. 1975; 13:14.
- [29]. Gouder T, Eloirdi R, Wastin F, Colineau E, Rebizant J, Kolberg D, Huber F. *Phys Rev B*. 2004; 70:235108.
- [30]. Sternberk J, Hrebik J, Menovsky A, Smetana Z. *J Phys (Paris)*. 1971; (Suppl. 32):C1-744.
- [31]. Kaczorowski D, Troc R. *J Phys: Cond Mat*. 1990; 2:4185–4196.
- [32]. Schoenes J, Fumagalli P, Ruegsegger H, Kaczorowski D. *J Magn Magn Mater*. 1989; 81:112.
- [33]. Johansson B, Skriver H. *J Mag Mag Mater*. 1982; 29:217.
- [34]. Rundle RE. *J Am Chem Soc*. 1951; 78:4172.
- [35]. Bartscher W, Boeuf A, Caciuffo R, Fournier JM, Kuhs WF, Rebizant J, Rustichelli F. *Solid State Commun*. 1985; 53:423.

Fig. 1.

TEM micrographs for $(\text{UH}_3)_{0.88}\text{Mo}_{0.12}$ (left) and $(\text{UH}_3)_{0.85}\text{Zr}_{0.15}$ (right) illustrate the difference in microstructure. While the Zr alloying leaves visible quite homogeneous grains of about 20 nm, the Mo alloying yields within the achievable resolution areas exhibiting some contrast variations on few nm scale, but the granularity is not well developed.

Fig. 2. Concentration dependence of the Curie temperature in the series $(\text{UH}_3)_{1-x}(\text{Zr-Mo})_x$.

Fig. 3.

Temperature dependence of lattice parameter for $(\text{UH}_3)_{0.85}\text{Zr}_{0.15}$ representing the α - UH_3 structure compared with $(\text{UH}_3)_{0.96}\text{Mo}_{0.04}$ ($T_C \approx 180$ K), which has pure β - UH_3 structure, and with literature data for UD_3 [11], both rescaled to match the lattice difference. The lines represent the Debye type of lattice expansion and serve as a non-magnetic background.

Fig. 4.

Magnetoresistance measurements for the amorphous β - UH_3 material at $T = 250$ K and 50 K. The experiment was actually performed using $(\text{UH}_3)_{0.78}\text{Mo}_{0.12}\text{Ti}_{0.10}$, which has the same amorphous structure and very similar magnetic properties as $(\text{UH}_3)_{0.78}\text{Mo}_{0.22}$. The inset shows the temperature dependence of resistivity for very similar material, $(\text{UH}_3)_{0.85}\text{Mo}_{0.15}$.

Fig. 5.

Variations of U spin and orbital moments in α -UH₃, calculated by means of the FPLO method, as a function of the lattice parameter a normalized to the experimental value a_0 . The values of a/a_0 corresponding to the Hill limit and to γ -U are indicated by arrows.

Fig. 6.

Calculated total energies (per formula unit) of hypothetical *bcc* UH_3 as functions of the unit cell parameter a in the ferromagnetic (FM, full diamonds) and disordered-local-moment (DLM, open circles) states. The total energy minimum of the FM state has been taken as zero on the vertical axis. The experimental lattice parameter is $a = 416$ pm. The vertical shift was used to estimate the Curie temperature, the horizontal shift to estimate the volume magnetostriction.