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Electronic properties of α -UH₃ stabilized by Zr

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Abstract

Pure hydride of the α -UH₃ type without any β -UH₃ admixture was prepared by high-pressure hydrogenation of *bcc* U stabilized by Zr. Such material, characterized by a general formula (UH₃)_{1-x}Zr_x, is stable in air at ambient and elevated temperatures. H release is observed between 400-450 °C similar to β -UH₃. Its stability allowed to measure magnetic properties, specific heat, and electrical resistivity in a wide temperature range. Despite rather different crystal structure and inter-U spacing, the electronic properties are almost identical to β -UH₃. Its ferromagnetic ground state with Curie temperature $T_C \approx 180$ K (weakly and non-monotonously dependent on Zr concentration) and U moments of 1.0 μ_B indicate why mixtures of α - and β -UH₃ exhibited only one transition. Magnetic ordering leads to a large spontaneous magnetostriction $\omega_s = 3.2 \cdot 10^{-3}$, which can be explained by the increase of the spin moment between the paramagnetic (Disordered Local Moment) and the ferromagnetic state. The role of orbital moments in magnetism is indicated by fully relativistic electronic structure calculations.

I Introduction

Interaction of hydrogen with uranium is one of serious issues in the field of nuclear energy and weapons. Any contact with H is detrimental for mechanical integrity and in addition a very fine powder of uranium hydride tends to self-ignition if exposed to air.¹ On the other hand, uranium hydride provides a tool to observe the impact of expansion of the U lattice, allowing the formation of U moments and their ferromagnetic ordering.

Its stable allotropic form, β -UH₃, is a ferromagnet with magnetic moments $\mu \approx 1 \mu_B/U$.² Its magnetic ordering contrasts with the Pauli paramagnetic behaviour of U metal, which has a low magnetic susceptibility $\chi \approx 5.0 \cdot 10^{-9} \text{ m}^3/\text{mol}$ for the orthorhombic α -U form.³ The difference can be qualitatively ascribed to the enhanced U-U spacing in the hydride, which yields a *5f*-band narrowing, necessary for fulfillment of the Stoner criterion. The crucial role of the *5f*-*5f* spacing in determination of the ground state (magnetic contra superconducting) was recognized by Hill⁴, who besides U drew a similar systematics for Ce, U, and Pu compounds. At present it is evident that occurrence of magnetic order in Ce compounds is

primarily affected by the Kondo physics (depending on $4f$ hybridization with ligand states 5), while more complicated many-body effects and fine balance between $5f^5$ and $5f^6$ are primary for Pu systems.^{6,7} Nevertheless, the U and Np alloys and compounds are assumed to be depending on the An-An spacing $d_{\text{An-An}}$. The $5f$ ligand hybridization as a possible second delocalization mechanism⁸ (besides the direct $5f5f$ overlap), becomes prominent for large $d_{\text{An-An}}$. The critical value $d_{\text{An-An}}$ for U, which should be taken with some spread, is assumed around 340 pm. β -UH₃ with $d_{\text{An-An}} = 330$ pm must be therefore somewhere just at the real minimum distance. One can compare for example with $d_{\text{An-An}} \approx 300$ pm for γ -U, being as weakly paramagnetic as α -U.⁹ It is, however, surprising, that a compound close to the verge of magnetism can have a relatively very high Curie temperature $T \approx 170$ K. Ferromagnetism is at such $d_{\text{An-An}}$ more typical than antiferromagnetism, which prevails at $d_{\text{An-An}} > 400$ pm, but T_C over 100 K can be found only in cases like UGa₂ ($T_C = 126$ K) with much higher U moments, which can develop due to large $d_{\text{An-An}} = 401$ pm. Other U compounds in the range of the Hill limit have, if ferromagnetic at all, much lower T_C values.¹⁰

The cubic structure of β -UH₃ can apparently accept some doping. It was found by hydrogenating of U₆Fe that one of the U positions can accept Fe atoms,¹¹ yielding U₆FeH₁₇ (corresponding to (UH_{2.8})_{0.86}Fe_{0.14}). The resulting Curie temperature 173 K practically coincides with that of β -UH₃. Conspicuously similar $T_C = 185$ K was reported for U₆CoH₁₈ formed in the same structure.¹²

An interesting comparison is offered by the existence of α -UH₃, which forms as metastable in the early stage of hydrogenation and transforms fast at elevated temperatures into β -UH₃.¹³ The latter has the Cr₃Si structure type, there are 2 different U sites, and the H atoms occupy distorted tetrahedral interstitials. The cubic unit cell is large ($a = 664$ pm), containing 8 f.u., and the H positions depend on internal structure parameters. The cubic unit cell of α -UH₃ is smaller (416 pm), contains only 2 f.u., and H atoms adopt the Cr positions, there are no internal parameters.¹⁴ The U sublattice represents the *bcc* lattice, it can be therefore taken as expanded γ -U structure (70 % volume expansion).

The fact that α -UH₃ was never studied in a pure form but always in a mixture with β -UH₃ is a reason of uncertainty as to the type of ground state. While earlier works, reviewed in Ref. 2, deduced magnetic ordering with T_C coinciding with that of β -UH₃, in a later neutron diffraction work it was identified as non-magnetic.¹⁵ That would seriously contradict to the concept of the U magnetism depending on the $5f5f$ overlap. The density of α -UH₃ (11.12 g/cm³) is slightly higher for β -UH₃ (10.92 g/cm³), but the shortest U-U spacing 360 pm is considerably larger than 330 pm for β -UH₃. It is therefore strongly desirable to clarify basic electronic properties of α -UH₃.

We undertook a hydrogenation study of γ -U phases doped by Mo or Zr, which helps to retain the *bcc* structure to low temperatures. Both types of alloys are very stable with respect to hydrogen, and high H₂ pressures are needed to form a hydride. While the Mo doping leads to amorphized hydrides of the β -UH₃ type, we found that the Zr doping leads to a stable single phase α -UH₃ type of hydride, which opens an avenue for investigation of basic magnetic, transport, and thermodynamic properties. In the present work magnetic and

magnetoelastic properties of α -UH₃ as well as the Sommerfeld coefficient γ are experimentally determined. A deeper insight into electronic properties is provided by different types of electronic structure calculations, which reveal, *i.a.*, an important role of orbital magnetic moments, which are necessary to explain phenomena originating from high magnetic anisotropy.

II Materials synthesis and experimental methods

Starting U_{1-x}Zr_x alloys were prepared by arc melting of pure elements (U-2N8, Zr-3N) in argon atmosphere using an arc furnace. 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 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 UO₂), residing mostly at the surface. The lattice parameters are listed in Tab. 1. 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. The surface was prepared by mechanical polishing, followed by Ar ion gun bombardment using the voltage 4 kV. For pure U splat very small grains of the *bcc* phase were detected.¹⁶

For higher Zr concentrations, the ultrafast cooling is not necessary, and normal cooling in the arc furnace is sufficient to retain the single-phase *bcc* structure. Therefore we could alternatively work further on with ingots. In this case the XRD study was not performed, the lattice parameters are therefore not included in Tab. 1. The sample with 40% Zr concentration exhibited an inhomogeneous Zr distribution in the bulk form, it was therefore excluded from further study.

For the hydrogenation, the samples were placed in an alumina crucible into a reactor, which could be pressurized to 150 bar of H₂. The reactor was first evacuated down to 10⁻⁶ mbar and then H₂ gas was introduced. We found that minimum H₂ 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 allow better monitoring of the process (by recording pressure variations in a closed volume) and its completion, we used as a standard the H₂ pressure of 5 bar.

The desorption in a closed evacuated volume was performed with the temperature ramping 2 K/min. As all H is released from β -UH₃ at 450 °C, we took 500 °C as an upper limit. In selected case heating up to 800 °C was tested, which however did not yield any further H release. We typically observed a release in the range 400-450 °C in two close steps, which we assign to two competing processes proceeding at very similar temperatures. H is either released from the ternary hydride, or Zr segregates, leaving β -UH₃, which releases H₂ in the

next step. As $U_{1-x}Zr_x$, which would be left in the first case, decomposes at 500 °C into UZr_2 and α -U, the final products are the same in both cases.

The total amount of H_2 released corresponds to approximately 3 H atoms per 1 U atom (see Tab. 1). Therefore we adopted the formula $(UH_3)_{1-x}Zr_x$. 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.

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 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 which were in the form of powder pressed to make a pellet. Magnetization was measured on powder samples with grains fixed by a glue in a random orientation.

One of the hydride samples, $(UH_3)_{0.85}Zr_{0.15}$, consisted of elongated fragments 2-3 mm large, which allowed to attach electrical contacts by a silver paste and measure the temperature dependence of electrical resistivity, also using the PPMS system.

III Results

3.1 Crystal structure

XRD patterns of the $(UH_3)_{1-x}Zr_x$ hydrides are presented in Fig. 1. In contrast with the Mo doped hydrides studied previously,^{16,17} 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 expansion) with respect to the *bcc* precursors. The lattice parameters $a \approx 416$ pm are very close to the known α - UH_3 structure (Tab. 1). Small amount of ZrC impurity was also observed from diffraction patterns for all hydrides. A small amount of ZrH_2 is not excluded. 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. 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. The peak broadening indicates a grain size in the range 10-20 nm.

The XRD study was repeated after investigations of physical properties, i.e. after one month mostly at room temperature. The samples with low Zr concentration exhibited some changes. The α - UH_3 phase in pure-U hydride and $(UH_3)_{0.89}Zr_{0.11}$ has been partly transformed to UO_2 . No significant changes have been observed by XRD for samples with higher Zr concentrations.

3.2 Magnetization

As an example, we display (Fig. 2) the temperature dependence magnetization of $(\text{UH}_3)_{0.80}\text{Zr}_{0.20}$, which has undoubtedly the single phase of the α - UH_3 type. Measurements in various fields indicate ferromagnetism below $T \approx 175$ K, leading to spontaneous magnetization of $\approx 1.0 \mu_B/\text{U}$. A closer inspection of $M(T)$ dependence in the ordered state reveals that magnetization is not smoothly increasing with decreasing T , as usual in ferromagnets, instead a flat part is appears around 45 K, with possible slight decreases with further reducing T . One has to stress that all the T dependences were measured in the field-cooling mode. This effect can be perhaps attributed to a high anisotropy, progressively increasing with decreasing T , which forces some of the moments from the field direction towards easy magnetization directions. Alternatively one may consider that some antiferromagnetic components of exchange coupling (leading to non-collinear moments) develop at low temperatures, perhaps in relation with the variable U-U spacing introduced by the Zr doping.

The weak decrease of magnetization with decreasing T can be observed also on hysteresis loops, obtained for the same sample (Fig3a,b), using the field sweeping rate 0.0045 T/s in the range from -1 T to 1 T and 0.009 T/s outside this range. The prominent feature of the loops is that they do not reach the reversible behavior even in $\mu_0 H = 12$ T. At this stage we can only speculate about details of magnetization processes, which can be very complicated for nanostructured inhomogeneous ferromagnets. We can expect single domain grains of high and random anisotropy, but as deduced in Ref.18, they are exchange-coupled into larger interaction domains. The remagnetization happens in many grains in the same time, which can explain the magnetization jumps observable at the lowest temperatures (1.8 and 3 K). Their smearing at higher T reflects relatively easy thermally assisted excitation. Similar jumps also appear in the case of pinning of narrow domain walls. As shown e.g. for rare-earth compounds with transition metals, randomness on the transition-metal sublattice with relatively small magnetic moments yields a fundamental coercivity due to fluctuations of exchange interactions or anisotropy, which stabilize domain walls in given positions. The coercive field decrease follows the $-aT^{1/2}$ dependence deduced by Egami model of thermally activated movements of domain walls.¹⁹ Similar to the Egami model it deviates from this dependence and saturates at low temperatures. One should notice that the smooth demagnetization curve turns into large erratic steps, corresponding to re-magnetization avalanches. We use this word for stressing a kinetic effect, leading to a faster demagnetization even if T is lower when the avalanche is triggered comparing to somewhat higher temperatures with smooth thermally assisted motion.

Although the phenomenology is very similar e.g. to $\text{SmCo}_{1.4}\text{Ni}_{3.6}$,²⁰ in the U-Zr hydrides we consider the dilution of the U sublattice by Zr introducing "defects" in the exchange interaction and/or anisotropy. The most essential prerequisite of the model, the large anisotropy, is inherent to $5f$ itinerant systems. The strong magnetic anisotropy is traditionally associated with crystal-field phenomena of localized $4f$ states in lanthanides. In light actinides, where the $5f$ states are part of metal bonding, and the strong spin-orbit interaction induces large orbital moments, the anisotropy of different type is encountered, which is related to the directionality of the $5f$ - $5f$ bonding. This so-called two ion anisotropy, the

energy can be of the order of several hundred Kelvin, is particularly noticeable in low-symmetry structures,²¹ but can be expected even in cubic materials. The central idea is that when the involvement of the $5f$ into bonding is directional it leads to a population of the $5f$ states with orbital moments perpendicular to the strong bonding directions. Working of such anisotropy mechanism was deduced from the moments directions even for weak ferromagnets with d_{U-U} far below the Hill limit, as UNi_2 or U_2Fe_3Ge .²²

The magnetic hardness even increases with more Zr doping, reaching $\mu_0 H_c = 6$ T for $(UH_3)_{0.70}Zr_{0.30}$. The T dependence type remains the same. Using the relation $H_c(T)/H_c(0) = 1 - \eta T^{1/2}$ ¹⁹ we obtain the same value of $\eta = 0.082$ K^{-1/2} for both Zr concentrations. As seen from Fig. 4, the two-phase hydride with $(UH_3)_{0.89}Zr_{0.11}$ has the η -value smaller.

Naturally, the primary interest is the variation of T_C and μ_s with the Zr concentration. The values of Curie temperature was determined for each sample by several methods, using either the inflexion point of $M(T)$ in low magnetic fields or by the Arrott plots (M^2 vs. H/M dependences for temperatures bracketing the expected T_C value), or T dependence of the specific heat, $C_p(T)$. One can notice a certain increase of T_C for low Zr concentrations up to $T_C = 186$ K (see Tab. 1 and Fig. 5), which is reminiscent of the increase in Mo-doped UH_3 .¹⁶ Neither Zr nor Mo belong to traditional "magnetic" elements, but there are cases (as $(U,Y)B_4$), in which a small dilution can induce magnetic order.²³ In general, one can consider variations of the mean U-U spacing or changing the balance of conduction electrons, or combination of both responsible. Magnetic moments per 1 U atom deduced from $M(H)$ at low temperatures do not show any real tendency, being on the level of $0.9 \mu_B/U$ (see below).

The dilution of an active magnetic sublattice leads typically to a broadening of the transition, as seen in magnetization, and apparently it is the case even here. For low Zr concentrations it is the two-phase nature which can also produce a broadening. The result is the relatively large error bars displayed in Fig. 5. We can, however, conclude a very weak Zr concentration dependence of T_C , which is different than effects of the $5f$ dilution in regular band U-based ferromagnets, as $U(Th,Lu)RhAl$, in which the long-range order vanishes entirely for 15% Lu or 35% Th (the difference between the two is likely a volume effect related to much large Th atoms).²⁴ Thus besides the increase of T_C it is mainly the lack of suppression of the $5f$ magnetism with doping, which seem unusual and which suggest that the UH_3 -based hydrides are not just usual $5f$ band ferromagnets. Practically constant spontaneous moments and even similar variations of T_C resemble more the local-moment materials (please do not confuse with localized $5f$ states) as $(U,Th)CoSn$, in which the moments decrease dramatically only close to the dilution limit).²⁵

The slow saturation of $M(H)$ dependences makes also the derived values of spontaneous moments less accurate than usual. From the field dependence (up to 14 T) at $T = 1.8$ K, an estimate of the saturated moment can be done assuming a phenomenological relation $M(H) = M_s[1 - a/H^2] + \chi_{hf}H$, where the last term is accounting for the influence of field on the size of individual moments, while the first one accounts for the influence anisotropy. The values obtained given in Tab. 1 are similar to β - UH_3 (with approx. $0.9 \mu_B/U$) and somewhat smaller than those which can be reached in $(UH_3)_{1-x}Mo_x$ ($M_s = 1.15 \mu_B/U$ in

(UH_3)_{0.85}Mo_{0.15}). All those values are therefore quite similar and far below the ionic moments ($\approx 3.2 \mu_B$ for f^2 or f^3), which is in line with the strongly itinerant magnetism of the U hydrides. One should keep in mind that both spin and orbital components of total moments can differ from the free-ion prediction and they tend to orient antiparallel to each other in U compounds.

Magnetic susceptibility in the paramagnetic range (230-300 K) can be fitted by the Curie Weiss law, $\chi = C/(T - \Theta_p)$, giving the effective moment normalized per U atom $\mu_{\text{eff}} = (2.2 \pm 0.1) \mu_B/\text{U}$. The paramagnetic Curie temperature Θ_p reaches (187 ± 2) K for (UH_3)_{0.85}Zr_{0.15} and weakly decrease for higher Zr concentrations (see Tab.1). The parameters are practically independent of the Zr concentration within the experimental accuracy. The Θ_p -values are comparable with literature data for $\beta\text{-UH}_3$ or $\beta\text{-UD}_3$ (168-181 K), the μ_{eff} values are slightly lower than typical literature data ($2.2\text{-}2.4 \mu_B/\text{U}$). (For detailed summary of numerous studies one can consult Ref. 14).

3.3 Specific heat

The temperature dependence of specific heat, $C_p(T)$, has not been studied systematically for all samples over the whole temperature range, which would include both the low- T and high- T behavior. For Curie temperatures almost 200 K the magnetic part of specific heat is only a small fraction of the lattice part, which together with experimental uncertainties (e.g. due to the subtraction of specific heat of Apiezon mediating the thermal contact) and rather smeared (due to an inhomogeneity related to U dilution) anomaly at T_C (see Fig. 6) brings us to a situation, that very little can be concluded about magnetic specific heat itself. Comparing to the sharp anomaly for $\beta\text{-UH}_3$, we can deduce a spread of a part of magnetic entropy towards higher temperatures.

Fig. 6 gives an example of $C_p(T)$ for (UH_3)_{0.89}Zr_{0.11} and (UH_3)_{0.70}Zr_{0.30} compared with $\text{U}_{0.70}\text{Zr}_{0.30}$ and $\beta\text{-UH}_3$, the last showing a sharp cusp related to T_C . The alloy $\text{U}_{0.70}\text{Zr}_{0.30}$ exhibits a Debye-type saturation, Θ_D is estimated as 160-170 K from the $C_p/T = \gamma + \beta T^2$ plot at low temperatures, using the relation $\beta = 1944/\Theta_D^3$ for C_p in J/mol K divided by number of atoms in 1 mole.

Metal hydrides have typically the lattice specific heat affected by the Einstein vibration modes of the H atoms. As a result, a non-Debye character of $C_p(T)$ can be expected. However, an effective Debye temperature 280-310 K can be derived from the low- T slope of the plots for all hydrides (UH_3)_{1-x}Zr_x. These values are not far from $\Theta_D = 270$ K mentioned for $\beta\text{-UH}_3$ in Ref. 26.

The difference of the Debye temperatures between alloys and their hydrides may look surprising considering very similar behavior of $C_p(T)$ at low temperatures, from where the values are determined. The difference is a natural consequence of the normalization of the β -value per 1 atom - in H atoms are included in the balance, the slope per 1 atom decreases.

The similarity of the low- T part gives an alternative view of the lattice specific heat. The low lying phonon modes (acoustic) are similar for the alloys and hydrides. The vibrations related to H atoms are characterized as high energy optical modes, revealed only at higher

temperatures. Those were indeed observed by neutron scattering in the energy range 80-160 meV.²⁷ Only after the optical modes are populated one can reach the classical limit for specific heat $3R^*N$ (N is the number of atoms in formula unit), which should be in the range 75-100 J/mol K, depending on the actual concentration of H. For UH_3 , it is 98.4 J/mol K. The high energy of the optical modes is the reason why the experimental C_p values are below this limit still at $T = 250$ K.

The γ -coefficient of low-temperature specific heat, which reflects the density of states at the Fermi level, $N(E_F)$, weakly increases with increasing Zr concentration, if normalized per mole of U. This normalization makes sense as the $5f$ states should be the main contributor to $N(E_F)$. Our analysis shows that the γ -values change from 30.8 mJ/mol U K² for 11% Zr to 33.8 mJ/mol U K² for 30% Zr. On the other hand, considering that Zr and mainly its $4d$ states can contribute to the γ -value, we may get approximately constant contribution of U or even weakly decreasing, if we e.g. use the experimental value of γ for the Zr metal, 2.8 mJ/mol K². All values are very similar to those for pure $\beta\text{-UH}_3$ values presented in literature (29 mJ/mol K²,²⁸ or 33.9 mJ/mol K² ²⁹). This underlines an important (but not well understood) fact, that α - and $\beta\text{-UH}_3$ are almost identical not only as to magnetism, but also from the point of view of density of electronic states at the Fermi level in the ferromagnetic state.

3.4 Electrical resistivity

The temperature dependence of electrical resistivity, $\rho(T)$, of $\beta\text{-UD}_3$ was determined using a compact sample synthesized at high temperatures and very high pressures, which helped to avoid fragmentation.²⁶ $\rho(T)$, can be seen as highly anomalous for a system with metallic conductivity, as it reaches 600 $\mu\Omega\text{cm}$ in the paramagnetic state. Although such high absolute value can bring doubts about the geometrical factor (existence of cracks or voids), here we have to assume, considering the very low residual resistivity ρ_0 , that the values are indeed realistic. Both unrealistic geometrical factor and e.g. problems with metallicity (a low concentration of conduction electrons) would necessarily increase ρ_0 . As the T_C anomaly is very pronounced and $\rho(T)$ almost flat above T_C , we have to associate a large part of total resistivity (i.e. several hundred $\mu\Omega\text{cm}$) with spin-disorder scattering. It implies large U spin moments and a strong coupling of U spins, existing even in the paramagnetic state, to conduction electrons.

The $\rho(T)$ dependence of the $\gamma\text{-U}$ alloys with Zr (not shown here) is similar to other *bcc* U alloys with e.g. Mo.⁹ The atomic disorder leads to a large increase of ρ_0 up to $\approx 100 \mu\Omega\text{cm}$ and resulting non-additivity of electron-phonon scattering gives overall flattening of $\rho(T)$, and even a weak negative slope due to a weak localization. Ref. 16 shows that $(\text{UH}_3)_{0.85}\text{Mo}_{0.15}$ combines flat $\rho(T)$ with a weak negative slope with very high absolute values, about 1 m Ωcm (see inset of Fig. 7), with superimposed T_C anomaly in the form of a sharp but weak cusp, below which $\rho(T)$ resumes an increase with decreasing T . This suggests that a spin disorder contribution does not decrease below T_C , probably because the crystallographic disorder induces a strong magnetic disorder on the state characterized by bulk ferromagnetism.

(UH₃)_{0.85}Zr_{0.15} behaves differently. Fig.7 demonstrates that resistivity drops below T_C with ρ_0 corresponding to 50% of the high T values. Cycling of temperature increases the resistivity value, which may be the impact of thermal expansion and spontaneous magnetostriction, described in the next paragraph, which open cracks in the brittle material, changing the effective geometrical factor. The anomaly related to T_C appears only as a knee, which is less pronounced than that for β -UH₃,²⁶ and which is further broadened and shifted somewhat to higher temperatures in the applied field $\mu_0 H = 3$ T, applied when the sample was at $T = 300$ K. The 3 T data reveal a similar irreversibility due to additional cracks opening, its character remains similar to the zero field data, as seen when comparing with the 0 T heating data, normalized to the residual resistivity of the 3 T data (upper curve in Fig. 7). Both data sets exhibit the quadratic T -dependence of resistivity up to ≈ 140 K.

3.5 Spontaneous magnetostriction

The temperature dependence of the lattice parameter a was measured in the temperature range 10 - 300 K using X-ray diffraction. Results are presented in Fig. 8 together with data published for β -UH₃.²⁶ Our data set, which has much lower scatter, reveals the similar expanding tendency, starting below $T \approx 200$ K, and leading to a pronounced invar effect, i.e. compensation of decreasing the lattice volume with decreasing T by an expansion due to a magnetic contribution. The latter has to be associated with spontaneous magnetostriction, i.e. the volume expansion due to magnetic ordering. The size of magnetostriction can be estimated if we assume that a regular lattice thermal expansion, which is followed in the paramagnetic state, can be extrapolated down to $T = 0$ K. Using a Debye type of lattice expansion, used in Ref. 26 (the effective Debye temperatures for β -UH₃ and (UH₃)_{1-x}Zr_x are quite similar) we obtained the spontaneous volume magnetostriction $\omega_s = 3.2 \cdot 10^{-3}$. This value is even higher than that estimated for β -UH₃, $2.7 \cdot 10^{-3}$,²⁶ and represents a truly remarkable value among the $5f$ systems. It is interesting to compare the effect with the temperature dependence of magnetization. Fig.9 displays the magnetic contribution, separated using the tentative background from Fig. 8. Using the spontaneous magnetization M_s estimated as $M_{4T} - 2 \cdot M_{2T}$, we see that the volume effect follows well M_s^2 , as expected for itinerant magnets. On the other hand, it gives a support to the background used. The data allow to determine also the coefficient of thermal expansion of (UH₃)_{0.85}Zr_{0.15}, $\alpha_v = 21 \cdot 10^{-6} \text{ K}^{-1}$.

3.6 Electronic structure calculations

First theoretical analysis of electronic structure (using the APW method) was performed by Switendick,³⁰ who noticed the properties of α - and β -UH₃ may be very similar despite different U-U spacing. 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^{13,31} 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 a lower U-U spacing. Although the equilibrium lattice parameters are well reproduced in the calculations, there remains a large disagreement as to the equilibrium bulk modulus B_0 , which was calculated as 104 GPa for α -UH₃ and 144 GPa for β -UH₃, while the only experimental data³² indicate much softer lattice with $B_0 = 33 \pm 5$ GPa for β -UH₃. The

value of B_0 does not change considerably even if LDA+U type of calculations are used. 33 Experimental value of B_0 for α -UH₃ is unknown.

In the present work we decided to employ 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. In addition, Disordered Local Moment calculations were used to calculate 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.

First we used the full potential local orbitals code (FPLO) 34 applied on α -UH₃. This code solves Dirac equation in the framework of density functional theory, local spin density approximation, using the widely used Perdew and Wang exchange-correlation potential.35 At the experimental volume of α -UH₃, we found almost complete compensation of large spin $M_S = 2.7 \mu_B$ and orbital $M_L = -2.72 \mu_B$ magnetic moments. The density of states is displayed in Fig. 10. Magnetic moments of hydrogen were negligible. We assume 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 of our particular local spin density approximation (LSDA) calculations for 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. The calculated total energies versus volume were fitted by Murnaghan equation of state. The obtained bulk modulus $B_0 = 101$ GPa is similar to all calculations mentioned above, and exhibits therefore a similar discrepancy with the experimental report of Halevy et al. 32

Occupancies of individual states (Tab. 2) 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. Its occupancy increases from 1.0 to 1.74. This leads to the depletion of the U-7*s* states, while the U-6*d* states lose about 50% of their occupancy. The 5*f* states are affected very little, in fact their occupancy slightly increased in our calculations. The almost complete loss of U-7*s* electrons and partial depopulation of U-6*d* states can be taken responsible for high values of electrical resistivity. H-1*s* 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 6*d* states shifted up in energy reduces the 5*f*-6*d* hybridization and supports the formation of ordering of the 5*f* magnetic moments.

The Density of States (Fig.10) for the experimental volume corresponds qualitatively to those given in Ref. 31 for the magnetic state, with almost all occupied 5*f* states only in spin-up sub-band. A large gap between -1 and -3 eV separates the states in the Fermi level region from the density between -3 and -9 eV, which should contain the occupied H-1*s* states. The calculated Sommerfeld coefficient of the electronic specific heat $\gamma = 7.42$ mJ/mol K² is by the factor of 4 lower than the experimental value. The discrepancy may originate in the many-body effects not included in the LSDA method. The other reason may be in the fact

that the Fermi level is located in the deep narrow minimum of DOS in our calculations. Any Fermi level shift or DOS broadening may thus bring the γ -value close to the experimental value ≈ 30 mJ/mol K².

Studies of the volume dependence 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 this limit is reached, 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.

It would be interesting to find out whether the lower pressure sensitivity of spin moments comparing to orbital moments in U-based systems is a real phenomenon. As the spin magnetism originates naturally from band models, orbital magnetism has been perceived as a fingerprint of certain localization, and it should be therefore faster afflicted by pressure driven delocalization. Neutron form factor studies indeed indicate lower $|\mu_l/\mu_s|$ values for more delocalized actinide systems.³⁶ On the other hand, substantial orbital susceptibility has to be considered, due to the strong s-o interaction, aside the spin susceptibility even in wide-band U systems, such as U metal.³⁷ The situation is not clear yet, partly because there is not yet a consensus about which computational method (different varieties of LDA+U, LSDA with orbital polarization) is more appropriate for different situations. An instructive discussion of the situation for U alloys can be seen e.g. in Refs. 38,39.

On the quantitative level, we face an apparent disagreement between U moments of 1 μ_B and moments almost zero obtained from calculations. The fact that the total moment is obtained as a difference between antiparallel spin and orbital moments, being themselves much higher, makes the discrepancy merely quantitative, not qualitative. The picture can be modified e.g. if orbital polarization is included. In such case the orbital moments can be more pronounced.⁴⁰

Another issue, which could be addressed by computations, is whether the relative insensitivity of electronic properties to Zr alloying, which is unusual in band magnetism, can be understood by *ab-initio* techniques. For the theoretical study of the effect of Zr alloying on magnetism of *bcc* U-based systems we employed the tight-binding linear muffin-tin orbital (TB-LMTO) method in the atomic-sphere approximation (ASA) combined with the coherent-potential approximation (CPA) for an efficient treatment of substitutionally disordered alloys.^{41,42,43} We have studied the random binary $U_{1-x}Zr_x$ alloys with Zr concentrations $x < 0.5$ on a *bcc* lattice with the lattice parameter equal to that of *bcc* UH₃ ($a = 416$ pm). Using this crude model neglecting the role of hydrogen but allowing to focus on the substitution of U by Zr makes it computationally more tractable. In addition, we have studied not only the ferromagnetic state of the alloys, corresponding to their ground state, but also the so-called disordered-local-moment (DLM) state featured by randomly oriented U moments, which is relevant for the paramagnetic state.⁴⁴ This state has been simulated by a pseudoternary random alloy $(U^{+}_{0.5}U^{-}_{0.5})_{1-x}Zr_x$, where U^{+} and U^{-} denote

respectively U atoms with two different orientations of their magnetic moments. The obtained values of the magnetic moments of U atom in both states are plotted in Fig. 11.

One can see that the large negative orbital moment of U is very stable with respect to Zr alloying. The positive spin magnetic moment in the ferromagnetic state depends slightly on the Zr concentration, but the spin moment in the DLM state is very stable again. It should be noted that the Zr atom in the ferromagnetic alloys exhibits a positive spin moment, 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 $(\text{UH}_3)_{1-x}\text{Zr}_x$ system (Tab. 1). However, the theoretical investigation of finite-temperature magnetic properties goes beyond the scope of the present work.

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 $\mu_{\text{U}} = 1.0 \mu_{\text{B}}$ 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 studies⁴⁰) we cannot be conclusive as to the relevance of the calculated orbital moments in the DLM state.

For assessment of the magnetovolume effects in the $(\text{UH}_3)_{1-x}\text{Zr}_x$ system, especially of its large observed spontaneous magnetostriction, we have employed the same approach as in the case of systems containing transition and rare-earth metals.^{45–47} This approach rests on a treatment of the magnetically ordered state (ground state) and of the DLM state (paramagnetic state) and on the different equilibrium lattice parameters (alloy volumes) in these states, which give rise to the spontaneous volume magnetostriction. In the case of *bcc* UH_3 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 valence basis comprises *spdf*-orbitals of U atoms while only *sp*-orbitals have been attached to H atoms and vacancies. The ratio of the Wigner-Seitz radii of the H and U spheres has been taken as $s_{\text{H}}/s_{\text{U}} = 0.4$. The volume dependence of the total energies of both magnetic states is displayed in Fig. 12. One can clearly see that the DLM state is featured by a slightly reduced equilibrium lattice parameter comparing to the ferromagnetic state; the calculated equilibrium properties are summarized in Tab. 3. 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), while the bulk modulus comes out significantly higher than in experiment, in line with other calculations. 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 spin moment of U is reduced by about 10 % due to the magnetic disorder (see Tab. 3). The obtained semi-quantitative agreement between the theoretical and measured spontaneous magnetostriction corroborates the itinerant nature of magnetism of the UH_3 system; a more accurate theoretical description, including the effect of spin-orbit interaction and of Zr alloying, remains the task for future studies.

4 Discussion and concluding remarks

The new and well established data on $\alpha\text{-UH}_3$ complements interesting but fragmentary information on U hydrides in general. The relatively very high T_C values (in the context of actinide magnetism) of $\beta\text{-UH}_3$ has not been perceived as anomalous, because it was actually the first pure $5f$ -ferromagnet discovered. It was preceded only by $\text{UFe}_{2,48}$ in which similar $T_C = 160 \text{ K}$ is mainly due to the involvement of Fe- $3d$ states. The $\beta\text{-UH}_3$ type compounds, $\text{U}_6\text{FeH}_{17}$ and $\text{U}_6\text{CoH}_{18}$ 11,12 have been taken simply as analogs of $\beta\text{-UH}_3$. Our discovery of U hydrides with amorphous or $\alpha\text{-UH}_3$ structure, which all exhibit similar ordering temperatures and U moments around $1 \mu_B$ as well as the Sommerfeld coefficient $\approx 30 \text{ mJ/mol K}^2$ bring up the question about the reason for such uniformity in a material, assumed to be an itinerant $5f$ -ferromagnet, while the band $5f$ states in light actinides are normally very sensitive to all variables. Certain hints seem to be provided by the preliminary electronic structure calculations presented in this work. The shift of the electronic states of uranium to higher energies is applicable to U- $6d$ and $7s$ states only, and the $5f$ states remaining below the Fermi energy have less opportunity to hybridize with non- f states. In such situation, the Hill limit of 340 pm ,⁴ which was empirically determined assuming number of intermetallics with hybridized $5f$ states, has to be "renormalized" and the critical U-U spacing needed for magnetic ground state must be much smaller. More systematic work using various computational methods would bring more quantitative understanding.

The calculations performed so far (ours or in Ref. 31) exhibit a certain disagreement with the high-resolution UPS data,⁵⁰ which show the occupied part of the $5f$ band in UH_3 to almost 2 eV binding energy exceeding thus the calculated DOS not reaching more than 1 eV binding energy. More advanced calculations using LDA+U, LDA+Hubbard I or DMFT should determine whether the ground-state DOS is modified if the e-e correlations are treated more explicitly or whether it is actually the f^2 final-state multiplet appearing in the valence-band spectra, as suggested in Ref. 46, stressing possible similarities with NpH_3 and PuH_3 .

An important feature of the $5f$ magnetism in UH_3 is the sizeable orbital moment, revealed by the calculations, which is a necessary ingredient of high magnetic anisotropy. The fact that light actinides have large orbital moments (antiparallel to spin moments due to strong spin-orbit interaction) despite the band character of the $5f$ states was pointed out by Brooks and Kelly.⁵¹ Our LSDA calculations give only semi-quantitative prediction of the magnitude of spin and orbital moments, but existence of sizeable orbital moments cannot be doubted. The

related anisotropy is explaining the high coercivity and slow approach to saturation of magnetization in high fields. Orbital effects in $5f$ -band ferro- or antiferromagnets have been naturally more visible in bulk properties in case of low symmetry structures.⁵² Macroscopic studies of cubic materials do not reveal such striking anisotropy due to possible higher multiplicities of easy-magnetization direction, but it does not mean that the anisotropy energy must be lower. Determination of the U moments direction (easy magnetization direction) is one of the tasks for future experiments. Those experiments may benefit from the fact that while the alloyed UH_3 hydrides have very similar properties to their pure precursors, their stability (resistance to oxidation and mechanical decrepitation) is much better and even monolithic pieces can be used.

At present it is not clear what is the main reason for this stability. The decrepitation of U metal upon hydrogenation can be associated with very low solubility of H in α -U. The absence of solid solution of H in U, representing an intermediate step in hydrogenation, makes the volume increase to UH_3 so dramatic and abrupt, forming a sharp interface between U and UH_3 , proceeding fast inwards. The solubility of H in γ -U is much higher,⁵³ which makes the interface wider and perhaps better accommodating mechanical strains. We may assume that substituted bcc U alloys retain this feature.

The fact that high H pressures are needed for hydrogenation of alloyed bcc U can dwell both in thermodynamic (different enthalpy of formation) or kinetic (difference in H diffusion, passivation of surface by segregated dopants) reasons. A surface science study is planned to explain this effect, which makes U hydrides much more user friendly material.

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Fig.1.

X-ray diffraction pattern of the $(\text{UH}_3)_{1-x}\text{Zr}_x$ hydrides. The ticks indicate positions of diffraction lines expected for $\alpha\text{-UH}_3$ (red ticks - lower line) and $\beta\text{-UH}_3$ (blue ticks - upper line). In addition, weak lines of ZrH_2 can be distinguished.

Fig. 2.

Temperature dependence of magnetization of $(\text{UH}_3)_{0.80}\text{Zr}_{0.20}$ measured in various magnetic fields. Measurement for $\mu_0 H = 0.05$ T were performed in the field-cooled (FC) and zero-field-cooled mode (ZFC), the latter exhibiting very weak response except the temperature range in the vicinity of T_C .

Fig.3.

Hysteresis loops of $(\text{UH}_3)_{0.80}\text{Zr}_{0.20}$ measured at various temperatures. The panel a) covers higher temperatures, the panel b) compares the lowest temperatures, revealing how the smooth behavior of magnetization changes into erratic steps below $T = 6$ K.

Fig.4.

Values of the coercive field for the hydrides $(UH_3)_{1-x}Zr_x$ obtained from the hysteresis loops follow the scaling of the $1 - \eta T^{1/2}$ type in the high- T part.

Fig.5. Concentration dependence of the Curie temperature for the hydrides $(\text{UH}_3)_{1-x}\text{Zr}_x$. The full line is a guide to the eye.

Fig. 6. Temperature dependence of specific heat of selected hydrides $(\text{UH}_3)_{1-x}\text{Zr}_x$ compared with $\beta\text{-UH}_3$ 11 and $\text{U}_{0.70}\text{Zr}_{0.30}$.

Fig. 7.

Temperature dependence of electrical resistivity of $(\text{UH}_3)_{0.85}\text{Zr}_{0.15}$ measured when cooling down (red) and heating up (blue) in zero field (thick line) and in applied field $\mu_0 H = 3 \text{ T}$ (thin line). The upper line represents the 0 T data with heating, renormalized to match the residual resistivity of the 3 T data. For comparison, resistivity data on $(\text{UH}_3)_{0.85}\text{Mo}_{0.15}$ are displayed in the inset.

Fig. 8.

Temperature dependence of the lattice parameter of $(\text{UH}_3)_{0.85}\text{Zr}_{0.15}$ compared with $\beta\text{-UH}_3$, (from Ref. 26) with extrapolated dependence from the paramagnetic state. The data on $\beta\text{-UH}_3$ are rescaled to match approximately those on $(\text{UH}_3)_{0.85}\text{Zr}_{0.15}$, which allows to compare mutually the magnetostriction and thermal expansion.

Fig. 9. Temperature dependence of the lattice parameter a with the non-magnetic contribution subtracted (the background in Fig. 8 - empty circles). The red crosses correspond to M_s^2 , both normalized arbitrarily to fit into the figure.

Fig. 10.

Total (black) and spin-resolved (green and red) density of states for α - UH_3 calculated using fully relativistic FPLO method.

Fig. 11.

Calculated spin, orbital, and total magnetic moments of U atoms in a random bcc $U_{1-x}Zr_x$ alloy (with expanded volume) as functions of Zr concentration in the ferromagnetic (full diamonds) and the disordered-local-moment (DLM, open circles) states.

Fig. 12.

Calculated total energies (per formula unit) of hypothetical *bcc* UH_3 as functions of the Wigner-Seitz radius s_U of U atom in the ferromagnetic (FM, full squares) and disordered-local-moment (DLM, open circles) states. The experimental lattice parameter ($a = 416$ pm) corresponds to the value of $s_U = 3.47$ atomic units (1 atomic unit equals to the Bohr radius $a_B = 52.92$ pm). The curves are shifted vertically to have the minimum at the same energy,

taken as zero on the vertical axis. The total energy minimum of the DLM state comes out by 1.5 mRy/f.u. above that of the FM state.

Table 1

Room temperature lattice parameter a , H concentration, paramagnetic Curie temperature Θ_p , Curie temperature T_C , spontaneous magnetization M and Sommerfeld coefficient of electronic specific heat γ for hydrides of various $U_{1-x}Zr_x$ alloys.

compound	a (pm) precursor	a (pm) - hydride	H conc. (at./U)	Θ_p (K)	T_C (K)	M (μ_B/U)	γ (mJ/molU K ²)
$U_{0.89}Zr_{0.11}$ -H	354.2	416.1	-	177	174	1.03	30.8
$U_{0.85}Zr_{0.15}$ -H	353.8	414.3	2.8(2)	187	186	0.90	-
$U_{0.80}Zr_{0.20}$ -H	356.0	414.3	2.8(2)	181	167	1.02	33.2
$U_{0.70}Zr_{0.30}$ -H	354.3	414.2	2.7(3)	184	163	0.85	33.8

Table 2

Site projected occupancies of individual states for α -UH₃ (at experimental lattice parameter) and *bcc* U with the same lattice parameter. Occupancies of particular states in interstitial areas are not included.

State	α -UH ₃	<i>bcc</i> U
U-6 <i>d</i>	0.63	1.22
U-7 <i>s</i>	0.03	0.42
U-5 <i>f</i>	2.71	2.62
H-1 <i>s</i>	1.74	

Table 3

Values of equilibrium lattice parameter a , bulk modulus B , spin magnetic moment of U atom m_U and total spin moment per formula unit M in the ferromagnetic (FM) and the disordered-local-moment (DLM) states of hypothetical bcc UH_3 (see the text for details) as obtained from scalar-relativistic TB-LMTO-CPA calculations.

State	a (pm)	B (GPa)	m_U (μ_B)	M (μ_B)
FM	417.99	109	2.14	2.24
DLM	416.95	116	± 1.94	0