

Electronic structure of UH₃ thin films prepared by sputter depositionT. Gouder,^{1,*} R. Eloirdi,¹ F. Wastin,¹ E. Colineau,¹ J. Rebizant,¹ D. Kolberg,² and F. Huber¹¹European Commission, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-76125 Karlsruhe, Germany²Institut für Halbleiterphysik und Optik, Technical University of Braunschweig, Mendelssohnstrasse 3, D-38106 Braunschweig, Germany

(Received 7 August 2004; published 6 December 2004)

UH₃ thin films have been prepared by dc sputtering of uranium in presence of hydrogen, and studied *in situ* by valence band and core level spectroscopy. X-ray diffraction measurements showed formation of β -UH₃, and magnetization experiments demonstrate that the films are ferromagnetic with $T_C=178$ K. Valence band spectra showed that the films are metallic. The $5f$ states are positioned at the Fermi level, proving their itinerant character. Broadening of the $5f$ peak is attributed to correlation effects, or possibly the appearance of final-state multiplets. U $4f$ core level spectra showed a main peak at slightly higher binding energy (BE) than U metal, accompanied by a broad correlation satellite at 6 eV high BE.

DOI: 10.1103/PhysRevB.70.235108

PACS number(s): 71.20.Gj, 71.28.+d

I. INTRODUCTION

UH₃ was one of the first ferromagnetic uranium compounds observed.^{1,2} It exists in two allotropes, α - and β -UH₃. α -UH₃ is the metastable low-temperature phase. β -UH₃, the high-temperature phase, is a ferromagnet with a transition temperature around 173 K. Although the spacing of the uranium atoms ($d_{U-U}=0.331$ nm) in the β phase is considerably larger than that in U metal ($d_{U-U}=0.276$ nm), it is still below the Hill limit ($d_{U-U}=0.340$ nm) and the $5f$ electrons are expected to be itinerant. The magnetism was therefore surprising. It has been discussed either in terms of localized moments (incompatible with the itinerant nature of the $5f$ electrons) or itinerant magnetism. Whereas nuclear magnetic resonance (NMR) measurements seem to suggest localized $5f$ states for β -UH₃ and thus localized magnetism,³ the magnetoelastic properties and pressure dependence of the magnetic moment point to the itinerant nature of magnetism.⁴ Band structure calculations (nonrelativistic, non-self-consistent) came to the conclusion that there are both itinerant and localized f states.⁵ The localized f states, in a $5f^1$ configuration, would be responsible for magnetism, whereas the itinerant f states are strongly hybridized with the H $1s$ states.

Even though photoelectron spectroscopy is an ideal tool to differentiate localized and itinerant states, very few data exist. This is primarily due to the very high reactivity of UH₃, which is pyrophoric in powder form, and the absence of a protective overlayer preventing oxidation. Moreover, UH₃ is not stable and easily decomposes under vacuum: its dissociation pressure at 375 K is 0.27 Pa.⁶ So any surface cleaning by heating or ion bombardment can itself result in the decomposition of the sample. Also, breaking under vacuum or scraping⁷ may lead to dirty surfaces, because the breaking plane often contains impurities.

In this work, we avoided these problems by preparing the UH₃ films *in situ* at low temperature (room temperature and below), and performing the photoemission measurements without breaking the vacuum. The films were prepared by reactive sputter deposition of uranium in presence of a partial pressure of H₂. The same deposition technique has been used

previously to prepare uranium nitride films (UN_x,⁸ in the presence of Ar-N₂) and uranium oxide films (UO_x,⁹ in the presence of Ar-O₂). It was not clear, however, if the hydride could be prepared by this technique, or if due to its low stability it would decompose under vacuum or in the plasma. Below we will show that indeed stoichiometric UH₃ films have been prepared. The photoemission study of UH₃ showed that the $5f$ electrons form a narrow band of extended states at the Fermi level. This points against the localized nature of magnetism in UH₃.

II. EXPERIMENT

Thin films of UH₃ with less than 1% of C and 1% of oxygen were prepared *in situ* by dc sputtering of U in an Ar-H₂ atmosphere. We used ultrahigh-purity (99.9999%) Ar at a pressure of 0.67 Pa. The partial pressure of H₂ (99.999% purity) varied between 0 and 10⁻² Pa. The target was a U metal disk (99.9% purity, 5 mm radius, 1 mm thickness), put at a negative potential of -900 V. It was kept at room temperature by air cooling. The plasma in the diode source was maintained by injecting electrons of 50 to 100 eV kinetic energy. Shields were installed to expose only the sample to the Ar-H₂-U plasma and keep the contamination of the chamber as low as possible. The deposition rates were about 0.1 nm s⁻¹. Photoemission measurements were done on films of about 20 nm thickness, deposited at room temperature on a Si(111) wafer. The background pressure in the plasma chamber was 1.33 × 10⁻⁷ Pa.

Photoemission data were recorded *in situ* using a Leybold LHS-10 hemispherical analyzer. X-ray photoemission spectroscopy (XPS) spectra were taken using Mg $K\alpha$ (1253.6 eV) radiation with an approximate resolution of 0.9 eV. Ultraviolet photoemission spectroscopy (UPS) measurements were made using He I and He II (21.22 and 40.81 eV) excitation radiation, produced by a windowless uv rare gas discharge source. The total resolution in UPS was 0.1 to 0.05 eV for the high-resolution scans. The background pressure in the analysis chamber was 2.6 × 10⁻⁸ Pa. The x-ray diffraction (XRD) measurements were made with a conventional Philips PW3830 powder diffractometer using Cu $K\alpha_1$ radiation

($\lambda=0.1540560$ nm). For XRD and superconduction quantum interference device (SQUID) measurements, the films were deposited on a Si(111) and on a quartz substrate respectively, and had a thickness of about 180 nm. They were covered *in situ* with a protective Mg overlayer, to slow down the oxidation during contact with the laboratory atmosphere. The assignment of the diffraction peaks has been done using the PCPDFWIN database. The dc magnetization measurements were carried out on a Quantum Design SQUID magnetometer (MPMS-7) in the temperature range of $2\text{ K} \leq T \leq 310\text{ K}$, and in applied fields up to 70 kOe.

III. RESULTS

A. Formation of UH_3

It is not possible to determine the composition of the hydride directly by photoemission spectroscopy, because hydrogen has no characteristic core-level peak. Nevertheless, formation of UH_3 was proven indirectly. Spectroscopic data (see below) showed that presence of hydrogen changes the spectra, i.e., U metal features are modified. The overview spectra do not show any other element than U, in spite of the changes of the valence band and U $4f$ core-level lines. As hydrogen is the only element, which XPS does not see, we conclude that the new compound must be a hydride. The changes of spectra with hydrogen pressure soon saturate, and stay constant between 2.5×10^{-4} and 2.5×10^{-3} Pa hydrogen. At higher pressures, oxide impurities appear, presumably due to the interaction of hydrogen with the chamber walls, which release oxygen. Saturation points to the formation of a stable hydride with one well-defined stoichiometry. Thus, unlike for the U-N (Ref. 8) and U-O (Ref. 9) systems, where we did observe intermediate compounds for certain gas pressures, for the U-H system we obtain only one type of hydride spectrum with H_2 gas pressure. This hydride has been assigned to UH_3 , because this is the only stable uranium hydride, as shown by the phase diagram.⁵

Formation of UH_3 was further supported by XRD measurements. The thick hydride film (180 nm) was covered with a Mg overlayer to reduce oxidation during exposure to

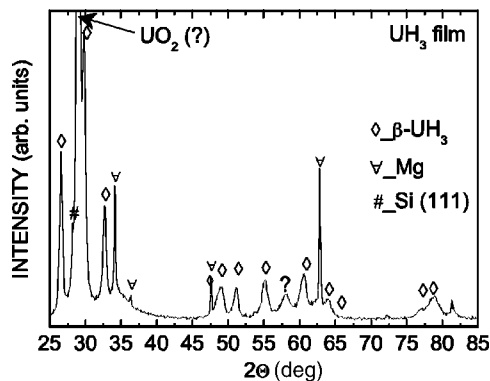


FIG. 1. XRD of a UH_3 film deposited on a Si(111) substrate at room temperature, and covered by a Mg overlayer. The diffraction peaks are assigned to the $\beta\text{-UH}_3$ phase (\diamond PDF: 74-0908), to the Si(111) ($\#$ PDF: 80-0018) and to the Mg phase (∇ PDF: 04-0770).

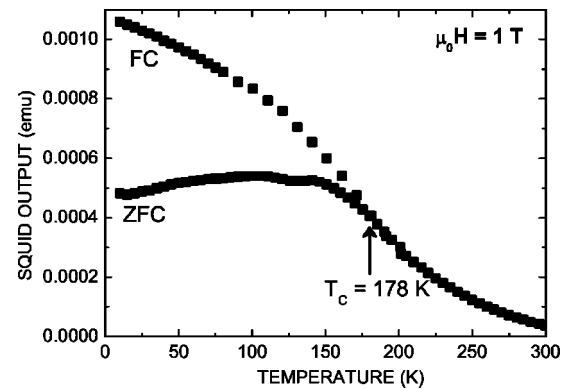


FIG. 2. Temperature dependence of the magnetic susceptibility M of a UH_3 film. The noticeable difference between zero-field-cooled (ZFC) and field-cooled (FC) data at low temperature indicates ferromagnetism. The T_C of 178 K is in agreement with the T_C obtained for UH_3 bulk.

the laboratory atmosphere. The XRD analyses (Fig. 1) showed formation of the $\beta\text{-UH}_3$ phase (cubic, $Pm\bar{3}n$). The diffraction peaks are well fitted by the reference peaks of the bulk β phase (PDF: 74-0908 file in PCPDFwin database). The lines of UH_3 films were shifted to low angle, indicating a cell parameter of about 0.670 nm, which is 1.1% larger than the cell parameter of bulk $\beta\text{-UH}_3$ (0.663 nm).

Formation of UH_3 was also confirmed by the magnetic susceptibility measured at magnetic field $\mu_0 H = 1\text{ T}$. Comparison of field-cooled (FC) and zero-field-cooled (ZFC) curves (Fig. 2) shows a typical ferromagnetic behavior. A transition temperature $T_C = 178\text{ K}$ was found. This is close to the transition temperature of bulk $\beta\text{-UH}_3$ ($T_C = 173\text{ K}$). The T_C was shown to depend on the H_2 pressure. T_C values of up to 220 K were observed at higher H_2 pressure. Recent work¹⁰ made on $\beta\text{-UH}_3$ showed the changes in the electronic structure as a function of H_2 pressure. For thin films, the relationship between magnetic properties, structure, and composition (H_2 pressure) will be further investigated in the near future.

B. UPS valence band spectra

Figure 3 compares the He II and He I valence band spectra of UH_3 and U metal. A large peak at the Fermi level dominates the U-metal spectrum. It corresponds to itinerant $5f$ states forming the conduction band. The peak is narrow and does not show any additional structure, pointing to the absence of correlation or many body effects.¹¹ UH_3 has two features, a broad band between 8 and 3 eV, and a narrower peak with a flat top between 1 eV and E_F . The broad band is composed of two peaks (4.4 and 6.1 eV). It is characteristic of hydride compounds¹² and attributed to the valence band formed by hybridization of the H $1s$ states with metal states. Compared to lanthanides hydrides¹³ this band is closer to E_F by about 1 eV.

The plateau at the Fermi level is attributed to $5f$ states. This is concluded from the comparison of He II and He I spectra. The characteristic energy dependence of their cross sections indeed allows identification of the various sublevels¹⁴ (s, p, d, f) (Table I). In particular the f states are

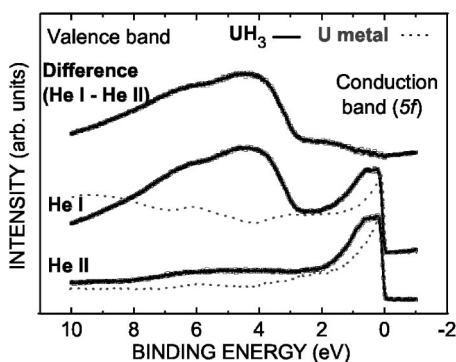


FIG. 3. He I and He II spectra of a U film (dotted line) and a UH_3 film (full line). Comparison of the He II and He I spectra of the UH_3 film enables assigning the peak at E_F to $5f$ states.

strongly suppressed in He I, while the d states are enhanced. The unchanged shape of the plateau for the two excitation energies suggests that it consists mainly of one type of state. Because the entire plateau is strongly suppressed in He I (compared to the H $1s$), we attributed it to U $5f$ states. Their positioning at the Fermi level proves the itinerant character of the f states.

Calculations of the density of states (DOS) made in the local density approximation of the density function theory also shows two energy bands for UH_3 (Fig. 4).¹⁵ The one at high binding energy (4–8 eV) indeed has H $1s$ character. It coincides with the measured spectrum. The U $5f$ states are concentrated at the Fermi level, thus confirming the metallic character of UH_3 . There is an overall good agreement between the DOS and the measured spectrum.

C. U $4f$ core-level spectra

Figure 5 compares the U $4f_{5/2}$ spectra of UH_3 with those of an itinerant f system (U metal) and a localized, oxidized f system (UO_2). Peak shapes and positions for the three systems are different. U metal has a narrow, asymmetrical $4f_{5/2}$ emission at 388 eV binding energy. The asymmetry is characteristic of a high density of states at E_F , which, in the actinides, is due to a narrow band formed by itinerant $5f$ states.¹⁶ UO_2 has a symmetrical peak at 391 eV ($4f_{5/2}$) accompanied by a shake-up satellite, fingerprint of stoichiometric UO_2 ,^{17,18} located at about 7 eV higher in binding energy than the main peak. The symmetry of the main peak points to a low density of states at E_F , which is consistent with the fact that UO_2 is a semiconductor. The shift to high binding energy of the U $4f$ in UO_2 is due to the increased

TABLE I. Theoretical cross sections (barns) in He I, He II, and Mg $K\alpha$ (Ref. 14).

	He I	He II	Mg $K\alpha$
H $1s$	1.888	0.2892	0.046×10^{-5}
U $5f$	0.6423	6.047	0.20×10^{-1}
U $6d$	4.01	0.6794	0.99×10^{-3}
O $2p$	10.67	6.816	0.50×10^{-3}

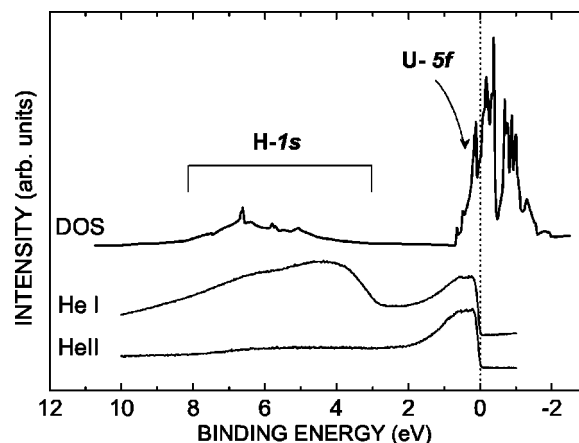


FIG. 4. Calculated DOS for $\beta\text{-UH}_3$ compared to experimental valence band spectra.

oxidation state of uranium (U^{4+}). The U $4f$ line of UH_3 is more similar to that of U metal than that of UO_2 . Compared to U metal its maximum is shifted to 0.4 eV higher binding energy (BE). This implies a similar oxidation state of uranium in the hydride and in the metal. The hydride peak is broadened compared to that of the metal. Such broadening is observed for all metal hydride systems. It is explained by the crystal lattice expansion of the host metal after the introduction of hydrogen.¹⁹ Also the peak is asymmetrical, pointing again to a high DOS at the Fermi level in UH_3 , in agreement with the valence band spectra (Fig. 3). The U $4f$ asymmetry for UH_3 is more pronounced than that for U metal, and this is totally consistent with the larger electronic specific heat (Table II) of UH_3 compared to U metal.²⁰ In addition there is a broad, unresolved satellite around 395 eV binding energy. A very similar satellite has been observed in narrow-band uranium compounds, e.g., UPt_5 , UBe_{13} ,²¹ or URu_2Si_2 .²² It is generally attributed to the occurrence of final-state effects (poor screening), when the $5f$ states approach localization.

D. Previous XPS studies of bulk UH_3

A previous XPS valence band study on UH_3 bulk by Ward *et al.*⁷ shows the U $5f$ peak at about 1.5 eV binding energy

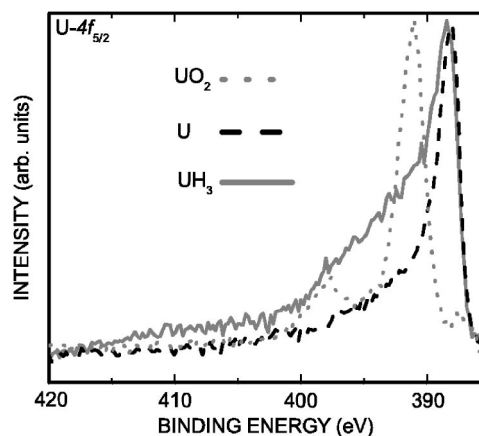


FIG. 5. U $4f_{5/2}$ core-level spectra of U, UH_3 , and UO_2 films.

TABLE II. Electronic specific heat constant (γ) and paramagnetic moment per U ion (μ_p) of the U pnictide series of β -UH₃ and of α -U.

	γ^a (mJ/mol K ²)	μ_p^b (μ_B)
UN	26	2.7–3.1
UP	32	3.1
UAs	53	3.5
USb	4	3.7
β -UH ₃	30	2.6
α -U	9	

^aReference 28.

^bReference 29.

(Fig. 6). Also a peak is observed at 6 eV, and it is attributed to the H 1s valence band. To compare this result with our study we did a similar XPS valence band measurement of a UH₃ film (Fig. 6), and we find the U 5f peak with a maximum at 0.6 eV, i.e., close to the Fermi level. It is unlikely to observe the H 1s peak in XPS, because of the extremely low H 1s cross section (Table I). We argue that the valence band spectrum of Ref. 7 is rather due to UO₂, with the O 2p emission at 6 eV and the localized 5f peak at 1–1.5 eV. The presence of appreciable amounts of UO₂ may be related to the high reactivity of the hydride. Even fracturing under vacuum, as done in Ref. 7, can result in dirty surfaces because cleavage preferentially occurs in plains containing large amounts of impurities. The corresponding U 4f spectrum has never been published, it was only stated that the U 4f_{5/2} peak is located at 389.8 eV. It is most likely due to the superposition of the broad hydride peak (4f_{5/2} at 388.2 eV) and an oxide peak (4f_{5/2} at 390.5 eV).

IV. DISCUSSION

The magnetism of UH₃ is not consistent with a broad *f* band, but instead points either to highly correlated *f* states in a narrow band, or localized *f* states. The striking difference

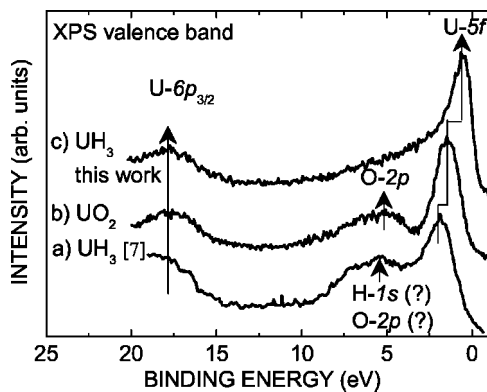


FIG. 6. Comparison of XPS valence band spectra: (a) previously measured UH₃ (Ref. 7), (b) a UO₂ film prepared by reactive sputter deposition of U metal in an Ar-O₂ gas mixture, and (c) a UH₃ film prepared by reactive sputter deposition of U metal in an Ar-H₂ gas mixture.

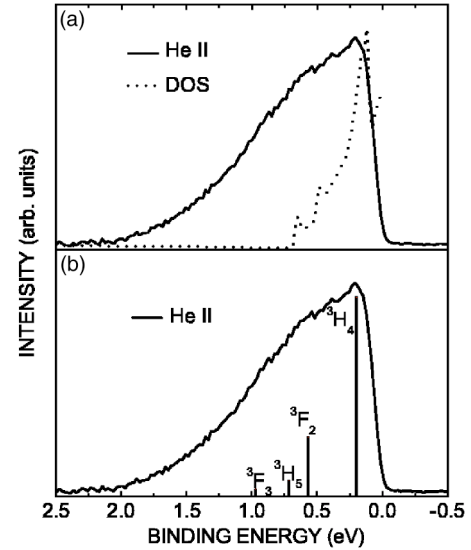


FIG. 7. (a) Comparison of the He II detail spectrum, after subtraction of the inelastic background, and the 5f ground-state DOS by the local density approximation. (b) Comparison of the He II detail spectrum, after subtraction of the inelastic background, and the $f^3 \rightarrow f^2$ multiplet transition calculated in the intermediate coupling scheme.

between the 5f signal of UH₃ and U metal (Fig. 3) must certainly be related to the appearance of magnetism in UH₃, which is a good indicator of the 5f band narrowing (comparing to U metal) due to the lattice expansion and reduced 5f-5f overlap. Therefore one central question is whether photoemission shows itinerant or localized *f* states. Below different interpretations of the 5f spectrum [(a)–(c)], in terms of localized and itinerant 5f states will be given.

(a) First one may consider if the 5f photoemission peak does not simply reflect the ground-state density of states, as for broad-band materials. Figure 7(a) compares the calculated DOS of 5f band with the He II photoemission line. The inelastic background of the photoemission line has been subtracted. The measured 5f band is significantly broader than the calculated one. This broadening cannot be ascribed to instrumental factors, because the resolution in UPS is better than 40 meV. Also lifetime broadening can be ruled out, because, if photoemission does reflect the ground-state DOS in the vicinity of E_F , then the final state is the stable ground state and there are no decay effects. The strong broadening of the photoemission spectrum is thus not compatible with a direct comparison to the ground-state DOS, but correlation effects have to be considered.

(b) Narrow-band uranium systems indeed show a broadened *f* emission at the Fermi level, having an itinerant component (directly at E_F , as in U metal) and a correlation satellite at higher binding energy, typically 0.5–1 eV.²³ In these systems, the ground state has weakly itinerant 5f electrons, often via hybridization with the conduction band, e.g., in the heavy-fermion or Kondo systems.²⁴ Photoemission of a 5f electron, leaving a 5f photohole, then leads to two different final states. In the first the 5f photohole is directly filled by a screening electron coming from the conduction band and restoring the ground state. This is the itinerant component, di-

rectly at E_F , as in U metal. In the second final state, the $5f$ photohole is screened by the filling of an empty $6d$ state.²³ Energetically this situation is less favorable, and the corresponding photoemission line lies at higher binding energy (poorly screened component). With approaching localization of the f state, when hybridization with extended states decreases, the probability of the d screened final state increases. Thus growth of the correlation satellite is directly related to the approaching localization of the f states. The broadening of the $5f$ peak in UH₃ would thus reflect narrowing of the $5f$ band to a point where correlation effects become important and photoemission no longer reflects the ground-state density of states. The $5f$ correlation satellite also appears in other U narrow-band systems, e.g., URu₂Si₂ or UPd₂Si₂.²² These systems also have the 6 eV satellite in the U $4f$ spectra (Fig. 5), and again main peak and satellite are attributed to two differently screened final states.²⁵

(c) We present an alternative interpretation, where the broad $5f$ peak corresponds to the unresolved multiplet of one localized final state [instead of two final states in paragraph (b)]. Indeed the $5f$ line can be fitted by an $f^3 \rightarrow f^2$ multiplet transition [Fig. 7(b)]. After removal of the inelastic background, the broad $5f$ peak compares well to the multiplet transition, calculated in the intermediate coupling scheme,²⁶ where the lowest term (3H_4) lies close to E_F . However, such multiplet requires $5f$ localization and, at first sight, this seems incompatible with the large γ constant of the electronic specific heat (Table II), indicating a narrow (f) band at the Fermi level. The problem can be solved by assuming that in the ground state the f states are itinerant (large γ), and it is photoemission itself, which induces $5f$ localization in the final state. The suddenly increased core potential, after creation of the photohole, pulls down the f states, which feel the potential stronger than the more extended d or s states. This results in the decoupling of the f states from the conduction band, and their localization. A similar model was proposed for the uranium pnictides,²⁷ which incidentally are also magnetic. Within the pnictide series (UN, UP, UAs, USb), the transition from $5f$ itinerancy to localization occurs gradually. The sudden drop of the electronic specific heat as indicated in Table II between UAs and USb may be related to the $5f$ localization in USb ground state. However, the multiplet structure appears already in UAs,²⁷ i.e. for a system, which is

still itinerant in the ground state. In USb the multiplet shifts away from the Fermi-level, which may indicate a total or at least a partial localization of $5f$ electrons as suggested by Kumigashira *et al.*³⁰ Multiplets, whose lowest term is very close or even at the Fermi level, are typical for narrow-band or intermediate valence systems, whereas in truly localized systems they shift to higher binding energy.

The picture of a weakly itinerant system, which, after the photoemission process, becomes localized is consistent with the reduced magnetic moment of UH₃, which is not compatible with a localized ground-state configuration ($5f^3$) like USb. Also the magnetoelastic properties rather point to an itinerant magnetic behavior.⁴ Localization in the final state, as a consequence of the photoemission process, was also suggested in the interpretation of the valence band spectra of Ce (Refs. 31 and 32) and PuSi_x (Ref. 33), where again final-state multiplets are developed in systems, which in the ground state have itinerant states.

V. SUMMARY AND CONCLUSIONS

UH₃ films were produced by reactive sputter deposition of uranium in presence of hydrogen. The films are stable under UHV conditions and virtually oxygen-free. X-ray diffraction shows formation of β -UH₃ for films deposited at room temperature and saturation hydrogen pressure. Magnetization measurements indicate ferromagnetic behavior, just like in the bulk systems, but the critical temperature depends on the hydrogen pressure and is larger than in bulk UH₃. Core-level and valence band spectroscopy indicate itinerant character of the $5f$ states. The U $4f$ lines are only slightly (0.4 eV) shifted compared to U metal, showing the U atoms to have a similar oxidation state. The valence band spectra show a $5f$ signal at the Fermi level, which is again consistent with the itinerant nature of the $5f$ states. The supplementary broadening of the f signal compared to U metal may be interpreted either in terms of a $f^3 \rightarrow f^2$ multiplet transition, or the presence of a final-state correlation satellite.

ACKNOWLEDGMENTS

We thank M.S.S. Brooks and P. Boulet for fruitful discussions. R.E. acknowledges the European Commission for support in the frame of the program "Training and Mobility of Researchers."

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¹W. Trzebiatowski, A. Sliwa, and B. Stalinski, *Rocz. Chem.* **28**, 12 (1954).

²R. Troc and W. Suski, *J. Alloys Compd.* **219**, 1 (1995).

³J. Grunzweig-Genossar, M. Kuznietz, and B. Meerovici, *Phys. Rev. B* **1**, 1958 (1970).

⁴A. Andreev, S. Zadorkin, M. Bartashevich, T. Goto, J. Kamarad, Z. Arnold, and H. Drulis, *J. Alloys Compd.* **267**, 32 (1998).

⁵A. Switendick, *J. Less-Common Met.* **88**, 257 (1982).

⁶R. Meyer, E. Pietsch, and A. Kotowski, *U. Erg.-Bd. C1*, Gmelin Handbuch der Anorganischen Chemie (Springer-Verlag, Berlin, 1977).

⁷J. Ward, L. Cox, J. Smith, G. Stewart, and J. Wood, *J. Phys. (Paris), Colloq.* **40**, 4 (1979).

⁸L. Black, F. Miserque, T. Gouder, L. Havela, J. Rebizant, and F. Wastin, *J. Alloys Compd.* **315**, 36 (2001).

⁹S. V. den Berghe, F. Miserque, T. Gouder, B. Gaudreau, and M. Verwerf, *J. Nucl. Mater.* **294**, 168 (2001).

¹⁰I. Halevy, S. Salhov, S. Zalkind, M. Brill, and I. Yaar, *J. Alloys Compd.* **370**, 59 (2004).

¹¹S. Molodtsov, J. Boysen, M. Richter, P. Segovia, C. Laubschat, S. Gorovikov, A. Ionov, G. Prudnikova, and V. Damchuk, *Phys. Rev. B* **57**, 13 241 (1998).

¹²H. Smithson, C. Marianetti, D. Morgan, A. V. der Ven, A. Predith,

- and G. Ceder, Phys. Rev. B **66**, 144107 (2002).
- ¹³J. Weaver, D. Peterman, and D. Peterson, *Electronic Structure of Metal Hydrides: A Review of Experimental and Theoretical Progress* (Plenum, New York, 1983).
- ¹⁴J. Yeh and I. Lindau, At. Data Nucl. Data Tables **32**, 1 (1985).
- ¹⁵M. Brooks (private communication).
- ¹⁶J. Naegele, J. Ghijsen, and L. Manes, *Actinides—Chemistry and Physical Properties*, Vol. 59/60 of *Structure and Bonding* (Springer, Berlin, 1985).
- ¹⁷G. Allen, P. Tucker, and J. Tyler, J. Phys. Chem. **86**, 224 (1982).
- ¹⁸M. Hedhili, B. Yakshinskiy, and T. Madey, Surf. Sci. **45**, 512 (2000).
- ¹⁹H. Peisl, *Hydrogen in Metals I*, Vol. 28 of *Topics in Applied Physics* (Springer-Verlag, Berlin, 1978).
- ²⁰J. Lashley *et al.*, Phys. Rev. B **63**, 224510 (2001).
- ²¹C. Laubschadt, W. Grentz, and G. Kaindl, Phys. Rev. B **37**, 8082 (1988).
- ²²A. Grassmann, Physica B **163**, 547 (1990).
- ²³A. Arko *et al.*, J. Less-Common Met. **133**, 87 (1987).
- ²⁴D. Malterre, M. Griioni, and Y. Baer, Adv. Phys. **45**, 299 (1996).
- ²⁵J. Allen, Physica B **171**, 175 (1991).
- ²⁶F. Gerken and J. Schmidt-May, J. Phys. F: Met. Phys. **13**, 1571 (1983).
- ²⁷B. Reihl, J. Less-Common Met. **128**, 331 (1987).
- ²⁸H. Rudigier, H. Ott, and O. Vogt, Phys. Rev. B **32**, 4584 (1985).
- ²⁹P. Erdös and J. Robinson, *The Physics of Actinide Compounds* (Plenum, New York, 1983).
- ³⁰H. Kumigashira, T. Ito, A. Ashihara, H.-D. Kim, H. Aoki, T. Suzuki, H. Yamagami, T. Takahashi, and A. Ochiai, Phys. Rev. B **61**, 15 707 (2000).
- ³¹S. Hüffner and L. Schlappbach, Z. Phys. B: Condens. Matter **64**, 417 (1986).
- ³²S. Hüffner, *Photoelectron Spectroscopy, Principles and Applications* (Springer-Verlag, Berlin, 2003).
- ³³T. Gouder, F. Huber, F. Wastin, and J. Rebizant (unpublished).