

Characterization of U-based thin films: the UFe_{2+x} case

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Abstract. We have characterized UFe_{2+x} films prepared by sputter deposition onto fused silica (SiO₂) and Si(111) substrates with the film thickness ranging from 75 nm to 900 nm. The X-ray diffraction results showed an amorphous character of the deposited material. Some of the films showed in addition a pattern of highly textured cubic Laves phase. Rutherford Backscattering Spectroscopy with 2 MeV He⁺ ions has been used to determine the composition, thickness and concentration depth profile of the films. A large ageing affect was observed within 1 month after that the films were exposed to air. Magnetic measurements revealed T_C increasing with relative Fe concentration and reaching approx. 450 K in UFe_{3,0}.

1. Introduction

Actinide elements with incomplete f -shell exhibit many interesting properties when alloyed with the transition metals or other elements, as e.g. strongly-correlated-electron behavior combined with superconductivity and magnetism. Increasing interest has been recently paid to actinide thin film systems with a great potential of tuning electronic and magnetic properties in comparison with the corresponding bulk materials.

UFe₂ is one of examples of combination of $3d$ and $5f$ magnetism in a compound with a relatively high Curie temperature ($T_C = 162$ K) and very small total U magnetic moments ($\mu_U = 0.01 \mu_B/\text{f.u.}$), as a consequence of the cancellation of spin and orbital moment. Iron magnetic moment is also reduced ($\mu_{Fe} = 0.60 \mu_B/\text{f.u.}$) due to a strong $5f$ - $3d$ hybridization) [1]. An Fe-excess (i.e. off-stoichiometric UFe_{2+x} compounds with $x > 0$) is expected to increase the T_C value markedly. However, it is difficult to prepare the Laves phase with Fe excess. The quenching technique did not work. An attempt was made using a ball milling [2], which led to enhancement of T_C to 207 K in an amorphous UFe_{2+x} sample. We tried then the ultrafast cooling method (splat cooling) to incorporate more Fe into the Laves phase [3,4]. A nanocrystalline material was obtained up to the stoichiometry UFe_{2,3}, with the

excessive Fe atoms entering the U sublattice. T_C was enhanced up to 230-240 K in this case. More Fe leads to the segregation of α -Fe. Recently, we continued the effort to embed more U into the UFe_{2+x} phase by sputter deposition of thin films (despite of amorphisation): the UFe_{2+x} thin film deposited on Si (111) substrate with $x \approx 2.0$ and with the film thickness of about 450 nm (sample I) reveals a ferromagnetic behavior with the T_C value of 240 K [5].

In the present work we concentrate to characterize various UFe_{2+x} films sputter deposited onto SiO_2 substrates. The thickness and composition of the layers especially the concentration depth of the films was determined by using Rutherford Backscattering Spectroscopy (RBS). We focus on analyzing the correlation between the film composition and the corresponding magnetic properties. In particular we have underlined the ageing effect in these films.

2. Thin-film synthesis and experimental techniques

UFe_{2+x} films were obtained by DC sputter deposition in a UHV chamber (base pressure better than 10^{-10} mbar) from U and Fe targets onto fused silica (SiO_2) and Si(111) substrates kept at the room temperature. The co-sputtering from the two U- and Fe targets allows the stoichiometry control. Sputtering time was in the range from 10 minutes to 3.5 hours. The stoichiometry of the films, before exposing the films to air, was estimated from in-situ X-ray photoelectron spectroscopy (XPS) and then confirmed by electron microprobe analysis (Table 1).

The X-ray diffraction (XRD) in the glancing angle geometry with an variable angle of incidence in the range of 3-15 degrees and in the Bragg-Brentano (B-B) geometry were used to characterize the film structure.

The RBS experiments were performed at the Institute of Nuclear Physics of the University Frankfurt/Main using 2 MeV He^+ ion beam with a 171° backscattering angle. Details of our RBS experiment conditions were reported elsewhere [6,7]. For the data evaluation the computer code SIMNRA [8] was used. It is more convenient to have the estimated layer thickness in nm and thus the simulated RBS areal density values ($at./cm^2$) were converted into the layer thickness value (nm) by using the bulk density of the stoichiometric UFe_2 (13.0 g/cm^3). However, the real layer thickness of different layers would be somewhat different, since the films do not have the same stoichiometry. Besides, as it turned out, the film composition is far from 1:2 ratio. The RBS measurements were performed about 1 week after the films were exposed to the atmosphere. In order to check the stability of the films, RBS has been performed again on selected films after 1, 6, 9, 12, and 18 months.

Magnetic properties were studied in the temperature range 2-500 K by means of a Vibrating Sample Magnetometer (VSM) in the Quantum Design PPMS System. For the high-temperature measurement ($T > 300 \text{ K}$), the samples were fixed by the Zircar cement and tightly wrapped by the copper foil. The temperature dependence of magnetization was measured in the magnetic field of 0.1

Table 1. The composition ($2+x$) and thickness of the main U-Fe layer of the UFe_{2+x} amorphous films estimated from combined analysis of XPS, electron microprobe and RBS data.

Sample number	$x \approx$	$d \approx$ (nm)	Sample notation
I	2.0	450	$UFe_{4.0}/Si(111)$
II	2.0	310	$UFe_{4.0}/SiO_2$
III	6.0 (+ α -Fe)	370	$UFe_{6.0}/Si(111)$
IV	0.3	520	$UFe_{2.3}/SiO_2$
V	0.7	75	$UFe_{2.7}/SiO_2$
VI	0.7	900	$UFe_{2.7}/SiO_2$
VII	1.0	120	$UFe_{3.0}/SiO_2$

Tesla. Exposure of the samples to higher temperature $T > 500$ K led to a degradation of the films by the oxidation, which is revealed by an abrupt, irreversible increase of magnetization, this is why we suspect the segregation of α -Fe.

We notice here that it is very difficult to compare the in-situ XPS and other ex-situ data. Besides, the RBS data for instance can give the information about the element content in different sub-layers (depth profile), which is certainly different from other techniques estimated the average value for the entire film. For the sake of comparison, we concentrate on the main U-Fe layer. The composition of the films revealed in the film notation was determined as an average value of the Fe-content in the entire films from different methods (Table 1). Our results showed that x -value of the U-Fe layer varied between 0.3 and 2.0 (with the exception of the sample III indicating clearly the existence of the α -Fe phase) and the film-thickness is in the range from 75 nm to 900 nm. During the discussions of magnetic data when we regard only the U- and Fe content, we would skip the notation for the SiO_2 substrate, e.g. instead of $\text{UFe}_{3.0}/\text{SiO}_2$ film we label it as $\text{UFe}_{3.0}$ sample.

3. Results and discussion

3.1. Structure study

Figure 1 shows the XRD patterns obtained in the conventional B-B geometry for the UFe_{2+x} samples with $x = 0.3$ and 0.7 (i.e. $\text{UFe}_{2.3}/\text{SiO}_2$ (sample IV) and $\text{UFe}_{2.7}/\text{SiO}_2$ film (sample VI)), exhibiting a broad bubble between 35 - 40 deg., which is a fingerprint of an amorphous phase. The comparison with data obtained in the glancing angle geometry reveals that it is not only the amorphous substrate (in case of fused silica) giving rise to this feature, but that the deposited film must be largely amorphous. In some of the films we observed besides the amorphous feature also several sharp peaks, which can be attributed to the cubic Laves phases structure with the lattice parameter of $a = 7.15$ Å. The dominance of the (111) peak can be understood as strong texturing with the [111] direction perpendicular to the substrate. The same peaks are also revealed in the glancing-angle XRD patterns for $\text{UFe}_{2.7}/\text{SiO}_2$ film shown in figure 2. The diffraction lines of UO_2 were also detected. They partially overlap with the lines coming from the Laves phases. For all other remaining samples, XRD patterns in both geometries show no sharp diffraction peaks, indicating that the samples are purely amorphous. As an example, we showed in figure 2 the glancing-angle XRD patterns for amorphous $\text{UFe}_{3.0}/\text{SiO}_2$ film (sample VII).

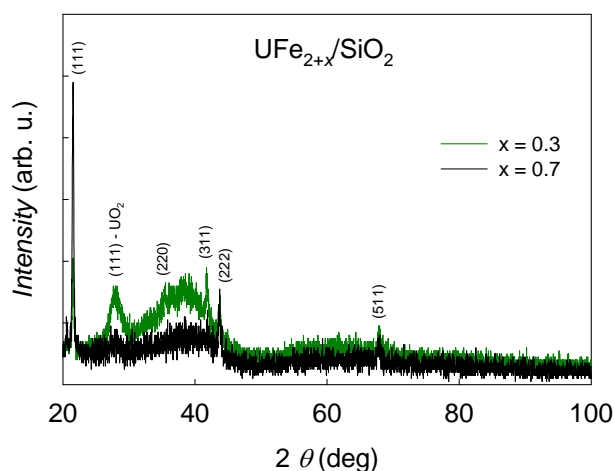


Figure 1. XRD patterns for $\text{UFe}_{2+x}/\text{SiO}_2$ films ($x = 0.3$ (sample IV), 0.7 (sample VI)) obtained in conventional Bragg-Brentano geometry using $\text{Cu-K}\alpha$ radiation. The data were collected with 2θ -step size of 0.02° in a 2θ -range of 20° - 100° .

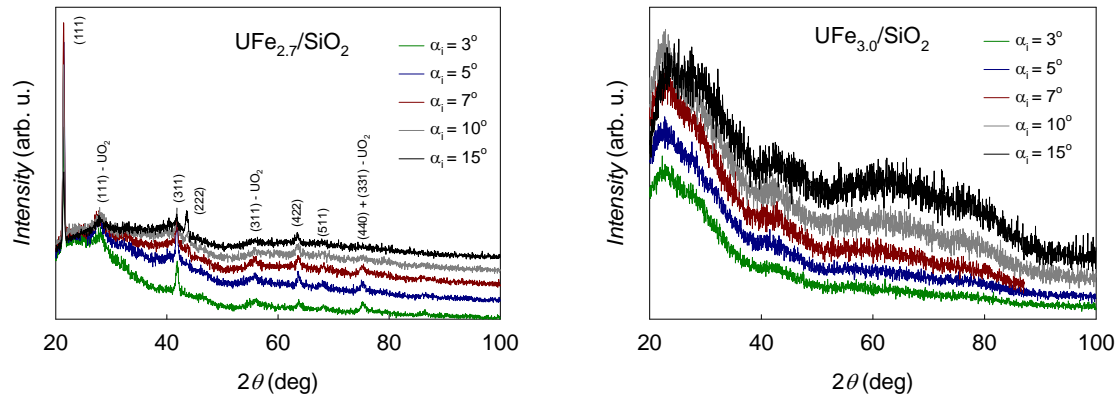


Figure 2. XRD patterns for $\text{UFe}_{2.7}/\text{SiO}_2$ (sample VI, left panel) and $\text{UFe}_{3.0}/\text{SiO}_2$ film (sample VII, right panel) obtained in the glancing angle XRD using $\text{Cu-K}\alpha$ radiation with a variable angle of incidence increasing from 3° (bottom) to 15° (top).

3.2. RBS measurements

In figure 3, random RBS spectra of various films revealing some characteristic features are shown: the RBS spectrum with a sharp U- and Fe peaks completely separated from each other ($\text{UFe}_{3.0}/\text{SiO}_2$ film; sample VII), the spectrum with large but separated U- and Fe signals ($\text{UFe}_{4.0}/\text{SiO}_2$ film; sample II) (figure 3, left panel) and the spectrum with a partial overlap of the U- and Fe signals implying some fine structure of the combined large film-signal ($\text{UFe}_{4.0}/\text{Si}$ film; sample I, figure 3, right panel). The simulated spectra by SIMNRA are shown as solid lines in the same figures. The estimated layer thickness and composition are given in table 1. We notice here that one main difference between films deposited on Si(111) and SiO_2 substrate was that we observed only the backscattered signal from Si (Si-edge; Si(sub.) in the RBS spectra for films deposited on the Si(111) substrate, while both Si- and O-edge were observed for films deposited on SiO_2 ones (Si(sub.), O(sub.)). For the thin films with the thickness $d < 120$ nm, i.e. samples V and VII, a well-separated and sharp U- and Fe peak from the UFe_{2+x} film (U(film), Fe(film)) is always observed. The increase-slope of the peak at the right-hand side locates at 1850 keV and 1500 keV, i.e. the energy value related to the binary collision of the He ions with U- and Fe atoms in the front surface of the films, respectively. From the relative peak-intensity ratio, it was clear that the uranium-iron ratio is larger than 1:2. The Si- and O-edge from the SiO_2 substrate were revealed in the RBS spectra around respectively 1130 keV and 725 keV. Increasing the film thickness leads to a large increase of the peak widths. If the film is still not so thick, for instance for sample II with $d \approx 310$ nm (figure 3), the U- and Fe signal is still well separated and thus there exists a visible minimum between them. However, in this case, the O- and Si-edge moved down to a much lower energy. Increasing further the film thickness implied an overlap of the U- and Fe signal. For the film with the thickness $250 \text{ nm} < d < 500$ nm, a partial overlap of the U- and Fe signals leads to a formation of a wide peak but with some features(step-rises) observed in the RBS spectrum (sample I and III). In figure 3, the step-rise at 1850 keV and the step-decrease around 1300 keV revealed the signals of the He ions backscattered from the U atoms from the front and rear surface of the films respectively (U(film-front), U(film-rear)), whereas those at 1550 keV and 980 keV was related to the backscattered signals from Fe in the films respectively ((Fe(film-front), Fe(film-rear)). A total overlapping of U- and Fe signal resulted in a single but huge and very wide peak was observed for thicker films (sample IV with $d \approx 520$ nm and sample VI with $d \approx 900$ nm).

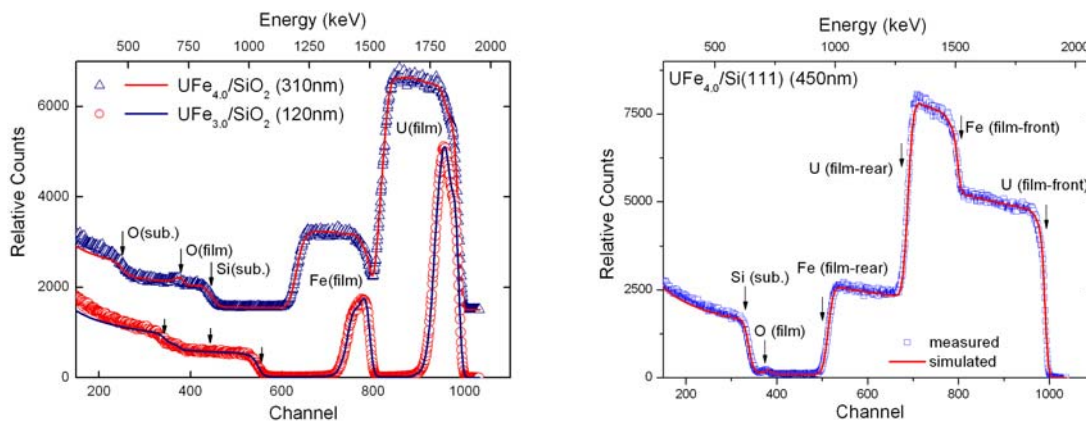


Figure 3. Random (markers) and simulated (lines) RBS spectra for selected UFe_{2+x} films: left) 120 nm-thick $\text{UFe}_{3.0}/\text{SiO}_2$ (sample VII) and 310 nm-thick $\text{UFe}_{4.0}/\text{SiO}_2$ (sample II), right) 450 nm-thick $\text{UFe}_{4.0}/\text{Si}(111)$ (sample I). The exemplary spectra revealed different features of the U- and Fe backscattered signals: well-separated and sharp U- and Fe signals (U(film), Fe(film)) for thin films with $d < 120$ nm (as for sample V and VII), separated but wide U- and Fe signals for the film with $d \approx 310$ nm (sample II), a partial overlap of the U- and Fe signals implying some fine structures of the spectra such as steps in the large peak (sample I and III). In all films the existence of the surface oxidized layer was revealed by a visible oxygen signal from the film (O(film)) which was well separated from the Si- and O-edge from the SiO_2 substrate (Si (sub.), O(sub.)).

For all investigated films, a very pronounced oxygen peak from the film (O(film)) was revealed in the RBS spectra (the small peak around 720 keV), which was well separated from the oxygen signal from SiO_2 substrates. It is attributed to the presence of oxygen in the topmost surface layers of the films (i.e. oxidized surface). For a more detail analysis of the film composition we have constructed the depth profile. As example we show in figure 4 the depth profile for sample I. The surface oxidation leads to a formation of a mixed U-Fe-O layer with a thickness of 65 nm in which the O-content decreased from 40% (at the topmost layer) to zero (Figure 4). Probably it is UO_x mixed with the U-Fe phase. Beneath such the mixed layer, we obtained the pure U-Fe layer (oxygen-free layer) with the thickness $d \approx 450$ nm. At the interface (beneath the $\text{UFe}_{4.0}$ layer), an U-Fe-Si intermixing region (≈ 60 nm) could be detected. Probably it is USi_3 indicated also by XRD data. For the films deposited on the SiO_2 substrates, the RBS results reveal clearly the oxidation of the film surface as well as the Si diffusion and especially oxygen diffusion in the interface region. Besides, some oxidation of the main U-Fe layer for the films with thickness $d < 400$ nm (e.g. sample II, III, V and VII) was also observed. Only in the case of the film deposited on Si(111) (sample I), the composition of the main U-Fe layer determined from RBS with a thickness of about 450 nm is $\text{U}_{16}\text{Fe}_{84}$, in a good agreement with that from the in-situ XPS ($\text{U}_{14}\text{Fe}_{86}$). XPS also revealed 3 at. % Oxygen on the surface layer in this case. One cannot be conclusive about whether this effect can be related to the surface oxidation and subsequent diffusion. Increasing the deposition time and thus increase the film thickness, the pure U-Fe layers can be obtained. For example for sample IV, the main layer with a thickness of about 520 nm has the $\text{U}_{30}\text{Fe}_{70}$ composition (stoichiometry determined by RBS), while for sample VI, the main

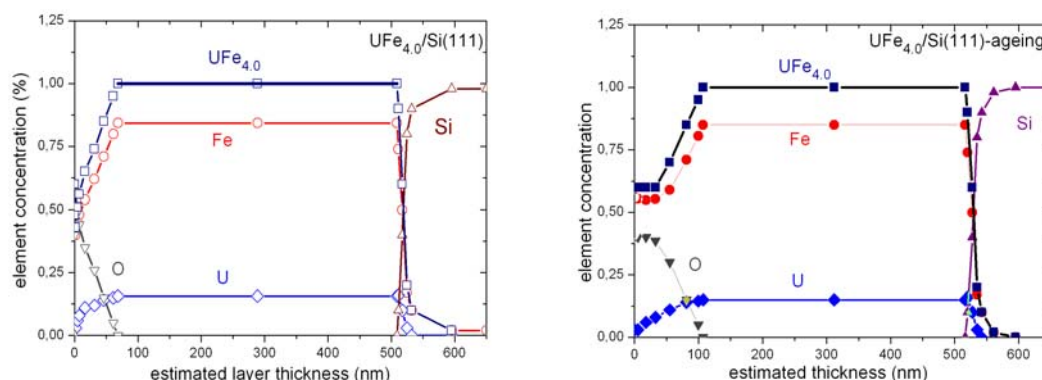


Figure 4. The concentration depth profile constructed from the RBS data for $\text{UFe}_{4.0}/\text{Si}(111)$ film after one week (left) and after one month exposed to air (right) revealing a large ageing effect indicating by an increase of the thickness of the oxidized surface layer from ≈ 65 nm to 110 nm.

layer with a thickness of about 900 nm has the $\text{U}_{25}\text{Fe}_{75}$ composition, i.e. in a good agreement with the XPS data ($\text{UFe}_{2.3}$ and $\text{UFe}_{2.7}$ respectively). However, we notice here that the RBS data revealed for both these films an oxidized surface, i.e. the mixed U-Fe-O layer with the thickness up to 100 nm. At the interface to the substrate, there exists a mixed U-Fe- SiO_x layer with the thickness in the range 200-300 nm. Certainly there is a difference in the U- and Fe content determined from different techniques. For instance the Fe-content determined from RBS for the main U-Fe layer is often higher than that from XPS. (A good reason for that is that this phase was with the highest temperature of magnetic ordering, besides α -Fe.) However, if taking into account the oxidized surface layer and the interface zone with a lower U-content, the average value for both U- and Fe content in the entire film certainly different to that of only the main U-Fe layer.

The RBS spectra performed on selected films after 1 month from the deposition have revealed a strong ageing effect of the films. A large increase of the oxygen signal in the film was observed within the first month. The depth profile analysis revealed clearly an increase of the thickness of the surface oxidized layer in e.g. $\text{UFe}_{4.0}/\text{Si}(111)$ film (Figure 4), the thickness of the surface mixed U-Fe-O layer increased from 65 nm to 110 nm and the $\text{UFe}_{4.0}$ layer decreases from 450 nm to 410 nm. However, RBS measurements after 6, 9, 12 and 18 months indicated that no visible change in the RBS spectra was observed with further exposure to air (in comparison to that after one month). The results indicated that the ageing affect saturates relatively fast and the oxidation does not progress into the bulk. We may attribute it to the mechanical stability of the sputter deposited films, preventing the cracking. For a compact surface, any oxidation of uranium would stop the moment the surface is covered by UO_2 , as the O molecule does not dissociate on UO_2 [9].

It is also interesting that a small amount of Fe (2%) and/or U (<2%) was found to diffuse into the Si and SiO_2 substrates in the investigated films, leading to a observed non-zero background between U- Fe peaks and Si-edge. This Fe can be possibly in the form of α -Fe, which is not easily detected by XRD due to the overlap with diffraction lines of USi_3 .

3.3. Magnetic measurements

Although the studied films are heterogeneous objects, it is not difficult to identify the contribution of the U-Fe phase. They are all ferromagnetic at room temperature, unlike the Fe-rich splats, which have only a weak ferromagnetic signal at room temperature (room- T), clearly due to parasitic α -Fe [3,4], and the main increment corresponding to the bulk ferromagnetism is observed somewhat below 300 K. So as to recognize whether the observed room- T ferromagnetism is not due to a possible admixture of α -Fe, and to determine the actual T_C values, we had to undertake the magnetometry experiment using a furnace. The question was the upper temperature limit, which can be reached without desintegration of rather reactive deposited material in exchange gas, which contains besides He also traces of air. The experience showed that the magnetization measurement is reproducible up to approx. 450 K. Above this temperature, magnetization starts to increase with time even if temperature stays constant. Apparently this is the moment when excessive Fe forms a phase, while U forms either crystalline UFe_2 or more likely UO_2 . Temperature dependence of magnetization shown in figure 5 for UFe_{2+x} films with $x = 0.3, 0.7, 1.0$ ($UFe_2, UFe_{2.7}$ and $UFe_{3.0}$ film) reveals that T_C values are enhanced and above the room temperature. $T_C = 400$ K was found for $UFe_{2.3}$, while it is further enhanced up to at least 450 K for $UFe_{3.0}$. For a comparison we show in figure 5 also the magnetization of the rather defected film V with a broad distribution of T_C values.

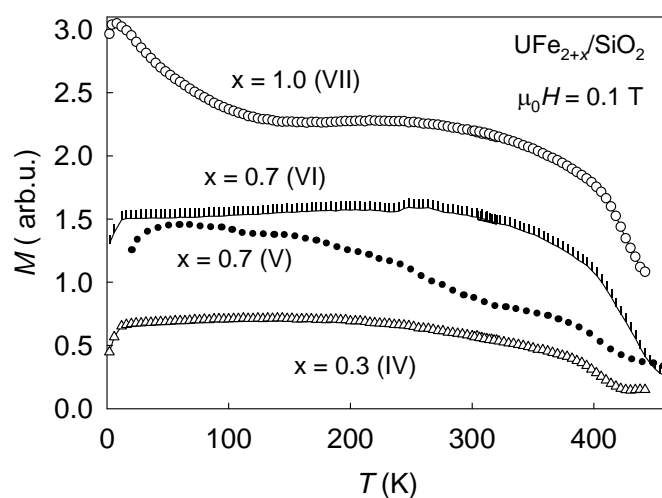


Figure 5. Temperature dependence of magnetization of sputter deposited UFe_{2+x} films on SiO_2 substrate with x ranging from 0.3 to 1.0. The very thin sample V is included to show that it exhibits a distribution of Curie temperatures. The absolute values of magnetization are irrelevant, as each sample was of different mass.

4. Summary

The obtained results on various UFe_{2+x} films indicate that films containing a U-Fe phase as a main ingredient could be successfully prepared by sputter deposition. Whether they are purely amorphous or show additional diffraction lines belonging to a Laves phase deposited with [111] direction perpendicular to the substrate, they reveal a pronounced enhancement of T_C values scaling with the excess of Fe over the UFe_2 stoichiometry and reaching approx. 450 K for the $UFe_{3.0}$, i.e. 1:3 ratio. The fact that ordering temperatures are not suppressed by the disorder well corresponds to the fact that Fe-Fe exchange interactions are responsible for the T_C value. The Fe magnetism is known to be quite insensitive to deviations from ideal crystal periodicity. The contribution of Fe moments remain to be determined by microscopic techniques.

Acknowledgments

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