

## Uranium compounds prepared by sputter deposition: $\text{UFe}_{2+x}$

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**Abstract.**  $\text{UFe}_2$  is one of rare examples of combination of  $3d$  and  $5f$  magnetism in a compound with relatively high  $T_C = 162$  K. U-excess is known to reduce the  $T_C$  value markedly. To prepare the Laves phase with an Fe excess is much more difficult. It can be achieved by sputter deposition, but the structure becomes amorphous.  $T_C$  can increase at least to 240 K (for  $\text{UFe}_4$ ), but the segregation of  $\alpha$ -Fe cannot be avoided for very high Fe concentrations.

### 1. Introduction

Uranium cubic Laves phase  $\text{UFe}_2$  was the first known actinide compound exhibiting ferromagnetism [1]. Its Curie temperature  $T_C$  reported by various authors was typically between 160-170 K [2]. Although both U and Fe carry magnetic moments [3], the Fe sublattice can be taken responsible for relatively high  $T_C$ . The fact that U moments are small ( $0.01 \mu_B$ ) is, besides the cancellation of spin and orbital part, undoubtedly connected with the small U-U spacing. The strong  $5d$ - $3d$  hybridisation leads to Fe moments ( $0.60 \mu_B$ ) [3] greatly reduced with respect to those in Fe metal or  $\text{REFe}_2$  Laves phases [4]. That is why the potential of a combination of the  $5f$  and  $3d$  magnetism in one material is not materialized in  $\text{UFe}_2$ .

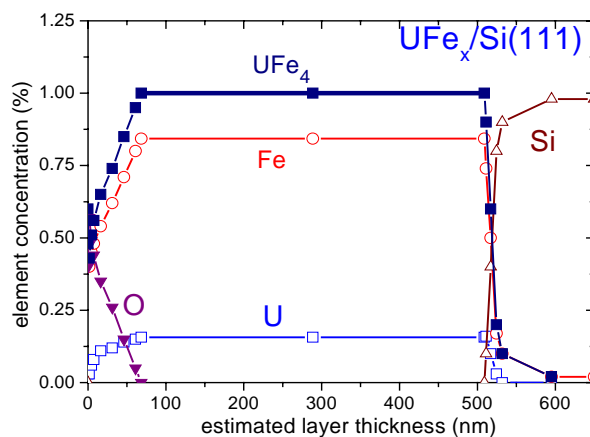
Studies on off-stoichiometric  $\text{UFe}_x$  compounds prepared by quenching [2] showed that the reduction of the Fe concentration leads to a suppression of  $T_C$  from 162 K in  $\text{UFe}_2$  to 112 K in  $\text{UFe}_{1.7}$ . The opposite deviation from the ideal 1:2 stoichiometry, i.e. stabilizing the Fe excess, could not be realized by a simple quenching. However, an increase of  $T_C$  to more than 200 K was achieved by a ball milling with excessive Fe, despite the concomitant amorphisation [5]. This finding was in contrast with results of reference [6], reporting on amorphous  $\text{UFe}_{2.7}$  prepared by sputtering, which exhibits only weak ferromagnetism with spin-glass features at low temperatures (below 32 K). More detailed study on splat-cooled  $\text{UFe}_{2+x}$  [7] indicated that incorporating additional 0.3 Fe atoms into the Laves phase structure leads to increase of  $T_C$  to about 230 K. In this case, Fe occupies the U sites, and such antistructure Fe atoms can have substantially higher magnetic moments. The structure remains crystalline, approaching nanocrystallinity. A larger Fe excess led to a segregation of  $\alpha$ -Fe

The aim of the present study is to use sputter deposition to test if even more Fe can be incorporated into the U-Fe phase, leading possibly to additional  $T_C$  increase. It is particularly intriguing to determine whether possible amorphisation would not affect the ferromagnetism in a negative way, as shown before for magnetic systems of purely  $5f$  type.

## 2. Thin-film synthesis and structure

$UFe_{2+x}$  films were obtained by sputter deposition in a UHV chamber (base pressure  $10^{-11}$  mbar) from U and Fe targets on Si (111) and fused silica ( $SiO_2$ ) as substrates, kept at the room temperature. The co-sputtering from two targets allows the stoichiometry control. In-situ XPS was used for the primary diagnostics. We succeeded to prepare films with  $x$  varying between 0.3 and 8, with typical thickness of 500 nm. Approximate sputtering time was 4 hours. After the XPS analysis, the films were exposed to atmosphere.

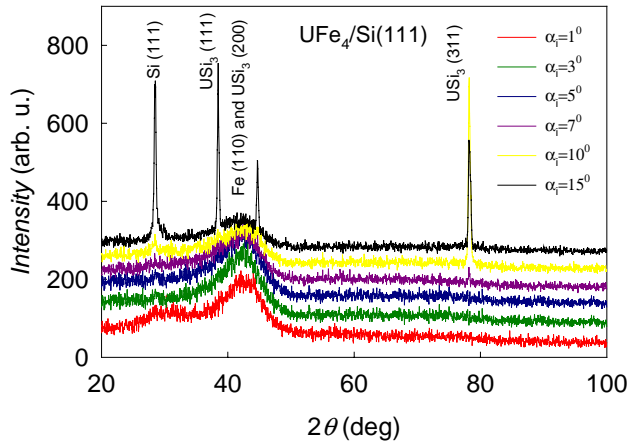
The composition and thickness of the films were studied by means of Rutherford Backscattering Spectroscopy (RBS). As an example, figure 1 shows the depth profile for the film  $UFe_x$  (the stoichiometry 1U-4Fe was estimated from XPS and electron microprobe analysis and confirmed by RBS) deposited on Si (111). Moreover, RBS indicated the presence of very thin (65 nm) surface layer of  $UO_2$  mixed with the U-Fe phase. At the interface, an U-Fe-Si intermixing region ( $\approx 60$  nm) could be detected. A small amount of Fe (2%) diffused into the Si substrate. This Fe can be possibly in the form of  $\alpha$ -Fe, which is not easily detected by XRD due to the overlap with diffraction lines of  $USi_3$ .



**Figure 1.** Concentration depth profile derived from the RBS areal density using the mass density of the “bulk” stoichiometric  $UFe_2$ . The analysis for the  $UFe_4$  deposited on Si (111). The plot shows both the elemental profiles as well as the tentative composed profile of the  $UFe_4$  phase.

A similar structure pattern was found for the U-Fe film deposited on fused silica under the same conditions. The main slab of approx.  $UFe_4$  composition contains in this case also small amount of uranium oxide. Much more uranium oxides occur at the interface in this case, pointing to the effect of the oxygen originating from the silica substrate and reacting with highly reactive uranium. Moreover, the surface oxidized layer was thicker than in the previous case. The results suggest that the surface film is not only due to post-deposition oxidation, but small amount of oxygen may segregate at the surface during the deposition already.

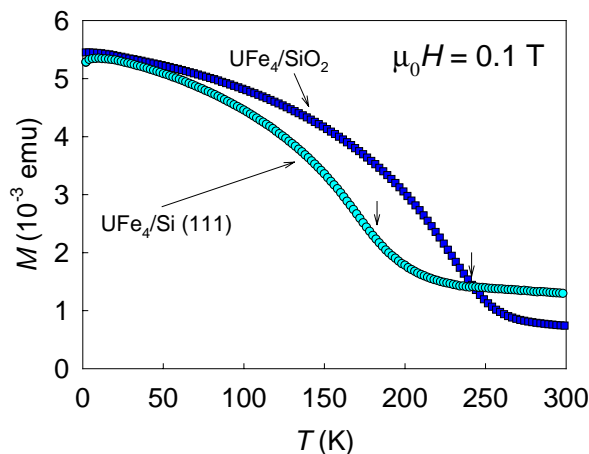
The film prepared with a larger Fe excess (approx.  $UFe_8$ ) exhibited a large amount of crystalline  $\alpha$ -Fe.



**Figure 2.** XRD patterns for UFe<sub>4</sub> (the same as in figure 1) obtained in the glancing angle XRD using Cu-K $\alpha$  radiation with a variable angle of incidence (given in the figure), increasing from 1° (bottom) to 15° (top). For small angles of incidence, the diffracted beam originates from the film only. For higher angles the interface and the substrate are included into the effective information depth.

### 3. Magnetic properties

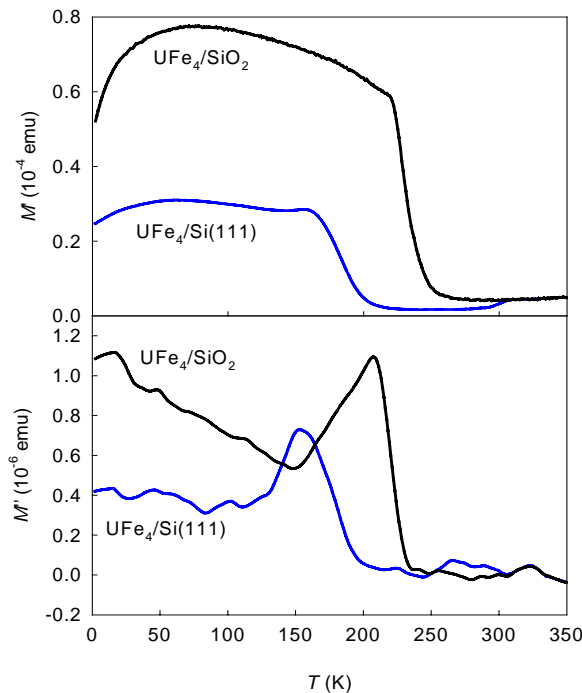
Magnetic properties were studied in the temperature range 2-300 K by means of a vibrating sample magnetometer and *ac* susceptibility magnetometer in the Quantum Design PPMS system. The diamagnetic signal of the substrates can be neglected in weak magnetic field. Therefore no correction was applied. Figure 3 shows the total magnetization in magnetic field of 0.1 T. Its temperature dependence indeed exhibits a ferromagnetic transition, which is not very far from critical temperature assumed for UFe<sub>2</sub>. The film deposited on Si exhibits  $T_C$  approx. 180 K, while  $T_C$  for the SiO<sub>2</sub> substrate is higher, approx. 240 K. The sample with larger Fe concentration (not shown here) exhibits a ferromagnetic behaviour throughout the whole temperature range. This is undoubtedly due to the dominance of  $\alpha$ -Fe, but also the present U-Fe phase is likely to have the  $T_C$  value exceeding 300 K.



**Figure 3.** Temperature dependence of the magnetization for the UFe<sub>4</sub> films deposited on Si and SiO<sub>2</sub>, respectively, measured in magnetic field 0.1 T. The arrows indicate the respective Curie temperatures.

The small amount of  $\alpha$ -Fe as ferromagnetic impurity is the reason for the relatively higher magnetization of the UFe<sub>4</sub> sample on Si at 300 K, i.e. nominally in the paramagnetic state. The weakly paramagnetic USi<sub>3</sub> and low-temperature antiferromagnetic UO<sub>2</sub> cannot influence the data significantly.

The respective Curie temperatures are better seen from the figure 4, exhibiting the *ac* magnetization data (*ac* field 1 mT). For the real part, a broad plateau is observed below  $T_C$ , which is unusual in U-based ferromagnets with typically strong magnetocrystalline anisotropy and consequent pinning of narrow domain walls. The anisotropy of UFe<sub>2</sub> is relatively very weak and the *ac* magnetization forms such a plateau instead of a sharp peak even in a crystalline material.



**Figure 4.** Temperature dependence of *ac* magnetization in the *ac* field of 1 mT for UFe<sub>4</sub> in Si(111) and SiO<sub>2</sub>. The real part  $M'(T)$  is in the upper panel, the imaginary part  $M''(T)$  in the lower panel. Reader should note that the real part is higher by a factor of 100. Although the main slab has nominally the main composition UFe<sub>4</sub> in both cases, the film in SiO<sub>2</sub> has somewhat less free  $\alpha$ -Fe (seen in Figure 3) and more oxides, which can both amount in more Fe-rich U-Fe, increasing the actual  $T_C$  value.

#### 4. Discussion and conclusions

The  $T_C$  value of UFe<sub>2</sub> can increase if an excessive Fe can be embedded in the same phase. The fact that the sputter deposited material is amorphous apparently does not strongly affect the  $T_C$  value, which points to the dominance of the Fe-3*d* magnetism as the 5*f* magnetism was found much more easily suppressed with increasing disorder [9,10]. The issue remains what is the highest achievable Fe concentration at various deposition conditions (mainly the substrate temperature and deposition rates should play a role). In this preliminary work we were not able to identify what is the main reason that the significant  $T_C$  increase was recorded for the UFe<sub>4</sub> film deposited on fused silica. One can speculate that the higher oxidation leading to uranium oxides can stimulate the U depletion in the U-Fe phase. A deeper insight could be provided by a microscopic method as XMCD, which could reveal magnetic moments of individual components. The results apparently strongly contradict to [6].

#### Acknowledgement

This work was supported by the Grant Agency of the Academy of Sciences of the Czech Republic under the grant number IAA100100912 and by the Czech Research and Development project KAN101630651. N.-T.H.K.-N and A.G.B. acknowledge the financial support from German Academic Exchange Service (DAAD)-project D/08/07991.

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