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Effect of interstitial hydrogen on UFe_xAl_{12-x}

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Abstract

Polycrystalline samples of UFe_xAl_{12-x} with x=4.5, 4.7, 4.85 and 5.0 were obtained by induction melting followed by annealing at 800°C for 3 weeks. The structure of all the samples was checked by powder X-ray diffraction and the final composition estimated using the Rietveld method. The introduction of interstitial hydrogen was performed by a reaction at high pressure and the final compounds were characterized by X-ray diffraction, magnetization measurements and Mössbauer spectroscopy. These results showed a significant modification in the magnetic behaviour after the insertion of hydrogen. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: $ThMn_{12}$-type structure; Intermetallics; Uranium compounds; Interstitial atoms

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1. Introduction

The ternary intermetallic compounds with 5f elements, crystallizing in the $ThMn_{12}$-type structure, have been extensively studied due to their complex magnetic properties and are regarded as having a high potential for providing good hard magnetic materials.

The semi-ordered compounds UFe_xAl_{12-x} have been found to melt congruently, within the iron-content range of $3.8<x<5.8$ [1,2]. Previous studies on single crystals, by low-field magnetization, ac-susceptibility and Mössbauer spectroscopy have shown a drastic change in the magnetic properties in the case of $x>4$ compounds due to the occupancy of 8*j* sites by iron atoms [3]. This systematic study evidenced the existence of two magnetic transitions for samples with $4.0 \leq x \leq 4.7$, in disagreement with previous results for polycrystalline samples which only indicated a single magnetic transition.

In the frame of a systematic study on the magnetic behaviour of these compounds, insertion of interstitial elements was undertaken in the UFe_xAl_{12-x} system. In the case of iron-rich isostructural rare-earth compounds it is well known that the introduction of interstitial elements induces important modifications on the intrinsic crystallographic and magnetic properties. In $RFe_{9.5}Mo_{2.5}$ (R=Y, Dy, Ho, Er) system larger critical temperature and saturation magnetization values were detected [4].

In this work we report on the study of UFe_xAl_{12-x} polycrystalline samples with x=4.5, 4.7, 4.85 and 5 using X-ray diffraction, magnetization measurements and Mössbauer spectroscopy, performed before and after the insertion of hydrogen interstitial atoms.

2. Experimental details

The UFe_xAl_{12-x} samples with nominal compositions x=4.5, 4.7, 4.85 and 5 were prepared by repeated induction melting of stoichiometric amounts of uranium, iron and aluminium with purity of at least 99.9%, in a cold crucible under a pure argon atmosphere. In order to avoid uranium oxidation, argon with less than 1 ppm of O_2 was used and several purges of the furnace were performed before melting. The weight losses during melting were generally less than 1%. Following the melting, the ingots were wrapped in a tantalum foil, sealed under vacuum in a silica tube and annealed at 800°C for 3 weeks.

The hydrides were prepared using hydrogen produced at high pressure (4 GPa) obtained by decomposition of a precursor rich in hydrogen (naphthalene), inside a sodium chloride reaction cell. The sample was introduced in the centre of the cell and separated from the naphthalene by a disk of BN (0.2 mm thick), in order to avoid the diffusion of carbon to the compound. This cell was placed in a

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CONAC type equipment developed by the I.H.P. of Troïsk, Russia. The reaction was carried out at 400°C under a pressure of 4 GPa for 3 h.

The structural characterization of the samples with and without hydrogen was performed by X-ray powder diffraction using a Philips PW1700 diffractometer with Cu Kα_1 radiation. The data were measured with a 2θ-step size of 0.02° in a 2θ-range of 10.00–100.00° and a counting time of 12.5 s at each step. A least-squares structure refinement was undertaken with the Rietveld powder profile program [5].

The samples were studied by ^{57}Fe Mössbauer spectroscopy in the transmission mode using a constant acceleration spectrometer and a 25-mCi ^{57}Co source in Rh matrix. The measurements were performed in powder samples pressed together with lucite powder into Perspex holders, in order to obtain homogeneous and isotropic Mössbauer absorbers containing ~5 mg/cm^2 of natural iron. Spectra were collected at several temperatures between 300 and 5 K and analysed using a modified version of the non-linear least-squares computer method of Stone [6].

Magnetization measurements were performed on free powder samples and on pellets in the temperature range 5–300 K and under fields up to 5.5 T, using a SQUID magnetometer (Quantum Design).

3. Results and discussion

X-ray powder diffraction confirmed the $ThMn_{12}$-type structure with the *I4*/*mmm* space group for all the annealed samples. The estimated unit-cell parameters are listed in Table 1. These results show that the substitution of aluminium for iron induces a decrease of the *a* and *c* parameters, which is in agreement with the Al and Fe metallic radii values. A change of 0.2–0.3% is detected for *a*, for compounds with *x* from 4.5 to 5, whereas a change of 0.1% is detected for *c* values. After the process of hydrogen insertion, the XRD revealed that the samples crystallized also in the $ThMn_{12}$-type structure with slightly larger lattice parameters.

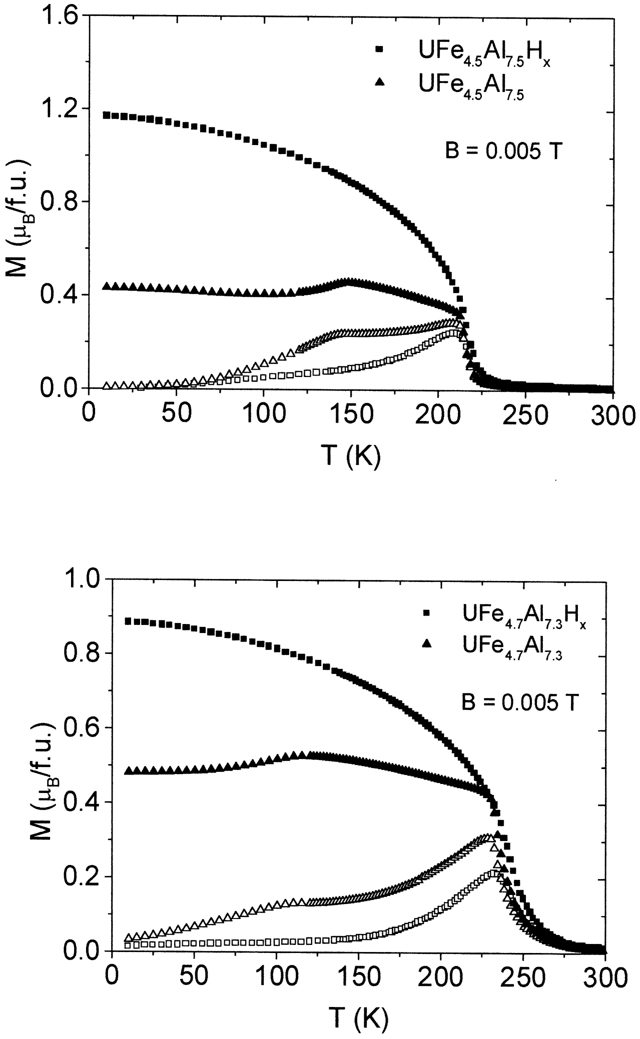

Fig. 1. Thermal dependence of the magnetization for $UFe_{4.5}Al_{7.5}$ and $UFe_{4.7}Al_{7.3}$ with and without hydrogen (open symbols: zero field cooled measurements; closed symbols: field cooled measurements).

Magnetization measurements show different magnetic behaviours for all the samples after the insertion of hydrogen, in particular for samples with $x=4.5$ and 4.7. In Fig. 1 the temperature dependence of magnetization for the sample $UFe_{4.5}Al_{7.5}$ before and after the interstitial insertion is presented. For the non-hydride sample two distinct anomalies are detected at temperatures around 131(2) and 216(2) K in agreement with the previous results on single crystals. For the hydride sample however, only one magnetic transition is detected at $T=218(2)$ K. A similar modification was observed for the hydride sample in the

Table 1
Estimated crystallographic parameters of UFe_xAl_{12-x} polycrystalline samples and their related hydrides

x	Cell parameters					
	Alloys			Hydrides		
	a (Å)	*c* (Å)	*V* (Å^3)	*a* (Å)	*c* (Å)	*V* (Å^3)
4.50	8.7216(4)	5.0286(2)	382.5	8.7233(2)	5.0287(2)	382.7
4.70	8.7141(4)	5.0274(3)	381.8	8.7168(3)	5.0285(3)	382.1
4.85	8.7061(6)	5.0245(4)	380.8	8.7194(5)	5.0315(5)	382.5
5.00	8.6976(1)	5.0224(1)	379.9	8.7021(8)	5.0243(5)	380.5

Table 2
The transition temperatures and saturation magnetization of UFe_xAl_{12-x} polycrystalline samples and their related hydrides

x	Transition temperatures ($\pm$5 K)		Saturation magnetization at 5 K (μ_B/f.u.)	
	Alloys	Hydrides	Alloys	Hydrides
4.50	131, 216	218	6.75	5.78
4.70	115, 234	242	6.62	6.46
4.85	250	254	5.51	6.24
5.00	260	262	7.05	7.81

case of $x=4.7$ (Fig. 1) showing that the hydrogenation process suppresses the lower temperature transition. In parallel with the suppression of the second anomaly the transition at higher temperature is clearly reinforced in both cases. The temperature dependence for this sample is typical of a ferromagnetic behaviour; the maximum in the ZFC (zero field cooling) magnetization curves is narrow and an abrupt change and huge increase in the FC (field cooling) magnetization values is detected for the lower temperatures. The isothermal magnetization curves also evidenced a ferromagnetic-type behaviour in both cases, with and without hydrogen, but with smaller saturation magnetization values for the hydride samples (Table 2). This fact is probably due to different conditions in the magnetization measurements; in the non-hydrogenated samples the measurements were performed on free powder, whereas in the hydrogenated samples they were performed on pellets, which means that the grains were not free to rotate with the applied field.

The hydrogenated $UFe_{4.5}Al_{7.5}$ sample was also studied by ^{57}Fe Mössbauer spectroscopy; the ^{57}Fe Mössbauer spectra were analyzed as described in Ref. [7]. The estimated parameters for the spectra recorded at 5 K are summarized in Table 3. The most striking difference between both samples is the significant increase (by ~10%) of the magnetic hyperfine fields, B_{hf}. The average B_{hf} estimated from the spectra obtained at different temperatures are represented for both samples in Fig. 2. This figure shows that the discontinuity observed in the curve of the $UFe_{4.5}Al_{7.5}$ sample disappears for the hydrogenated sample. The average B_{hf} are always larger for this sample and, due to the suppression of the lower temperature transition, the difference of the average B_{hf} increases significantly below this temperature. Considering that similar temperature dependences are expected for the B_{hf} and the corresponding Fe magnetic moments these results fully support the magnetization data.

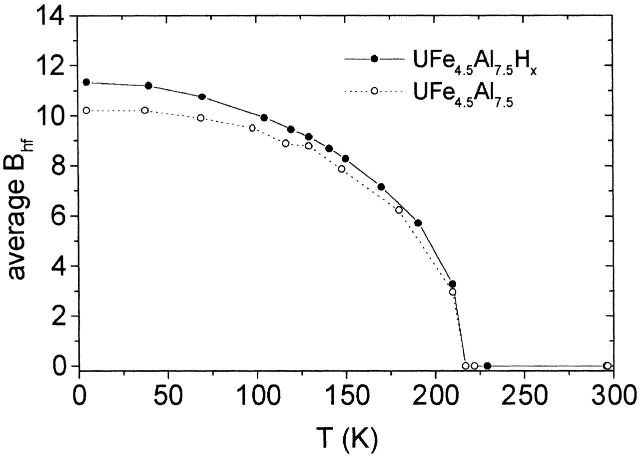

Fig. 2. The temperature dependence of the average B_{hf} for $UFe_{4.5}Al_{7.5}$ before and after the hydrogen insertion process.

For samples with $x=4.85$ and 5, there are also differences after the hydrogen insertion, which follow the same trend as for the lower iron content compound. For the starting samples with $4.85 \leq x \leq 5$ the temperature dependence of magnetization shows only one magnetic transition which can be identified with the ordering of the Fe and U sublattices [3]. However the FC curve shows for all the samples within this iron content, a kink for temperatures just below the transition. This particular variation disappears after the hydrogenation, the FC curves showing a temperature variation, which is once more characteristic of a ferromagnetic compound. It is clear from our results that the insertion of hydrogen leads to a magnetic behaviour

Table 3
Estimated parameters from the Mössbauer spectra of the $UFe_{4.5}Al_{7.5}$ samples taken at 5 K[a]

Compound	Site	z	I (%)	δ (mm/s)	ϵ (mm/s)	Γ (mm/s)	B_{hf} (T)
$UFe_{4.5}Al_{7.5}$	8j	≥4	11	0.18	0.54	0.24	13.7
	8f	≥4	5	0.21	0.19	0.24	12.1
	8f	3	28	0.23	0.15	0.24	11.2
	8f	2	56	0.28	0.10	0.24	8.9
$UFe_{4.5}Al_{7.5}H_x$	8j	≥4	11	0.19	0.54	0.24	14.7
	8f	≥4	5	0.22	0.11	0.24	13.5
	8f	3	28	0.25	0.18	0.24	12.3
	8f	2	56	0.29	0.11	0.27	9.9

[a] I, relative areas, are fixed, consistent with the calculated probabilities for the different number of Fe NN (z) of Fe atoms on the 8f and 8j sites. δ isomer shift relative to metallic α-Fe at 295 K; $\epsilon=(e^2V_{ZZ}Q/4)\,(3\cos^2\theta-1)$ quadrupole shift calculated from $(\phi_1+\phi_6-\phi_2-\phi_5)/2$ where ϕ_n is the shift of the nth line of the magnetic sextet due to quadrupole coupling. Γ, line-widths of the two inner peaks of a sextet; B_{hf}, magnetic hyperfine field. Estimated errors for the sextets with $I>11\%$ are ≤0.2 T for B_{hf}, ≤0.02 mm/s for δ, ϵ, Γ, and for the other sextets ≤0.4 T for B_{hf}, ≤0.03 mm/s for δ, and ≤0.04 mm/s for Γ and ϵ.

similar to the one observed in the compounds with higher iron content ($x>5$); the process modifies the magnetic structure of the compounds inducing a stronger ferromagnetic behaviour. However no significant modification is detected in the corresponding ordering temperatures. This is consistent with the very small modification detected in the lattice parameters.

In conclusion our results show that the insertion of hydrogen as interstitial atom suppresses the second magnetic transition detected at lower temperatures in the starting compounds. This transition was previously attributed to a reorientation of iron magnetic moments and explained as due to an indirect effect of the Fe 8f antiferromagnetic ordering. The hydrogenation process, even for very small quantities of interstitial hydrogen seems to favour the ferromagnetic ordering characteristic of the 8j Fe sublattice. One has to stress however that a pressure effect cannot be excluded from these preliminary results; further experiments, which will allow to clear out this point, are under progress.

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