Onset of magnetism stimulated by H absorption in UNiAl-UFeAl

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Abstract. Weak itinerant antiferromagnetism of UNiAl is rapidly suppressed by Fe doping. Magnetic order reappears as weak ferromagnetism in UNi0.75Fe0.25Al. The onset of magnetism can be shifted by H absorption. UNi0.85Fe0.15Al hydride is an antiferromagnet with TN approx. 70 K. Hydrogenating UNi0.70Fe0.30Al produces a ferromagnet (TC = 90 K). Here we describe the compound with 20% of Fe and its hydride. The proximity to magnetism shows up as non-Fermi liquid behavior, detected in specific heat as upturn, followed down to 0.3 K, which is gradually suppressed in magnetic fields of several tesla. The hydride was found rather unstable, releasing H at ambient conditions, which made it unsuitable for the specific heat measurement. Magnetization study detected that the hydride shows up as ferromagnet TC ≈ 98 K.

1. Introduction

U(Ni,Fe)Al compounds crystallize in the ZrNiAl structure type (space group P62m) as many UTX compounds (T - late transition metal, X – p-metal). It is a hexagonal structure with two types of basal planes, one with U and T atoms, and the other with T and X atoms. The group exhibits interesting variations of magnetic properties. Weak itinerant antiferromagnetism of UNiAl is rapidly suppressed by Fe doping. Magnetic order reappears as weak ferromagnetism for 25% Fe (figure 1) [1]. Previous studies [2,3] showed that compounds with less than 30% of Fe can absorb hydrogen. The crystal structure preserves its hexagonal symmetry upon hydrogenation or is only slightly distorted. In all studied cases the hydrogen absorption leads to the enhancement of magnetic interactions. So far no findings were reported about the effect of hydrogenation of UNi0.8Fe0.2Al, which is close to the onset of magnetism.
2. Experiments

Intermetallic compound UNi₀.₈Fe₀.₂Al was used as a starting material for the hydrogenation. The standard procedure of hydrogenation was performed. The sample was crushed into submillimeter particles, the surface of which was activated by annealing at \( T = 473 \) K for 2 h in a dynamic vacuum (\( 10^{-6} \) mbar) in order to desorb surface contaminants. The reactor was subsequently filled with a pressurized hydrogen gas (120 bar), and then exposed to thermal cycling up to \( T = 923 \) K. The hydrogen absorption was registered by a drop of the pressure. The crystal structure was studied by X-ray diffraction (XRD). Quantum Design PPMS equipment was used for magnetic studies and specific heat measurements. Magnetic measurements of UNi₀.₈Fe₀.₂Al and its hydride were performed in the temperature range 2-300 K and fields up to 9 T. The grains of the sample for magnetic measurement were fixed in random orientation by acetone-soluble glue. The specific heat was measured on the pellet, produced by pressing the powder, in the case of UNi₀.₈Fe₀.₂Al. The hydride was found rather unstable, releasing H at ambient conditions, which did not allow us to study specific heat, for which high vacuum conditions are needed.

3. Results and discussion

3.1 Crystal structure studies

The X-ray diffraction pattern of the hydrogenated sample shows that it consists of two phases, both hexagonal (the phase of the parent compound and the hydride phase, both having the same symmetry). It means that the hydride is unstable at ambient conditions and slowly decomposes. The hydrogenation leads to an anisotropic unit-cell expansion along the \( a \)-axis and compression along the \( c \)-direction what is the tendency revealed in all previously studied U(Ni,Fe)Al-hydrides. In the table 1 we compare the effect of hydrogen absorption on the crystal lattice of UNiAl [4] and UNi₀.₈Fe₀.₂Al. From the XRD we were not able to determine the amount of absorbed hydrogen. Also the instability of the hydride in time did not allow to perform controlled temperature-induced desorption in closed volume, what is usually used to determine the hydrogen concentration in the sample. But comparing the volume change upon hydrogenation with the volume change in UNiAl we can assume that the fully hydrogenated phase contains approx. 2 H atoms/f.u.
Table 1. Comparison of the crystal-structure parameters of UNiAl and UNi\(_{0.8}\)Fe\(_{0.2}\)Al and their hydrides: lattice parameters \(a\) and \(c\), unit cell volume \(V\) and volume change \(\Delta V/V\) with respect to the parent compounds.

|                | UNiAl   | UNiAl\(_{2.3}\) | UNi\(_{0.8}\)Fe\(_{0.2}\)Al | UNi\(_{0.8}\)Fe\(_{0.2}\)AlH\(_{2}\) |
|----------------|---------|-----------------|----------------------------|---------------------------------|
| \(a\) (Å)     | 6.733   | 7.181           | 6.736                      | 7.215                           |
| \(c\) (Å)     | 4.035   | 3.988           | 4.003                      | 3.858                           |
| \(V\) (Å\(^3\)) | 158.413 | 178.103         | 157.321                    | 173.940                         |
| \(\Delta V/V\) (%) | -       | 12.4            | -                          | 10.6                            |

3.2 Magnetic properties

The parent compound UNi\(_{0.8}\)Fe\(_{0.2}\)Al does not order magnetically. Magnetic susceptibility increases monotonously with decreasing temperature and can be fitted by the modified Curie-Weiss (MCW) law down to \(\approx 50\) K with the parameters \(\mu_{\text{eff}} = 1.9\) \(\mu_{\text{B}}/\text{f.u.}\), \(\theta = -41.5\) K and \(\chi_0 = 7.4\times10^{-9}\) m\(^3\) mol\(^{-1}\). Below that temperature the susceptibility deviates from the MCW law towards higher values and becomes field dependent (figure 3). The hydrogenation dramatically changes magnetic properties. In contrast to the parent compound the hydride orders antiferromagnetically with \(T_c = 98\) K. The temperature dependences of magnetization of the parent compound and of the hydrogenated sample are shown in the figure 2. We were not able to stabilize the hydride, hence we cannot see the pure hydride phase. We can see the ferromagnetic UNi\(_{0.8}\)Fe\(_{0.2}\)Al-H phase in the sample manifested as the anomaly at approx. 98 K corresponding to its \(T_c\).

Comparing the impact of hydrogenation to the whole series of U(Ni,Fe)Al, we find that the hydrogenation leads to the enhancement of magnetic interactions in all cases. The transition temperature increases regardless of the type of magnetic order. The Néel temperature of UNiAl increases from 19 K to 95 K upon hydrogenation [4]. Also in the case of the ferromagnetically ordered example UNi\(_{0.7}\)Fe\(_{0.3}\)Al the transition temperature increases from \(T_c = 15\) K to \(T_c = 90\) K for UNi\(_{0.7}\)Fe\(_{0.3}\)AlH\(_{4}\) [2]. The magnetic properties can be also tuned from nonmagnetic to antiferromagnetic or ferromagnetic depending on the Fe concentration as for UNi\(_{0.85}\)Fe\(_{0.15}\)Al and UNi\(_{0.8}\)Fe\(_{0.2}\)Al, respectively (table 2).
Table 2. Magnetic properties and ordering temperatures of U(Ni,Fe)Al compounds and their hydrides.

| parent compound   | UNiAl          | UNi0.85Fe0.15Al | UNi0.8Fe0.2Al       | UNi0.7Fe0.3Al       |
|-------------------|----------------|-----------------|---------------------|---------------------|
| hydride           | AF, \( T_N = 19 \) K | no order        | no order            | F, \( T_C = 15 \) K |
| \( \Delta V/V \)  | 12.4           | 14.9            | 10.6                | 7.3                 |
| absorbed H (H at./f.u.) | 2              | 2.4             | \( \sim 2 \)        | 0.8                 |

3.3 Specific heat measurement
The non-magnetic ground state of the parent compound UNi0.8Fe0.2Al is corroborated by the results of the specific heat studies, which do not reveal any anomaly originating in magnetic order. Instead a pronounced upturn in the specific heat appears at low temperatures, which can be followed down to 0.3 K (figure 4). The upturn in specific heat is gradually suppressed in magnetic fields of several tesla. The non-Fermi liquid (NFL) behavior manifested by the upturn can be in our case better described by the paramagnon term \( \delta T^2 \ln T \) than by \( -\delta T^{3/2} \), predicted for weakly interacting spin fluctuations (figure 5). The extrapolated \( \gamma \) value reaches 274 mJ/mol·K². Such a high \( \gamma \) value is relatively common at the verge of magnetism. The observed type of NFL behavior contrasts for example with \( \text{U}_2\text{Co}_2\text{InH}_{1.9} \), for which the other type of scaling, with \( -\delta T^{3/2} \) term, was identified [5]. Because of the instability of the hydride in time we were not able to obtain the specific heat data for the hydride.

4. Conclusions
We found that UNi0.8Fe0.2Al is very close to the onset of magnetism, which manifests in the NFL behavior with an enhanced \( \gamma \) value and \( T^2 \ln T \) scaling of \( C/T \). The volume increment of 10.6% due to the hydrogenation dramatically modifies magnetic properties, inducing ferromagnetism with \( T_C = 98 \) K. Such tendency is attributed to the 5f band narrowing.

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