Low-temperature Properties of $U_2Co_2InH_{1.9}$

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Dedicated to Dr. Bernard Chevalier on the occasion of his 60ᵗʰ birthday

$U_2Co_2InH_{1.9}$, synthesized by high-pressure hydrogenation of U_2Co_2In, crystallizes in the tetragonal structure similar to the parent compound, expanded by 8.4 %. Although U_2Co_2In is a weak paramagnet, its hydride shows properties suggesting a proximity to the magnetic order. Its magnetic susceptibility exhibits a maximum at $T = 2.4$ K, ascribed to spin fluctuations. Magnetization at low temperatures goes through a metamagnetic transition between $2 - 3$ T. The specific heat characteristics, with a pronounced upturn of C_p/T *vs.* T at low temperatures which can be fitted using an additional $-T^{1/2}$ term, resemble the behaviour of U_2Co_2Sn. The γ coefficient of the electronic specific heat, reaching 244 mJ mol^{-1} K^{-2}, is gradually suppressed by high magnetic fields.

Key words: Uranium, Hydrides, Magnetism

Introduction

Hydrides of U_2T_2X compounds (T = transition metal, $X = p$ element) have been studied intensively following the synthesis of the hydride of U_2Co_2Sn [1]. The systematic studies of hydrogenated U_2T_2X showed that the type of the transition metal predetermines the possibility for hydrogen absorption. Besides of U_2Co_2Sn hydrides, the hydrides of U_2Ni_2Sn and U_2Ni_2In have also been reported [2], showing markedly different magnetic properties as compared to the parent intermetallics. For example, the Néel temperatures T_N of $U_2Ni_2SnH_{1.8}$ and $U_2Ni_2InH_{1.9}$ considerably exceed those of all known U_2T_2Sn and U_2T_2In compounds. Moreover, the non-magnetic compound U_2Co_2Sn orders magnetically after hydrogenation. The variations can be in general attributed to the enhanced U-U spacing, which reduces the $5f$-$5f$ overlap. But more quantitative considerations suggest that reducing the $5f$-d hybridization, *i.e.* withdrawing partly the d states due to the d-$1s$ bonding, can also play a significant role.

A situation of fundamental interest is the regime close to the onset of magnetism. U_2Co_2Sn is located at the non-magnetic side, but the proximity to the quantum phase transition is indicated by a pronounced enhancement of the coefficient γ of the electronic specific heat, and by a non-Fermi liquid character of the specific heat [3]. Incorporation of hydrogen induces first a weak ferromagnetism in the α-hydride, and subsequently a more conventional antiferromagnetism in the β-hydride, $U_2Co_2SnH_{1.4}$ [1]. U_2Co_2In with its nearly temperature independent susceptibility is definitely more distant from the onset of magnetism than U_2Co_2Sn [4] and we can therefore assume that its hydrides will be located somewhere at the borderline between the magnetic and the non-magnetic regime. The formation of the U_2Co_2In hydride has been already reported [2]. In the present work we report on magnetic properties and the specific heat of the U_2Co_2In hydride.

Experimental Details

Hydrides were synthesized by means of hydrogenation of the intemetallic compound U_2Co_2In prepared by arc melt-

ing of pure metals (purity 99.9 % or higher) under an argon atmosphere. The samples obtained were then crushed into submillimeter particles and hydrogenation was performed at a hydrogen pressure of 110 bar, applying a thermal treatment up to $T = 923$ K, which are the conditions yielding the β-hydrides of the U_2T_2X compounds. The formation of the α-hydride, a solution of a small amount of H in U_2T_2X, requires only several bar of H_2 pressure. The phase composition before and after the hydrogenation was studied by X-ray powder diffraction analysis (XRD-3003 diffractometer (Seifert), CuK_α radiation, 2θ step: $0.02°$). The initial U_2Co_2In sample contained a small amount ($\approx 6\%$) of In metal as a spurious phase, as In was added in excess in order to compensate for In evaporation. The hydrogenated samples contained the U_2Co_2In hydride and non-modified In metal. After a preliminary estimate of the H concentration from weight changes, we performed a thermal decomposition in a closed volume by heating the samples up to 1073 K. The H content reached 1.9 ± 0.1 atoms per formula unit.

A Quantum Design PPMS extraction magnetometer was used, in the temperature range 1.8 – 300 K and in magnetic fields up to 9 T, for the measurements of magnetic susceptibility (magnetization) of both the hydride and the initial compound. The specific heat, C_p, measurement using the common microcalorimetry method could not be performed on the as-obtained fine powder. Instead, the powder was compacted into a thin pellet, 3 mm in diameter, using a hydraulic press and an anvil cell with WC faces, reaching 700 MPa. The sample of approximately 10 mg was attached to the substrate by a small amount of APIEZON N grease, and measured by a relaxation method using the specific heat insert in the PPMS equipment, in the temperature range 0.4 – 300 K and in magnetic fields up to 9 T.

This technique of the sample preparation has already been applied for the hydrides of TbMn$_2$ [5]. However, previously the mixing of the hydride powder with the micrometer-sized Cu (or later Ag) was applied. The drawback of the method is that the contribution of the sample itself was found to be relatively small in comparison with the contribution of Cu and the addenda giving rise to a relatively large error especially in the high-temperature range. We found that using high pressures one can obtain binder-free pellets suitable for the microcalorimetry measurement owing to good mechanical stability and sufficient thermal conductivity.

Results

$U_2Co_2InH_{1.9}$ crystallizes in the tetragonal Mo_2FeB_2 structure type which is similar to that of the initial compound U_2Co_2In, belonging to the large family of U_2T_2X compounds [6–8], and which is shared also by rare earths isotypes [8–10]. The crystal structure parameters are given in Table 1. Hydrogen positions

Table 1. Structure parameters of U_2Co_2In and $U_2Co_2InH_{1.9}$. Lattice parameters a and c, unit cell volume V, relative lattice expansion along the a direction, $\Delta a/a$, along the c direction, $\Delta c/c$, and a relative volume expansion, $\Delta V/V$, are given. $d_{U-U} \parallel c$ and $d_{U-U} \perp c$ are the nearest-neighbour U-U distances along the c axis and perpendicular to it, respectively. (x_U and x_{Ni} are the respective internal parameters).

	U_2Co_2In	$U_2Co_2InH_{1.9}$
a, Å	7.365(1)	7.590(2)
c, Å	3.434(1)	3.507(1)
V, Å^3	186.3(1)	202.0(1)
$\Delta a/a$, %	–	3.1
$\Delta c/c$, %	–	2.2
$\Delta V/V$, %	–	8.4
x_U	0.169(1)	0.175(1)
x_{Ni}	0.377(3)	0.376(2)
$d_{U-U} \perp c$ (Å)	3.521(10)	3.757(11)
$d_{U-U} \parallel c$ (Å)	3.434(1)	3.507(1)

could not be determined by X-ray diffraction, but the proximity of the stoichiometry of the U_2Co_2In hydride and the deuteride $U_2Ni_2SnD_{1.9}$, studied by neutron powder diffraction [11], allows us to predict hydrogen positions at the $8k$ site inside the U_3Co tetrahedra. Full occupancy of this site allowed by steric factors would give 2 H atoms per formula unit. The lattice expansion reaches 8.4 % (by volume), the expansion in the basal plane being somewhat larger than in the c axis direction. The relative lattice expansion is larger than the value observed for U_2Ni_2In (6.8 %) [2], resembling the tendency observed between the U_2Co_2Sn [1] and U_2Ni_2Sn [2] hydrides. The hydrogenation thus leads to a larger volume effect for the Co compound, in which a stronger $5f$-$3d$ hybridization can be assumed. The shortest interuranium distances are generally close to the Hill limit (3.4 – 3.6 Å), what makes U_2Co_2In very sensitive to lattice modifications such that a dramatic effect on magnetism can be expected due to hydrogenation.

Results of the measurement of the temperature dependence of the magnetic susceptibility $\chi(T)$ of U_2Co_2In agree well with the reported data [4]. U_2Co_2In exhibits no magnetic order and $\chi(T)$ is almost temperature-independent, being on the level $\chi \approx 3 \cdot 10^{-8}$ m^3 mol^{-1} (Fig. 1). However, the hydrogenation has a quite dramatic impact on the magnetism of U_2Co_2In and leads to an enhancement of magnetic interactions in the hydride. Measurements of $\chi(T)$ in various magnetic fields allowed to correct the susceptibility for the contribution of a small amount of UH$_3$, which is ferromagnetic with $T_C \approx 180$ K. The corrected susceptibility of $U_2Co_2InH_{1.9}$ strongly increases with
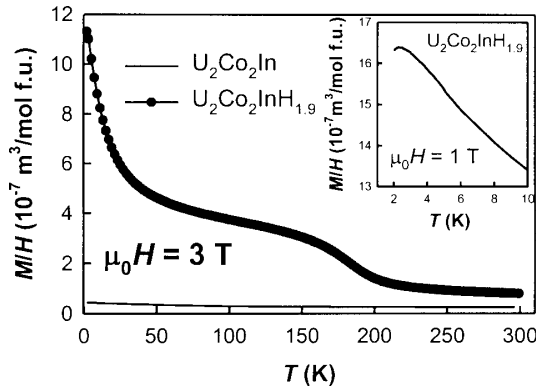
Fig. 1. Temperature dependence of the magnetic susceptibility of U$_2$Co$_2$In and U$_2$Co$_2$InH$_{1.9}$ measured in a magnetic field $\mu_0 H = 3$ T. The anomaly at $T = 180$ K can be attributed to a small amount of UH$_3$. The inset shows the low-temperature detail obtained in a magnetic field $\mu_0 H = 1$ T (measurement performed while cooling in the given field).
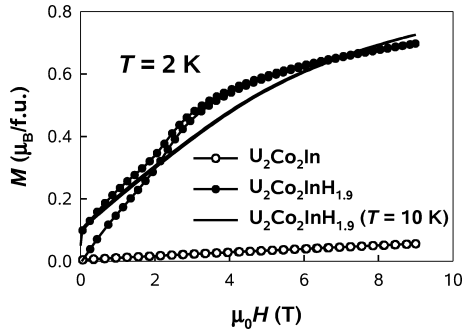

Fig. 2. Magnetization curves of U$_2$Co$_2$In and U$_2$Co$_2$InH$_{1.9}$ measured at $T = 2$ K. The solid line shows the magnetization curve of U$_2$Co$_2$InH$_{1.9}$ measured at $T = 10$ K.

decreasing T, and the dependence can be well described by a modified Curie-Weiss law with the parameters $\mu_{\mathrm{eff}} = 1.6$ μ_B per U atom, $\theta_P = 3$ K, $\chi_0 = 4.4 \cdot 10^{-8}$ m^3 mol^{-1}. A detailed analysis of the low-temperature part reveals the presence of a weak maximum in $\chi(T)$ located at $T = 2.4$ K, observed in low magnetic fields (*e. g.* 1 T, as seen in the inset of Fig. 1). The field dependence of magnetization, measured at $T = 2$ K, exhibits a metamagnetic shape with a transition in the range $2-3$ T (Fig. 2), which is close to the value observed for β-U$_2$Co$_2$SnH$_{1.4}$ [1]. The remanent magnetization observed can be attributed to the presence of ferromagnetic UH$_3$. The studies of the magnetization curves at different temperatures showed that the metamagnetic transition is shifted to higher fields with increasing temperature (Fig. 3). (The value of the metamagnetic field was determined by the maximum of dM/dH). This makes less likely that an anti-
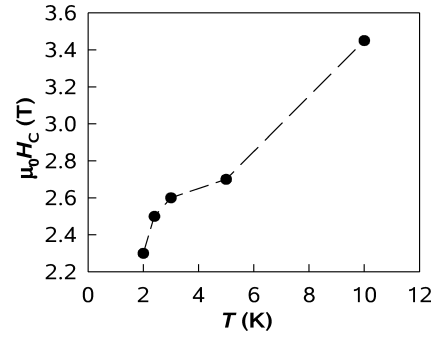

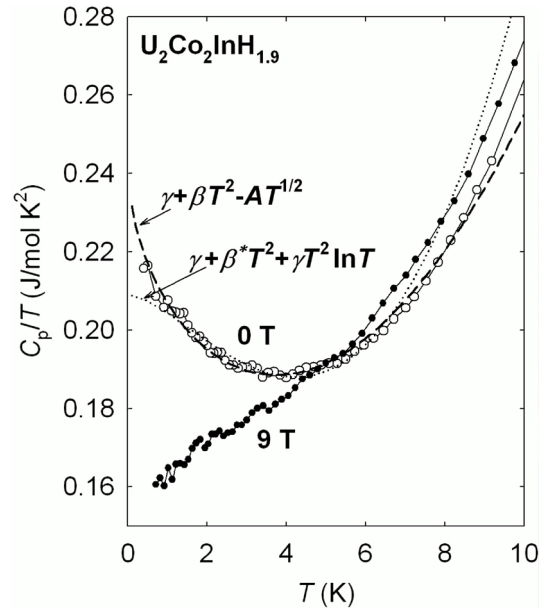Fig. 3. Temperature dependence of the critical metamagnetic field for U$_2$Co$_2$InH$_{1.9}$.

Fig. 4. Low-temperature part of the specific heat in the C_p/T representation of U$_2$Co$_2$InH$_{1.9}$ measured at $\mu_0 H = 0$ T (empty dots) and 9 T (full dots). The dashed and dotted lines represent two types of fits, as described in the text.

ferromagnetic ground state, for which the critical field typically decreases with increasing T, is responsible for the susceptibility maximum. Instead, the increase of the metamagnetic field is suggestive of a band metamagnetism, *i. e.* the situation, in which the ground state is non-magnetic, and a ferromagnetic-like magnetization is induced in essentially a band system by an external magnetic field [12]. The susceptibility maximum appears as a spin fluctuation effect, and the critical field increasing with T testifies that the entropy at a particular T is lower in the high-field state.

The non-magnetic ground state is also corroborated by the results of specific heat studies, which do not reveal any anomaly related to the feature in $\chi(T)$ (see Fig. 4). Instead, a pronounced upturn in the specific heat in the C_p/T representation appears at low temperatures, leading to a heavy fermion behaviour. Such behaviour has been observed in numerous nearly or weakly magnetic compounds, including some of the U_2T_2X compounds, in particular U_2Pt_2In and U_2Co_2Sn [3, 4]. The non-Fermi liquid behaviour, as manifested by the C_p/T upturn (originating from spin fluctuations), can be described by several models. Kim *et al.* [3] analyzed in detail the case of U_2Co_2Sn, where extrapolated γ reaches nearly 350 mJ mol^{-1} K^{-2}, concluding that it cannot be well described by a paramagnon term $C/T \sim T^2 \ln(T/T_{sf})$. Instead, the scaling $1 - T^{1/2}$, predicted for weakly interacting spin fluctuations [13 – 15], is describing the C_p/T data below 10 K. We have performed both types of analyses for $U_2Co_2InH_{1.9}$. The least-squares fits shown in Fig. 4 clearly demonstrate that the dependence including the $-T^{1/2}$ term describes the experimental data better and over a more extended temperature range. The extrapolated γ value reaches 244 mJ mol^{-1} K^{-2}. The values are expressed per mole f. u., *i. e.* to 2 U atoms. Similar to U_2Co_2Sn [3], the upturn is gradually suppressed by an applied magnetic field, and $\gamma \approx 160$ mJ mol^{-1} K^{-2} in $\mu_0H = 9$ T. The suppression illustrates the reduction of magnetic entropy as suggested in the previous paragraph. A more detailed measurement in various magnetic fields is necessary to quantify the field variations and their possible relation to the metamagnetic transition.

Discussion and Conclusions

The experimental data obtained on U_2Co_2In and its hydride confirm the tendency observed for other U-based systems. The hydrides, with a crystal structure related to the structure of the parent compound, with an expanded lattice volume, tend to have more pronounced magnetic properties. This is well under- stood assuming a $5f$ band character of the emerging magnetism, with the $5f$ bandwidth modulated by the U-U spacing. In such a regime, the volume expansion leads to the $5f$ band narrowing and an enhancement of the density of electronic states, supporting the formation of $5f$ moments. In this respect the situation is more straightforward than *e. g.* in Ce-based mixed-valent, magnetic, and Kondo systems, in which the impact of hydrogenation can be quite diverse (compare, *e. g.*, refs. [16] and [17]).

The comparison of $U_2Co_2InH_{1.9}$ and U_2Co_2Sn points to a universality of specific heat scaling in the critical regime of U_2T_2X compounds at the verge of magnetism. The bottom line of this universality is a similar character of spin fluctuations. On the other hand, the behaviour of magnetic susceptibility in these two materials is somewhat different. In U_2Co_2Sn, $\chi(T)$ increases monotonously with decreasing T, and the increase is gradually suppressed by an enhanced magnetic field. On the other hand, $U_2Co_2InH_{1.9}$ exhibits a susceptibility maximum and a metamagnetic behaviour. In order to study $U_2Co_2InH_{1.9}$ in more detail, one should avoid the formation of the spurious ferromagnetic UH_3 phase. Low temperature synthesis of the hydride, which is expected to suppress the UH_3 phase, is in progress. The resemblance of nearly magnetic $U_2Co_2InH_{1.9}$ and U_2Co_2Sn, whereas the U_2Co_2Sn hydride is magnetically ordered, underlines the fact that the U_2T_2Sn compounds are relatively more magnetic than the U_2T_2In isotypes [4, 7].

As a conclusion, we found that $U_2Co_2InH_{1.9}$ is located close to the verge of magnetism, and similar to U_2Co_2Sn is a non-Fermi liquid material with a γ enhancement and a $1 - T^{1/2}$ scaling of C_p/T.

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