Evolution of magnetism in UCoGe and UCoAl with Ru doping*

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Abstract

Intriguing magnetic properties of the UCo$_{1-x}$Ru$_x$Ge and UCo$_{1-x}$Ru$_x$Al pseudoternary systems studied on single crystals are presented and discussed in terms of anisotropic 5f-ligand hybridization as the principal driving mechanism. Ferromagnetism of the ferromagnetic superconductor UCoGe is initially stabilized by Ru substitutions for Co (superconductivity suppressed already for $x>0.01$) providing maximum Curie temperature ($T_C$), spontaneous magnetic moment ($\mu_s$) and magnetic entropy ($S_{mag}$) for 10% Ru. Further increasing Ru concentration leads to gradual suppression of these parameters towards a ferromagnetic quantum critical point (FM QCP) at $\approx 0.31$. Non-Fermi liquid scaling of specific heat and electrical resistivity is observed in the vicinity of FM QCP. The itinerant electron metamagnet UCoAl is transformed to a ferromagnet by only 0.5% Ru substituted for Co. The ferromagnetism is suppressed for $x>0.7$. On the descending branch of the dome-like $T-x$ magnetic phase diagram two distinctly different ferromagnetic phases are observed. The strong magnetocrystalline anisotropy leaving the hard magnetization directions Pauli paramagnetic like irrespective of magnetic ground states projected exclusively in the easy magnetization directions is accounted to the anisotropic 5f-5f wave-function overlap and 5f-ligand hybridization, and 5f-electron orbital moment.

Keywords: uranium compounds, ferromagnetism, metamagnetism, quantum criticality

Mathematics Subject Classification: 1.00, 5.02

1. Introduction

Recently physics of U compounds has attracted much interest owing to observation of novel phenomena such as a coexistence of ferromagnetism and superconductivity in UGe$_2$ [1], URhGe [2] and UCoGe [3] or itinerant f-electron metamagnetism with Ising type anisotropy of ferromagnetic fluctuations in UCoAl [4, 5]. These intriguing phenomena have been discovered owing to systematic investigation of UTX compounds (stoichiometry 1:1:1) which form one of the most extended families of U intermetallics comprising more than 50 ternary compounds of uranium with late transition metals (T) and p-elements (X) from the groups IIIA, IVA, and VA of the periodic table. The majority of ordered ternary UTX compounds crystallize either in the hexagonal ZrNiAl-type or in the orthorhombic ordered ternary TiNiSi-type [6]. The former group comprises mainly the UTAI (including UCoAl) and UTGa compounds, whereas the UTSi and UTGe (including UCoGe) counterparts adopt the latter structure type.

The prominent mechanisms affecting magnetism in U intermetallics, i.e. the size of U magnetic moments and their ordering, are the interaction of overlapping 5f wave functions of pairs of neighboring U ions and the 5f-ligand hybridization; the hybridization of the U 5f states with the s, p, d valence states of ligands (T and X ions). Both mechanisms induce two important effects:

(a) Delocalization of the U 5f states leading ultimately to the washout of U magnetic moments,
The overlap of neighboring 5f wave-functions and 5f-ligand hybridization are strongly anisotropic reflecting the anisotropic layout of U ions and ligands in a particular crystal structure. The close packing of U and T atoms in the basal plane of the ZrNiAl-type structure compresses the 5f charge density towards the basal plane. The strong spin–orbit interaction in U ions promotes orbital magnetic moments, which are indeed observed experimentally [7]. Consequently, the huge uniaxial anisotropy locks the 5f magnetic moments along the c-axis. This is an inevitable element of magnetism in these compounds which exhibit Ising like behavior. This is projected to uniaxial anisotropy of the magnetic susceptibility even in paramagnetic range. Whereas the c-axis susceptibility follows a modified Curie–Weiss law, the susceptibility in magnetic fields perpendicular to c (within the basal plane) is almost temperature independent (Pauli paramagnet like). The basal plane magnetization is very week exhibiting comparable values in all the isostructural compounds irrespective of the type of magnetic ground state realized exclusively along the c-axis. Consequently the magnetically ordered ground states consist of strictly collinear magnetic structures aligned along c. It should be stressed that the magnetocrystalline anisotropy is here intimately connected with the bonding anisotropy yielding anisotropic lattice properties [8].

The 5f-5f wave-function overlap and the 5f-d hybridization within the basal plane is a strong ferromagnetic coupling of the involved U magnetic moments. This situation leads to magnetic structures consisting of ferromagnetic basal-plane layers.

In the orthorhombic TiNiSi structure type, the moments are confined to the b-c plane, perpendicular to the a-axis along which the strong bonding chain of uranium ions propagates [6]. Consequently, in compounds of TiNiSi-type family the a-axis is the hard magnetization direction and the a-axis magnetization has features analogous to the basal-plane magnetization in the ZrNiAl-type compounds.

Evolution of magnetism within the two isostructural groups (ZrNiAl-type and TiNiSi-type) is analogous, which is reflecting evolution of the strength of the 5f-d (U—T) and 5f-p (U—X) hybridization, respectively. Namely, at the strong 5f-d hybridization limit (enhanced) Pauli paramagnets UFeX and URuX are observed. On the other hand, U 5f moment ferromagnets or antiferromagnets are by rule found for UNiX, URhX, UPdX, UIrX and UPtX. The UCo compounds apparently appear in the critical region for magnetism where the weaker of the 5f-p hybridization allows ferromagnetism in UCoGe [3] and UCoGa [9] contrary to paramagnetic UCoSi and UCoAI [6].

Ferromagnetism in UCoGe is particularly weak (U magnetic moment counts in hundredths of μB) and fragile with respect to chemical composition [10] or external pressure [11]; nevertheless, the strong easy-plane anisotropy of TiNiSi-type structure UTX compounds confines even the tiny U magnetic moments within the b–c plane making the a-axis be the hard magnetization direction in which the ferromagnetism is not at all reflected. Moreover, superconductivity emerges below 0.7 K [3], which makes UCoGe an archetype of superconducting very weak itinerant 5f electron ferromagnet. The Curie temperature (3 K for pure UCoGe) is strongly enhanced (and superconductivity eliminated) by small Fe or Ru substitution for Co [12, 13].

Paramagnetism of UCoAl is far from usual. The susceptibility in fields perpendicular to c is temperature-independent like the other counterparts with ZrNiAl-type structure, but the c-axis susceptibility follows a modified Curie–Weiss law (with reduced effective moment with respect to the U3+ free-ion value) and a pronounced maximum around 20 K. The maximum is apparently due to anisotropic spin fluctuations [4]. UCoAl remains paramagnetic down to lowest temperatures; application of magnetic field oriented along the c-axis larger than 0.6 T, induces metamagnetic state which mimics ferromagnetic ordering [4]. Ferromagnetism can be induced in UCoAl also by Ru substitution for Co as low as 1% [14]. On the other hand, metamagnetism in UCoAl can be suppressed by applying hydrostatic pressure [15].

The unusual magnetism in UCoGe and UCoAl and the its extreme sensitivity to the Ru substitution for Co motivated us to detailed investigation of the magnetic, transport and thermal properties of the entire series of UCo1_xRu_xGe and UCo1_xRu_xAl pseudoternary compounds on polycrystals and for the selected compositions on single crystals. Specific features revealed by this study are discussed in this paper.

2. Experimental

In order to study the development of the magnetic state in UCo1−xRu_xGe compounds we have primarily prepared a series of polycrystalline samples with different concentration of Ru for x from 0 to 0.9. Each sample was characterized by x-ray powder diffraction (XRPD) at room temperature. Composition of our samples was verified by EDX. The electrical resistivity and heat capacity measurements were performed in PPMS9T and PPMS14T (quantum design). Magnetization and ac susceptibility measurements were done in MPMS7T.

After inspecting the T−x magnetic phase diagram of UCo1−xRu_xGe system (figure 1) constructed from data delivered by measurements on numerous polycrystalline samples the representative compositions (x = 0.03, 0.12, 0.27) of interesting regions of evolution of magnetism have been determined for preparation of single crystals.

The single crystals were grown in tri-arc furnace under protective Ar (6N purity) atmosphere using Czochralski method and in optical furnace using floating zone method. The quality and orientation of all prepared single crystals was checked by Laue diffraction method. The growing process and single crystal characterization mostly followed our experience published in reference [10].

The T−x magnetic phase diagram of UCo1−xRu_xAl system determined by magnetization and ac susceptibility study of numerous polycrystals of various x has been published in
3. Results and discussion

3.1. UCo$_{1-x}$Ru$_x$Ge system

All samples of the UCo$_{1-x}$Ru$_x$Ge pseudoternary compounds were found possessing the same orthorhombic TiNiSi-type structure (space group Pnma) adopted by the boundary compounds UCoGe and URuGe. The unit cell volume of the ferromagnetic UCoGe is smaller (V = 208.3 Å$^3$) of about 5% than that of the Pauli paramagnet URuGe (V = 219.5 Å$^3$). The observed concentration dependences of all three lattice parameters and also the unit cell volume are linear, i.e. they obey the Vegard’s law. Parameters $b$ and $c$ increase with increasing $x$, whereas parameter $a$ simultaneously decreases.

The magnetization and specific-heat measurements revealed that the Ru substitution for Co in UCoGe leads to an initial sharp increase of the Curie temperature $T_C$ and the spontaneous magnetic moment $\mu_s$, whereas superconductivity observed in UCoGe ceases already for $x>0.01$ (see the magnetic phase diagram in figure 1). $T_C$ and $\mu_s$ increase up to the maximum values of 8.5 K and 0.1 $\mu_B$/f.u., respectively, for $x \approx 0.1$.

Further increasing Ru content leads to gradually decreasing both $T_C$ and $\mu_s$ to vanish at the ferromagnetic quantum critical point (FM QCP) at $x \approx 0.31$. Analogous non-monotonic concentration dependence is followed by the magnetic entropy $S_{mag}$ derived from specific-heat data. The maximum value at $S_{mag}$ for $x = 0.1$ reaches only 0.12 Rln2 and it falls to 0.006 Rln2 at $x = 0.30$. The strongly reduced magnetic moments and tiny magnetic entropy manifest itinerant nature of the magnetism in our UCo$_{1-x}$Ru$_x$Ge compounds. Note that for the ideal itinerant case we would expect magnetic entropy equal to zero [6].

From the specific-heat data analysis we also derived the Sommerfeld $\gamma$-coefficient that increases dramatically to the peak value of 160 mJ mol$^{-1}$ K$^{-2}$ as the system approaches the critical concentration, whereas the $\gamma$-coefficient of UCoGe amounts 57 mJ mol$^{-1}$ K$^{-2}$ [17].

Concentration dependence of the critical exponents of electrical resistivity and heat capacity together with scaling of the $T_C$ reveal signs of the non-Fermi liquid behavior of compounds with $x$ near 0.30 which is expected near FM QCP where the $T_C$ is suppressed to zero.

The non-monotonous concentration dependence of $T_C$, $\mu_s$ and $S_{mag}$ should be considered as a consequence of effect of varying 5f-ligand hybridization on formation of magnetic moments of U and ligands and on magnetic exchange interactions. A simple model considering varying widths and positions of the ligand d- and uranium 5f-band, respectively, has been successfully applied in the case of isoelectronic substitution in the system URh$_{1-x}$Co$_x$Ge exhibiting also a dome-type $T-x$ magnetic phase diagram [18]. A more sophisticated model is desired for treating non-isoelectronic substitutions in our UCo$_{1-x}$Ru$_x$Ge and UCo$_{1-x}$Ru$_x$Ge solid solutions as well as other systems exhibiting the dome-type $T-x$ magnetic phase diagram, e.g. UCo$_{1-x}$Fe$_x$Ge [13], URh$_{1-x}$Ru$_x$Ge [19], URh$_{1-x}$Ru$_x$Al and URh$_{1-x}$Ru$_x$Ga [20].

It should be emphasized that despite the non-monotonous evolution of magnetism, the strong easy-plane anisotropy with hard magnetization direction along the $a$-axis has been confirmed persisting in all UCo$_{1-x}$Ru$_x$Ge compounds as can be documented by magnetization curves measured on single crystals seen in figure 2. The hard magnetization direction ($a$-axis) signal remains almost identical overall the entire UCo$_{1-x}$Ru$_x$Ge series.

3.2. UCo$_{1-x}$Ru$_x$Al system

Since the ground state of both, UCoAl and URuAl, is paramagnetic we are dealing with two critical regions for ferromagnetism in the UCo$_{1-x}$Ru$_x$Al system. One is apparently in very low Ru concentrations and the other for 0.6 $< x < 0.8$.

In figure 3 hysteresis loops measured at 1.8 K on 4 single crystals, UCoAl and 3 of UCo$_{1-x}$Ru$_x$Al with $x=0.0025$, 0.005 and 0.01, respectively, are shown. One can see a gradual transformation metamagnet $\rightarrow$ ferromagnet with...
increasing Ru substitutions for Co. Whereas UCoAl and UCo$_{0.9975}$Ru$_{0.0025}$Al are paramagnetic and exhibit metamagnetism in fields along c-axis, ferromagnetism is unambiguously present in for Ru concentrations starting from $x = 0.005$.

The metamagnetism in UCoAl can be suppressed by applying hydrostatic pressure, which is manifest by increasing the critical field of metamagnetic transition with increasing pressure and finally transforming the first-order magnetic phase transition from paramagnetic to ferromagnetic state to a crossover behavior [15, 21]. Therefore, pressure experiments are desirable to test the ferromagnetic samples with $x \geq 0.005$, especially with respect to theories focusing on the ferromagnetic quantum criticality [21, 22]. The distinct uniaxial anisotropy remains intact irrespective the magnetic ground state. The basal plane magnetization is very weak and almost identical in all the four crystals.

The main issue of the behavior of UCo$_{1-x}$Ru$_x$Al compounds in the high Ru concentrations beyond the maximum $T_C$ in the $T-x$ magnetic phase diagram concerns the existence and nature of the two ferromagnetic phases. Hysteresis loops measured on the UCo$_{0.44}$Ru$_{0.56}$Al single crystal are shown in figure 4. One can see that for the field applied along the c-axis the magnetization is very small and varies linearly with magnetic field as in a weak paramagnet. This confirms that the a-axis (in the basal plane) is the hard magnetization direction. The magnetization behavior in fields applied along the c-axis is characteristic for a ferromagnet. The curve measured at lower temperature (4.5 K) resembles by its rectangular shape and clear hysteresis a hard ferromagnet, whereas that measured at higher temperature (37 K) is characteristic for a soft ferromagnet (round curve, no hysteresis).

When cooling from high temperatures one can distinguish the onset of spontaneous magnetization, anomaly in ac susceptibility, electrical resistivity and thermal expansion at a certain temperature, which we denote as the Curie temperature $T_C$. No anomaly at $T_C$ is observed in specific-heat data. Below this temperature soft-ferromagnet resembling curves are recorded. Therefore, we call this phase soft ferromagnetic phase (SFP). By cooling to lower temperatures the shape of magnetization curves changes suddenly to hard ferromagnet behavior at a temperature $T_1$. Consequently, the phase below $T_1$ is denoted as hard ferromagnetic phase (HFP). Surprisingly an anomaly is observed at $T_1$ in ac
susceptibility, electrical resistivity, thermal expansion but also specific heat.

In figure 5 one can see that the hard phase exists still in UCo$_{0.3}$Ru$_{0.7}$Al whereas UCo$_{0.22}$Ru$_{0.78}$Al is paramagnetic down to 1.8 K. The almost identical magnetization data measured on the two crystals in magnetic fields applied along the $a$-axis again manifest that, however, the strong uniaxial anisotropy is an inevitable property of the ZrNiAl-type UTX compounds irrespective of magnetic ground state, which is projected exclusively along the $c$-axis.

FM QCP is apparently located somewhere between $x = 0.70$ and 0.78. Further, single crystals should be grown in this concentration region to reveal details of approaching FM QCP and a proper representative composition for this concentration region to reveal details of approaching FM QCP. The strong easy-plane magnetocrystalline anisotropy leaves the $a$-axis magnetization very weakly intact by the varying ground state which is realized only in the $b$--$c$ plane.

Ru substitution immediately (already for 0.5% Ru) converts the itinerant electron metamagnet UCoAl to ferromagnet. For high Ru substitutions ferromagnetism becomes gradually suppressed towards FM QCP for $x > 0.7$. On the descending branch of the dome-like $T$--$x$ magnetic phase diagram with increasing Ru content, two distinctly different ferromagnetic phases (a soft and a hard one) have been observed. Ferromagnetic quantum criticality on the two ends of dome (for low and high $x$, respectively) is discussed. The strong uniaxial magneto-crystalline anisotropy makes the magnetic behavior of UCo$_{1-x}$Ru$_x$Al compounds Ising-like. Negligible magnetization (Pauli paramagnetic) is detected within the basal plane because the ferromagnetism and metamagnetism are projected exclusively along the $c$-axis of the ZrNiAl-type structure.

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