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Magnetic properties of $URuAl_{1-x}Sn_x$

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Abstract

Magnetic properties of the $URuAl_{1-x}Sn_x$ quasi-ternary solid solutions ($0 \leq x \leq 1$) were studied in magnetic fields up to 40 T. A strong non-linearity in concentration dependence of the lattice parameters was found. This was unexpected because of the single site for Al and Sn atoms in the hexagonal ZrNiAl-type structure. The boundary compounds URuAl and URuSn are a spin-fluctuating system and a ferromagnet respectively. The onset of ferromagnetism was found at $x = 0.2$ with further monotonous increase of both magnetic moment and Curie temperature with increasing Sn content.

Keywords: Uranium intermetallics; Magnetic properties

1. Introduction

Intermetallic compounds URuSn and URuAl are representatives of the UTX uranium ternaries (T is a late transition metal of the 3d, 4d or 5d series, X is a metal of groups 3–5 of the periodic table). Both compounds have a hexagonal crystal structure of the ZrNiAl type (the ternary variant of the Fe_2P structure, the $P\bar{6}m2$ space group). URuSn is a ferromagnet with a Curie temperature of $T_C = 55$ K and spontaneous magnetic moment $\mu_s = 1.1\ \mu_B$ per formula unit [1–3]. It has a very strong uniaxial magnetic anisotropy, as usually observed in compounds of this class. The estimated anisotropy field B_a far exceeds 100 T. In contrast, URuAl does not order magnetically (at least above 20 mK), despite the fact that its susceptibility χ obeys the modified Curie–Weiss law (with a temperature-independent term) above 70 K. It is a highly anisotropic paramagnet with the maximum susceptibility also along the c axis. A broad maximum at 50 K in the temperature dependence of magnetic susceptibility, an anomaly in the electrical resistivity below 50–70 K and a noticeable metamagnetic-like transition in 25 T allows classification of URuAl as a spin-fluctuation system [2,4,5].

In the UTX compounds, the ordered U magnetic moment varies from zero to 1.6 μ_B depending on the degree of itinerancy of the 5f electrons. Other components do not contribute much to the magnetic moment, but affect the magnetic properties of compounds influencing the 5f electron states. The 5f-ligand hybridization is the main mechanism causing delocalization of the 5f-electrons in actinide intermetallics and, consequently, determines the magnetic and other electronic properties of a particular compound [2]. The important feature of the UTX compounds in the context of uranium magnetism is a possibility of large substitutions in all three sublattices. One can change the local environment of U atoms in a chosen direction within the same crystal structure (for example, of the ZrNiAl type, as in the present paper), thus regulating the 5f-ligand hybridization. Several studies have been performed on quasi-ternary solid solutions of UTX with the ZrNiAl structure. They mainly deal with substitutions within the transition-metal sublattice, which leads to a change of ground state. The development of magnetic moment is often non-monotonous in such cases ($URu_{1-x}Rh_xAl$, $URu_{1-x}Rh_xGa$ [6,7], $URu_{1-x}Co_xSn$ [3], $UNi_{1-x}Fe_xAl$ [8,9], $UFe_{1-x}Co_xAl$ [8], $UNi_{1-x}Co_xAl$ [9], $UCo_{0.9}T_{0.1}Al$, $UCo_{0.9}T_{0.1}Sn$ [10]). Less attention was paid to the

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systems with substitution of the X metal; only data on $UNiAl_{1-x}Ga_x$ [2,11] and $UCoAl_{1-x}Sn_x$ [12,13] have been reported. In the present paper, we report on the magnetic properties of $URuAl_{1-x}Sn_x$ solid solutions.

2. Experimental details

The alloys with nominal compositions $URuAl_{1-x}Sn_x$ ($x = 0$, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0) were prepared by melting the corresponding amounts of the elemental components (uranium of 99.8% purity, other metals of 99.99%) in an arc furnace on a water-cooled copper bottom under a protective argon atmosphere. The ingots (of 3 g mass) were turned several times in order to avoid inhomogeneities, and afterwards they were wrapped in a Ta foil and annealed in vacuum at 750°C in a sealed quartz tube for 1 week. The $U_{1-x}Lu_xRuAl$ alloys, where U is substituted by non-magnetic Lu, were also prepared and heat-treated in the same way. The phase composition of the alloys and the lattice parameters of the compounds were determined by standard X-ray diffractometry.

Magnetization measurements were performed by an induction method in pulsed fields up to 40 T with a rise time of about 5 ms at 4.2 K on powder samples. The powders with randomly oriented particles were fixed by frozen alcohol to avoid an alignment of the particles in high field. This corresponds to an ideal polycrystal. URuAl was also measured in a single-turn coil in pulse field up to 90 T at 8 K in order to check for the occurrence of an additional transition. In this case, a fine powder of the compound was mixed with epoxy.

Magnetic susceptibility of several compounds was measured by the Faraday method in a superconducting magnet at 4.2–300 K in fields up to 2 T.

The Curie temperatures were determined from a.c. susceptibility measurements in a magnetic field of amplitude 1 mT and frequency 80 Hz.

3. Results and discussion

All alloys of the $URuAl_{1-x}Sn_x$ system were found to be of single phase with the ZrNiAl structure. With regard to the $U_{1-x}Lu_xRuAl$ system, only the sample with lowest Lu content ($x = 0.2$) contained an acceptable amount of extraneous phases (10–15%) and was further studied. This compound has lattice parameters $a = 701.0$ pm, $c = 392.0$ pm. Compared with URuAl (692 pm and 402 pm respectively), the lattice expands along the a axis, but shrinks along the c axis, and the unit-cell volume remains practically unchanged. A larger U–Lu substitution leads to a significant inhomogeneity of the alloys.

Fig. 1 shows the concentration dependence of lattice parameters. A very large deviation from linearity is observed for both a and c parameters, whereas the unit-cell volume increases almost linearly owing to the larger atomic radius of Sn (158 pm) compared with Al (143 pm). One of the most important characteristics of actinide compounds, the shortest interatomic distance between the actinide atoms, is approximately $0.52a$ for UTX with the ZrNiAl structure (four neighbours in the basal plane). In URuAl, this amounts in $d_U = 359$ pm. The next inter-U distance (along the c axis) exceeds d_U by 12%. The strong lattice contraction along the c axis, together with the large expansion within the basal plane for $x \leq 0.4$ results in significant reduction of the c/a ratio in this concentration range (Fig. 1). This does not lead to a crossover in inter-U distances in the basal plane and along the c axis, but the uranium sublattice becomes more isotropic (the difference between parameter c and d_U drops to 5.5% at $x = 0.4$ with further gradual decrease to 3.5% at $x = 1$), which may influence magnetic properties.

A similar behaviour of the lattice parameters was observed in several UXT systems upon substitution of the T metal ($URu_{1-x}Co_xSn$ [3], $UNi_{1-x}Fe_xAl$ [14]). However, atoms of the T metal occupy two non-equivalent positions in the ZrNiAl-type crystal structure. The observed anomalies in the concentration

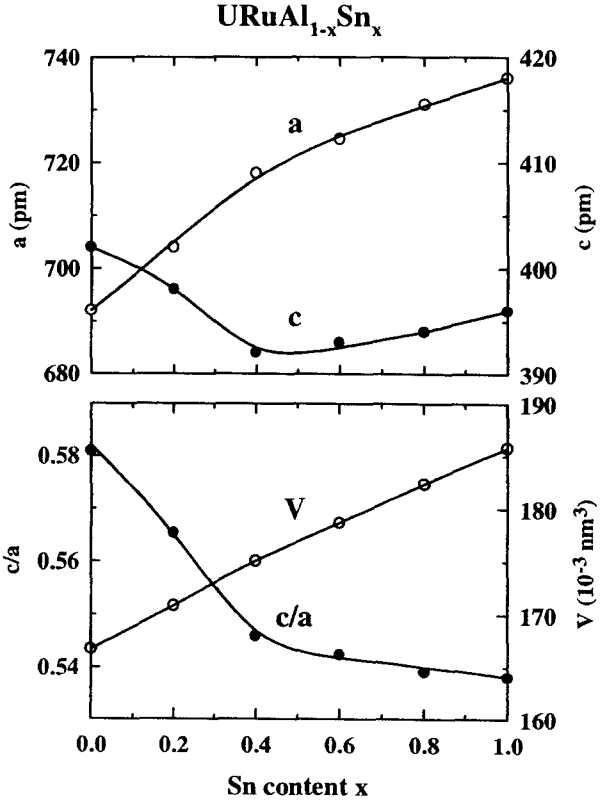

Fig. 1. Concentration dependence of the lattice parameters a and c, their ratio c/a and the unit-cell volume V.

dependences of lattice parameters were attributed to a non-statistical occupation of these positions by different T atoms. Moreover, in the case of the Fe containing system, this preference in site occupation was confirmed by Mössbauer effect study [8]. However, the X atoms have only one site in the ZrNiAl structure; therefore, such a reason should be dismissed. In systems with varying X metal studied previously ($UNiAl_{1-x}Ga_x$ [11] and $UCoAl_{1-x}Sn_x$ [12,13]), the lattice parameters depend on concentration practically linearly. However, similar and even more pronounced anomalies have been observed in some other quasi-ternaries upon substitution within only the crystallographic position, e.g. $R(Rh_{1-x}Ru_x)_3B_2$ with hexagonal $CeCo_3B_2$-type structure [15] (R = rare-earth metal). The reason for these anomalies is still unclear, but this shows that the explanation of such behaviour in $U(T^1,T^2)X$ systems based on the preference in site occupation should be reconsidered.

In Fig. 2, the virgin magnetization curves and hysteresis loops after application of a 6 T field at 4.2 K are presented. One can see a paramagnetic behaviour of URuAl, in agreement with literature data. A similar curve with a larger susceptibility was obtained for $x = 0.1$. Beginning from $x = 0.2$, a spontaneous magnetic moment appears and the magnetization isotherms become typical for ferromagnetic UTX compounds. They exhibit a rather low initial susceptibility, sharp increase of magnetization above a critical field and an almost rectangular hysteresis loop. These features of the magnetization process correspond to the narrow domain wall model, in which practically monatomic domain walls have very large intrinsic coercivity and are 'frozen' in the crystal [16]. The model may be applied to a ferromagnet with the anisotropy energy comparable with, or even exceeding, the exchange energy. The ZrNiAl-type UTX compounds with their huge uniaxial anisotropy and relatively low μ_U and T_C evidently belong to this class of ferromagnets. As seen from Fig. 2, the domain-wall movement does not finish even in $B = 6$ T in the samples with $x = 0.6$ and 0.8.

High-field magnetization curves (field-down branches) at 4.2 K are presented in Fig. 3. In agreement with Refs. [5,7], the metamagnetic transition in URuAl is seen poorly in the magnetization curve of the fixed powder. A deviation from the low-field linear extrapolation, starting at 20 T, reaches only 6% in 40 T. The magnetization of URuAl was studied earlier in fields up to 60 T [7]. We have extended the maximum applied field to 90 T, but no additional transition was found. The short pulse duration did not allow us to study with reasonable accuracy the powders free to rotate in an applied field, which simulates single-crystal measurements along the easy-magnetization direction. In this case, the metamagnetic transition is seen

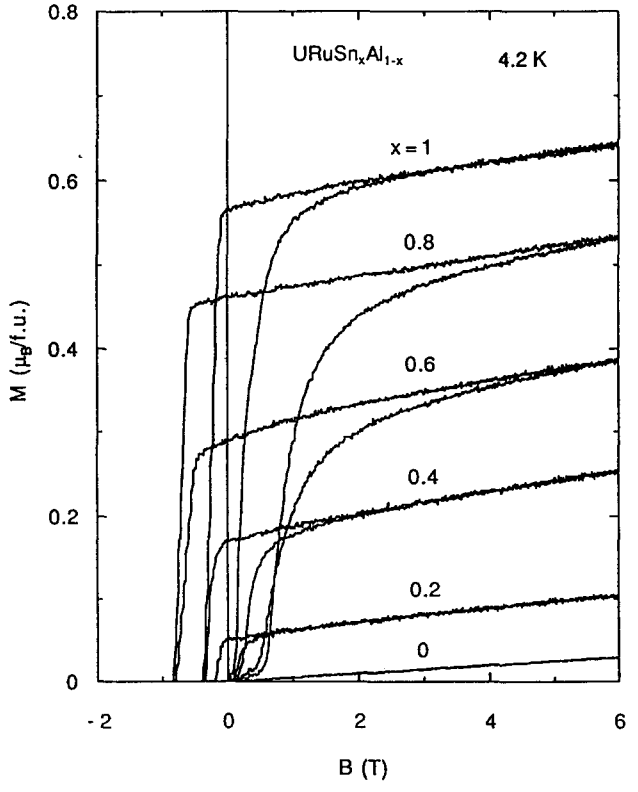

Fig. 2. Virgin magnetization curves and hysteresis loops at 4.2 K (with maximum applied field of 6 T).

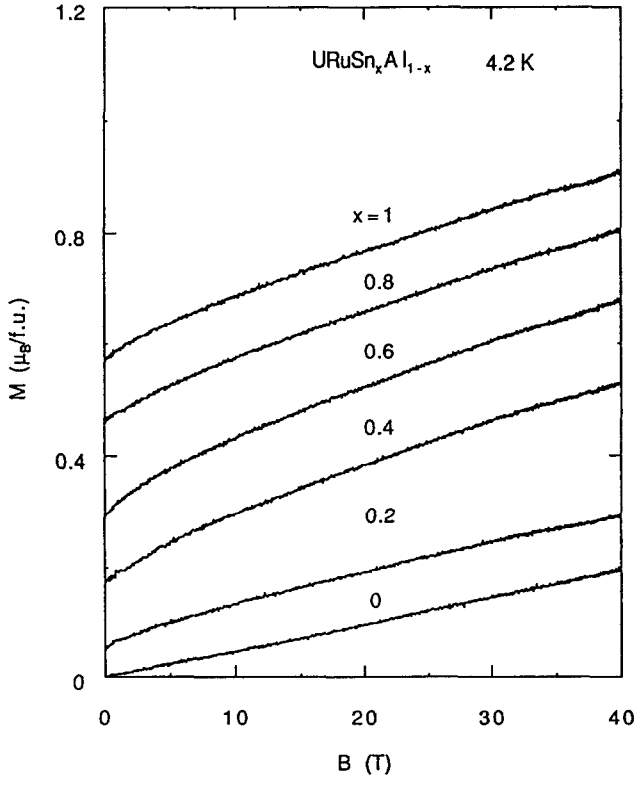

Fig. 3. High-field magnetization curves 4.2 K (field-down branch).

much better [5,7]. For the fixed powders, we can only say that the metamagnetic transition at least does not become more pronounced in compounds with $x = 0.1$ and disappears with the onset of ferromagnetism at $x = 0.2$. The enhancement of magnetic interactions is accompanied by the disappearance of the second feature of spin-fluctuating behaviour of URuAl, i.e. the broad maximum in temperature dependence of magnetic susceptibility χ (Fig. 4). The same effect was also observed upon dilution of the U sublattice by 20 at.% of non-magnetic Lu, i.e. with weakening of magnetism, but the value of susceptibility decreases in this case. This correlates with suppression of the metamagnetism.

The metamagnetism at low temperatures is thermodynamically connected with the maximum in χ(T). Such behaviour is traditionally attributed either to a special character of the energy dependence of density of electronic states in the close vicinity of the Fermi level [17] or to spin fluctuations, dominating the low-temperature dynamics of magnetic moments [18]. We would, however, also consider the possibility of short-range antiferromagnetic correlations leading to a maximum of q-dependent susceptibility χ(q) for non-integer q. In this scenario the metamagnetic transition is the consequence of breaking the antiferromagnetic correlations. Antiferromagnetism in UTX is, however, restricted to compounds with T = Ni, Pd, Pt, i.e. from the last transition-metal column of the periodic table, whereas earlier transition metals lead to a ferromagnetic-type coupling [2]. Therefore, the last explanation is less plausible, and we need to employ a neutron scattering technique to find the answer.

Fig. 5 shows the concentration dependences of magnetic properties. After the onset of magnetic order at $x = 0.2$, the values of spontaneous magnetic moment and the moment reached in the maximum field gradually increase. A similar behaviour is also found for the Curie temperature. A non-monotonous dependence of coercivity might reflect a decrease of uniaxial magnetic anisotropy with decreasing anisotropy of local environment of the U atoms. However, the c/a ratio is already practically the same for URuSn and the compound with $x = 0.8$, but the coercive field is lower by factor of two in the pure ternary. These two compounds have a similar high-field susceptibility (Fig. 3), which shows that their anisotropy does not differ considerably. Another mechanism for the coercivity involving microscopic inhomogeneity (clusters) and domain-wall pinning on such clusters can be applied to explain the

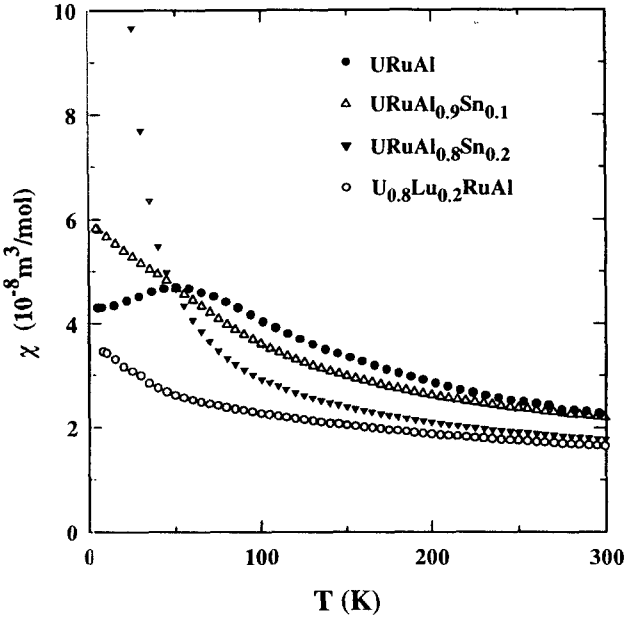

Fig. 4. Temperature dependences of magnetic susceptibility for paramagnetic compounds and for alloy on the onset of ferromagnetism ($URuAl_{0.8}Sn_{0.2}$).

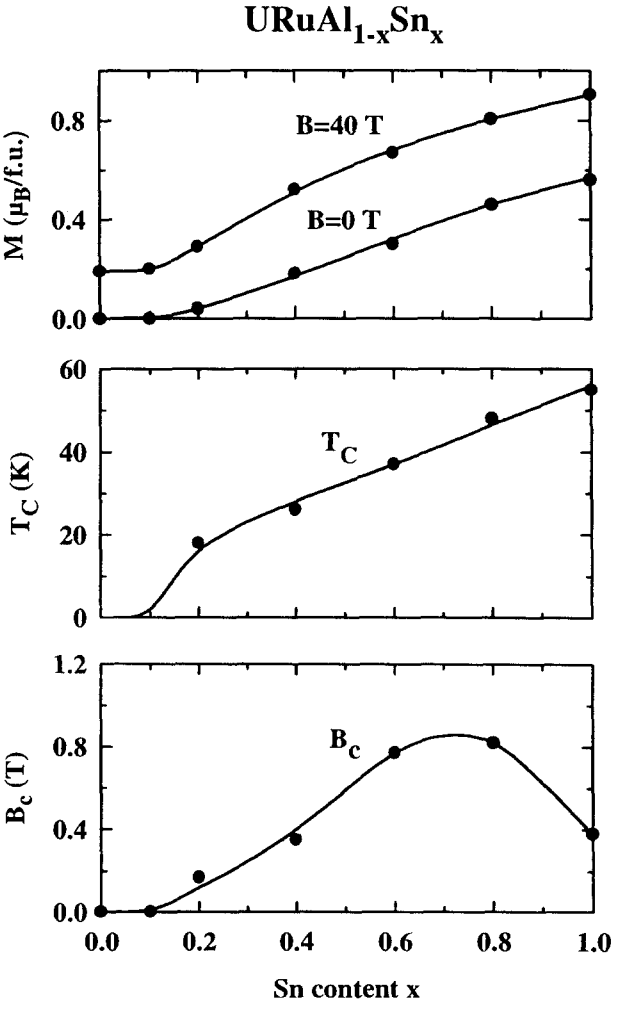

Fig. 5. Concentration dependence of the magnetic moment in 40 T and extrapolated to zero field, the Curie temperature and the coercive field at 4.2 K.

maximum in B_c for the intermediate compositions. Such a mechanism is supposed to be responsible, for example, for the very large coercivity of $R(Co_{1-x}Ni_x)_5$ and $R(Co_{1-x}Cu_x)_5$ compounds (e.g. Ref. [19]).

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