Magnetic properties of $UCo_{1-x}Fe_xSn$

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Abstract

The magnetic properties of $UCo_{1-x}Fe_xSn$ solid solutions in the limited homogeneity range up to $x = 0.15$ were studied. A monotonous increase of both T_C (from 83 K to 98.5 K) and the magnetic moment (from 1.21 μ_B f.u.$^{-1}$ to 1.29 μ_B f.u.$^{-1}$) with increasing Fe content has been observed. This behaviour is discussed in terms of a varying 5f–d hybridization.

1. Introduction

The uranium ternary equiatomic intermetallic compounds UTX constitute a large family of actinide materials. An extensive selection of the components X (p metals: Al, Ga, In, Si, Ge, Sn, Sb) and T (late transition metals: Fe, Co, Ni, Ru, Rh, Pd, Ir, Pt) provides a wide playground for the investigation of the uranium 5f states in various ligand environments. The UTX compounds involve Pauli paramagnets (e.g. UFeAl), spin-fluctuators (URuAl, URuGa), heavy-fermion antiferromagnets (UPdIn, UNiAl), as well as local-moment ferromagnets (UCoSn, URuSn) [1]. The uranium magnetic moment varies from zero to a maximum value of about 1.5 μ_B depending on the degree of itinerancy of the uranium 5f electrons. The other components (X and T) do not contribute considerably to the magnetic moment, but affect the magnetic properties of the compounds influencing the state of the 5f electrons. The 5f magnetism in UTX compounds is associated with a huge magnetic anisotropy and relatively weak exchange interactions. The type of anisotropy is intimately connected with the symmetry of the crystal structure and with the spatial arrangement of the U atoms, in particular. Each UTX compound crystallizes in one of four crystal structures (hexagonal ZrNiAl-, GaGeLi-, orthorhombic TiNiSi- and cubic MgAgAs-type).

The magnetic ordering temperature reflects the strength of inter-ionic exchange interactions, which depend on the size of magnetic moments and on the exchange coupling between moments. The principal mechanism affecting the coupling in this class of compounds is the hybridization of the 5f states with the electronic states of ligands. A stronger hybridization causes an increase of the exchange coupling, but ultimately it leads to a decay of the moments themselves. Thus one expects a strong non-linearity in the development of T_C with doping parameters, which can be related to variations of the 5f-ligand hybridization.

In the present work, we report the results of a study of Fe substitution for Co in UCoSn, which is the material with the highest T_C of 83 K in the whole UTX family.

2. Experimental details

The $UCo_{1-x}Fe_xSn$ alloys have been prepared by melting the components (U purity 99.8%; Fe, Co, Sn 99.99%) under argon atmosphere on a water-cooled copper bottom in an arc furnace. The ingots (of approx. 3 g) were turned and remelted several times to avoid inhomogeneities, and afterwards they were wrapped in a Ta foil and annealed at 750 °C in vacuum in a sealed quartz tube for 1 week. The phase composition and lattice parameters were determined by X-ray diffraction.

Magnetization data at 4.2 K were obtained in the Megagauss Laboratory of the ISSP in Tokyo by an induction method. The measurements were performed on two series of powder samples in pulsed fields up to 40 T with a rise time of about 5 ms. In the first series, the powder grains were free to rotate in the applied magnetic field, thus simulating measurements on a single crystal along the easy-magnetization direction. In the other series, the powders with randomly oriented particles fixed by frozen alcohol were studied, which corresponds to measurements on an ideal polycrystal. For three compounds, the reliability of the pulsed-field data has been confirmed by measurements up to 21 T in the Amsterdam High Field Installation, which provides fields constant for 0.1 s.

The Curie temperatures have been determined from a.c. and d.c. susceptibility measurements, both providing T_C values which coincide within 1 K for each compound studied. The data presented below (Fig. 3) have been obtained in an 80 Hz a.c. magnetic field of 1 mT.

3. Results

UCoSn has the hexagonal crystal structure of the ZrNiAl type (the ternary variant of the Fe_2P structure, space group $P\bar{6}m2$). A limited solubility of Fe is expected in the $UCo_{1-x}Fe_xSn$ system, since the ternary compound UFeSn does not exist [2,3]. Indeed, a homogeneity range up to only $x = 0.15$ has been found. Within this range, the lattice parameter c is constant, whereas a increases systematically with increasing x (Fig. 1). A certain disagreement of the lattice parameters of pure UCoSn ($a = 713.6$ pm, $c = 398.35$ pm) with previous data on a sample prepared in a similar way ($a = 715.3$ pm, $c = 400.1$ pm [4]) points to a possible wide homogeneity range of the parent compound. The observed increase of a with increasing x exceeds only slightly the spread
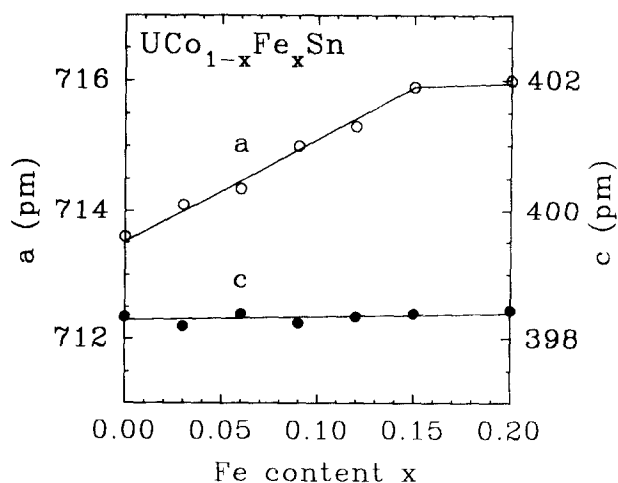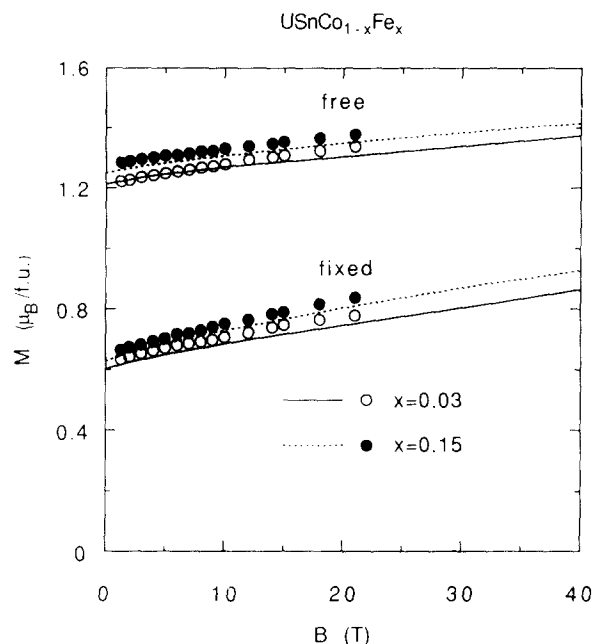
Fig. 2. Field dependence of the magnetic moment at 4.2 K for fixed and free-to-rotate powders with $x = 0.03$ and 0.15. The circles correspond to stepwise pulses with constant field during 0.1 s, lines to continuous pulses with 5 ms rise time.
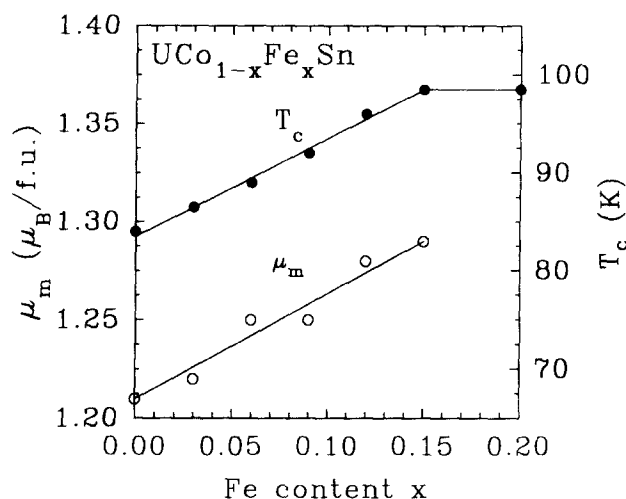
Fig. 3. Concentration dependence of the Curie temperature T_C and the spontaneous magnetic moment μ_m per formula unit.

in a values for UCoSn. Therefore, the variation of a alone cannot be considered as responsible for the changes in magnetic properties discussed below, because the properties of UCoSn of the present series and those reported in Ref. [4] for UCoSn with larger lattice parameters are very similar. The apparent disagreement in T_C is due to the fact that the T_C value of 88 K, reported in Ref. [4], has been derived from the temperature dependence of the magnetic moment in 0.1 T. The susceptibility measurements gave for this sample $T_C = 83$ K [1], which is nearly identical with the present result.

Fig. 1. Concentration dependence of the lattice parameters.

Fig. 2 shows selected magnetization curves at 4.2 K for fixed powder and powder free to rotate, both with low Fe content and at the limit of the Fe solubility. The ratio of low-field moments of fixed and free powders is equal to 0.5 for all compounds studied, which corresponds to the uniaxial type of magnetic anisotropy. The concentration dependences of T_C and of the spontaneous magnetic moment μm (free-powder value extrapolated to zero field), which is attributed to the uranium atoms in UTX, are presented in Fig. 3. One can see a slight increase of μm and a considerable increase of T_C with increasing Fe content. The T_C value of 98.5 K obtained for $x = 0.15$ represents the maximum ordering temperature reached within the whole UTX family.

4. Discussion and conclusions

The structure of uranium ternaries crystallizing in the hexagonal ZrNiAl structure consists of two types of basal-plane sheets, one containing U and T atoms, the other T and X atoms. It was found experimentally [5] that a substitution of Fe for Co in UCoAl leads to a preferential occupation of the latter type of transition-metal 2c sites by the Fe atoms, whereas the 1b sites within the U–T layers are occupied only after filling the 2c sites. This process is accompanied by a noticeable initial increase of the lattice parameter a. As a systematic increase is observed also in the $UCo_{1-x}Fe_xSn$ system, we may assume the same type of preferential occupation. A decisive role is probably played by the size factor; the somewhat larger substituting Fe atoms prefer the 'larger' 2c sites.

The hybridization of the 5f states with d states of the transition metals, which is the major delocalizing mechanism here, becomes stronger with reduced occupation of the transition metal d states, and leads to a decay of the 5f magnetism in some UTX compounds with T = Fe or Ru. A closer inspection shows weakly magnetic behaviour of UFeAl, UFeGa, URuAl and URuGa. From this point of view, the increase of both magnetization and T_C with Fe substitution is a rather surprising fact.

Compounds of the UTSn type display stronger magnetic features in comparison with their Al or Ga counterparts. Although UFeSn does not exist, we can compare the spin fluctuators URuAl and URuGa with URuSn, the latter being ferromagnetic below $T_C = 55$ K [1]. Thus, we can imagine that the onset of magnetic ordering is shifted to earlier d-metals for UTSn compounds compared with UTAl and UTGa compounds. Thus, the increase of the inter-uranium coupling can be understood as a consequence of a moderate increase of the U-ligand hybridization. Such an effect has also been observed in the $URu_{1-x}Rh_xAl$ system, in which

T_C passes through a maximum [6]. Polarized-neutron-diffraction experiments have shown an anisotropic 5f–d hybridization, which is the strongest within the U–T layers [7]. The substitution of Fe, which introduces generally a stronger 5f–d hybridization compared to the Co case, into the T–X layers may lead to a stronger magnetic coupling of the U atoms across the T–X layer, i.e. along the c-axis. The degree of the 5f delocalization, which is determined essentially by the situation within the U–T layer, where the U-atoms are closer together and where the U–T hybridization is stronger, remains unaffected.

A more problematic observation is the slight enhancement of the magnetic moment per formula unit. Firstly, we have to consider a variation of the moments on the transition metal atoms, which are essentially induced via the 5f–d hybridization. Polarized-neutron-diffraction experiments on compounds like URhAl [7] and UCoAl [8,9] show transition-metal moments of 0.3 μ_B and less than 0.1 μ_B, respectively, for the T(1b) sites, and these moments are parallel to the total magnetic moments residing on the U-ions. The moments on the T(2c) sites, which are in the planes between the strongly hybridized U–T(1b) layers, are even smaller. The increase of the bulk magnetization would mean much larger moments on the Fe atoms than on the Co atoms, which is in our opinion unrealistic. A more plausible explanation is, however, that the inter-ionic exchange coupling is important in the 5f-moment formation. Although this issue has not yet been studied systematically, some evidence of such an effect can be traced out, e.g. in the process of dilution of the uranium sublattice in UCoSn [10], which leads to a decay of the U moments in the dilute alloy limit.

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