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Formation of Kondo clouds in $U(Sn_{1-x}M_x)_3$ compounds (M = Al, Ga, Ge)

E.-W. Scheidt [a], G. Fraunberger [a], J.J. Rieger [a], A. Mielke [a], W.W. Kim [b], G.R. Stewart [a,b]

[a] *Institut für Physik, Universität Augsburg, 86135 Augsburg, Germany*
[b] *Department of Physics, University of Florida, Gainesville, FL 32611-2085, USA*

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Abstract

USn_3 has an unusually high γ value of 169 mJ $mole^{-1}$ K^{-2} in comparison with its neighboring compounds UAl_3, UGa_3, USi_3, and UGe_3. To study the formation of this high γ value we prepared pseudobinary $U(Sn_{1-x}M_x)_3$ compounds (M = Al, Ga, Si, Ge, and $x=0$, 0.1, 0.25, 0.5). From X-ray diffraction, specific-heat and susceptibility measurements we conclude that the high γ value is not only due to f-ligand hybridization, but also to the formation of Kondo clouds (40%).

Keywords: Heavy fermion; f-ligand hybridization; Kondo effect

1. Introduction

The classic feature of heavy fermion (HF) systems is the very large electronic specific heat corresponding to electronic effective masses as much as several hundred times the free electronic mass. These HF systems are intermetallic compounds containing f-electron elements (Ce, Yb, U, Np, etc.) with the exotic properties attributed to the nearly local behavior of the f-orbitals. UM_3 compounds (M being an element of group III and IV of the periodic table) are excellent systems to study the development of such a nearly local f-state. All these intermetallic UM_3 compounds crystallize in the fcc $AuCu_3$ structure, offering a particularly large set of systems for comparison with a common crystal structure, which holds constant one important parameter of the problem.

The U–U distance in these systems ranges from 4.035 Å in USi_3 up to 4.792 Å in UPb_3 [1], which is much larger than Hill's critical spacing for U systems [2]. Thus, in these compounds the electronic properties are mainly governed by hybridization of the f-electrons with the s-, p-electrons of neighboring non-f-atom sites (referred to hereafter as f-ligand hybridization) [1]. Dependent on the f-ligand hybridization strength, the electronic and magnetic properties in these compounds range from Pauli paramagnetism, with "enhanced" γ values about 40 mJ $mole^{-1}$ K^{-2} (M = Al, Si, Ge) to local-moment behavior (M = Tl, Pb) with itinerant antiferromagnetism (M = Ga, In) and spin fluctuation/heavy fermion state, for USn_3 in between. USn_3 [3,4] exhibits a large electronic specific-heat coefficient of 169 mJ $mole^{-1}$ K^{-2}, yet does not undergo a transition. Thus, USn_3 is obviously near the boundary region between itinerant and localized f-electrons, and therefore it might provide further information to investigate the various pseudobinary systems: $U(Sn_{1-x}M_x)_3$ with M = Al, Ga, In, Si, Ge, Pb.

Replacing 8% of the Sn by Pb will drive the compound into an antiferromagnetic state, which indicates that USn_3 is an exchange-enhanced paramagnet very near to a magnetic instability [5]. However, when doping USn_3 with In on the Sn site, antiferromagnetism does not occur until more than 55 at.% In is inserted into the Sn sublattice [6]. For lower In concentrations these substances show HF behavior in the vicinity of 40 at.% In, where C/T reaches a value of 530 mJ $mole^{-1}$ K^{-2} at $T = 1.35$ K. Dependent on temperature, this sample shows a low-temperature maximum in C/T. According to Lin et al. [6] this may indicate the development of a structure in the Kondo resonance at the Fermi level due to the onset of coherence [7]. From these two investigations it is not yet clear whether the large Sommerfeld coefficient in USn_3 is due to the onset of magnetic correlations (nearness to magnetic instability) or to the development of Kondo clouds leading to a

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Kondo resonance at the Fermi level. Thus, studies of pseudobinary systems $U(Sn_{1-x}M_x)_3$ with M elements of the non-magnetic UM_3 compounds (M = Al, Si, Ge) and with the weak itinerant antiferromagnetic compound UGa_3 are interesting systems to investigate the transition from usual weak paramagnetic systems to the strongly enhanced paramagnetic state in USn_3. Furthermore, it was not yet known whether the maximum of the specific-heat coefficient has been reached at USn_3 or whether minor changes in stoichiometry around that compound could increase it — as seen in $U(Sn_{1-x}In_x)_3$.

2. Experimental details

The polycrystalline samples used in this study were synthesized with a standard arc-melting technique under purified argon atmosphere. The purity of the depleted U was 99.95%, and 99.999% for Al, Ga, Si, Ge, and Sn. The elements were weighed stoichiometrically and after remelting the samples a total of three times, with the button turned over between meltings, they were checked for weight loss, which was always smaller than 0.5%. Afterwards, the samples were annealed in vacuum at 600 °C for three days.

Small pieces of these samples were used for X-ray powder diffraction studies. The room-temperature lattice constants were measured using a Siemens D5000 diffractometer in Bragg–Brentano geometry. The results of these measurements indicate that we were not successful in replacing small amounts of Sn by Si. This may be due to the small ionic radius of Si in comparison with Sn. With the exception of the U(Sn, Al)$_3$ system, where elementary Sn was detected, all the samples reported on below were single-phase. The lattice constant a_0 is equal to the U–U distance in these compounds. a_0 for U(Al, Ga, Ge)$_3$ increases linearly (Vegard's law) to $a_0 = 4.609$ Å for USn_3 (see Table 1). This indicates that the Al, Ga, and Ge atoms are going onto the Sn sites.

Magnetic d.c.-susceptibility measurements (from 1.8 K to 300 K) were performed in a Quantum Design SQUID susceptometer. Specific-heat measurements for $1.3\ \text{K} < T < 15$ K were performed on samples of 5 mg using a time relaxation technique [8,9].

3. Results and discussion

The temperature-dependent susceptibility was determined in a magnetic field of 0.5 T. Fig. 1 shows $\chi(T)$ vs. T for $U(Sn_{1-x}Ga_x)_3$ with $x = 0$, 0.1, 0.25, 0.5 as a typical result for all three systems investigated in this work. All samples below $x < 0.25$ show Curie–Weiss behavior above 70 K, with $1/\chi$ vs. T plots yielding an effective moment $\mu_{eff} \sim 2.5\ \mu_B$ (Table 1) which is close to the magnetic moment of one localized 5f electron. As is commonly seen in HF systems, this high-temperature evidence in the $1/\chi$ data for localized electrons does not result in local moment long-range order at lower temperature owing to a contribution of f-ligand hybridization and/or Kondo screening. At lower temperatures, below 50 K, the susceptibility (Fig. 1) first shows a strong enhancement which depends strongly on the Ga doping level. Finally, in the vicinity of 10 K, χ saturates. A few samples show a distinct peak at the lowest temperature (see Table 1, the samples marked with +) and also a slight saturation in the magnetization curve at $T = 1.8$ K. Therefore, we believe that the peak corresponds to magnetic correlations which may be caused by lattice distortions. For the Ge-doped com-

Table 1

Structural data for $U(Sn_{1-x}M_x)_3$ compounds (M = Al, Ga, Ge): U–U distance, $d_{U\text{–}U}$, and U–ligand, $d_{U\text{–}M}$. The Sommerfeld coefficient, γ, the magnetic susceptibility, χ, at $T = 1.8$ K (the values marked with $^+$ show a distinct peak in a χ vs. T plot at the lowest temperature) and the effective magnetic moment, μ_{eff}, are also shown. (*: data taken from the literature)

	$d_{U\text{–}U}$ (Å)	$d_{U\text{–}M}$ (Å)	χ (1.8 K) (m.e.m.u. mole^{-1})	μ_{eff} (μ_B)	γ (mJ mole^{-1} K^{-2})
USn_3	4.609	3.259	10^+	2.48	178
$U(Sn_{0.9}Al_{0.1})_3$	4.575	3.235	7.8^+	2.62	123
$U(Sn_{0.87}Al_{0.13})_3$	4.564	3.277	5.3^+	2.63	119
$U(Sn_{0.75}Al_{0.25})_3$	4.524	3.199	4.15	2.98	89
$U(Sn_{0.5}Al_{0.5})_3$	4.440	3.140	3^+	–	71
UAl_3*	4.265	3.016	1.48	–	41
$U(Sn_{0.9}Ga_{0.1})_3$	4.575	3.235	6.3	2.66	131
$U(Sn_{0.75}Ga_{0.25})_3$	4.529	3.202	5	2.90	105
$U(Sn_{0.5}Ga_{0.5})_3$	4.438	3.138	2.9	–	88
UGa_3*	4.257	3.010	2.3	–	52
$U(Sn_{0.9}Ge_{0.1})_3$	4.574	3.234	9.95^+	2.46	142
$U(Sn_{0.75}Ge_{0.25})_3$	4.520	3.196	8.1^+	2.53	96
$U(Sn_{0.5}Ge_{0.5})_3$	4.436	3.137	4.3	–	82
UGe_3*	4.206	2.974	1.15	–	20.5

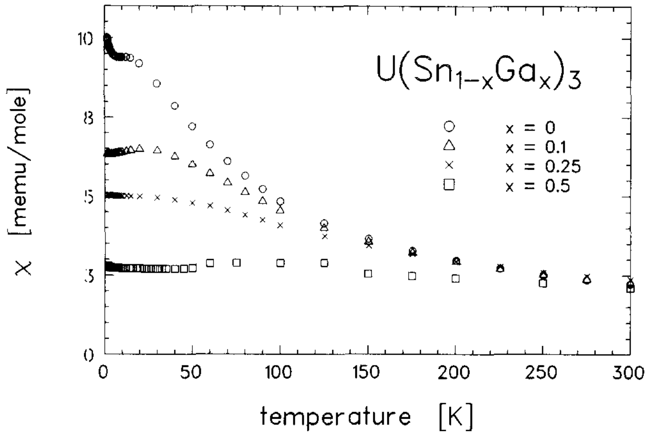

Fig. 1. D.C. magnetic susceptibility, $\chi(T)$, measured in an applied field of $B=0.5$ T. For low Ga concentration, $x \leqslant 0.25$, $1/\chi$ shows Curie–Weiss behavior above 70 K with $\mu_{eff} \sim 2.5\mu_B$.

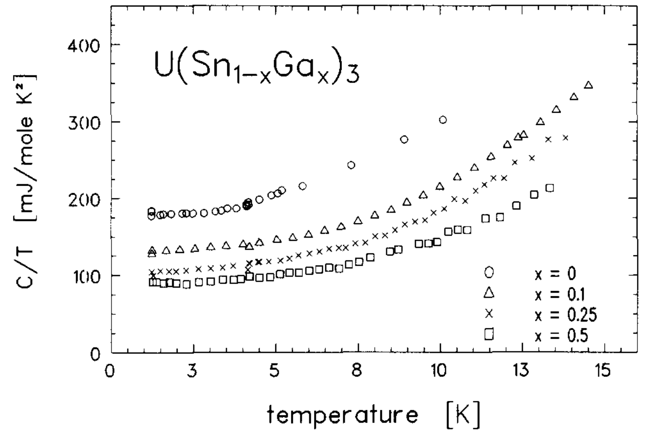

Fig. 2. Specific-heat measurements on $U(Sn_{1-x}Ga_x)_3$ plotted as C/T vs. T. The temperature dependence of C/T for USn_3 becomes constant below 4 K which may indicate the formation of a Fermi liquid state.

pounds it is very difficult to prepare samples without saturation effects in the magnetization curve. Thus, the $\chi(1.8$ K) values listed in Table 1 vary more than those of the other two systems. For all three systems the $\chi(1.8$ K) data decrease when replacing Sn by the other dopants.

In Fig. 2, heat capacity data for the $U(Sn_{1-x}Ga_x)_3$ system are displayed as C/T vs. T for the low-temperature region $T<15$ K. The data for USn_3 are in good agreement with the literature [2]. For USn_3 the temperature dependence of C/T becomes constant below 4 K. This was not observed in UAl_3, UGa_3 and UGe_3, which have normal metallic behavior in $C(T)$ (i.e. $C(T)=\gamma T+\beta T^3$) down to the lowest temperature [4]. Most of our samples with Sn concentrations down to $x>0.5$ show a tendency to become constant in C/T at low temperatures. This behavior and the observed saturation of the temperature-dependent χ data may indicate [10] the formation of a Fermi liquid state in USn_3. The Sommerfeld coefficients γ listed in Table 1 derived from a linear fit corresponding to $C(T)/T=\gamma+\beta T^2$ taking the data below 10 K.

For the following discussion the γ values are plotted vs. the U–U distances. As can be seen in Fig. 3, γ rises linearly with increasing a_0 (i.e. increasing Sn concentration) up to $d_{U-U}=4.55$ Å. From extrapolation of this straight line one would expect a γ value for USn_3 ($d_{U-U}=4.608$ Å) at around 110 mJ mole^{-1} K^{-2}. But with the rise of the U–U distance from 4.55 Å to 4.608 Å, γ increases strongly to 178 mJ mole^{-1} K^{-2}. The behavior of the susceptibility $\chi(1.8$ K) as a function of a_0 corresponds to that of γ only qualitatively. A rise of $\chi(1.8$ K) with increasing U–U distances (Table 1) can be observed, but no distinct change in the slope $\chi(1.8$ K) vs. d_{U-U} at $d_{U-U}=4.55$ Å. This was expected, because a few samples (Table 1) show a distinct peak in the susceptibility at the lowest temperature, and this peak (which is due to the small magnetic correlations discussed above) in some samples, but not in all, smears out any sharp changes.

Since d_{U-U} in all these systems is above the Hill limit of 3.4 Å [2], it is reasonable to assume that the f-ligand hybridization plays an important role for the high γ values in $U(Sn_{1-x}(Al, Ga, Ge)_x)_3$ systems [1]. Thus, the linear increase of γ up to $d_{U-U}=4.55$ Å may be due to a decreasing hybridization f-sp-band width. This is consistent with the increasing U–M distance (Table 1) as one moves from U(Al, Ga, Ge)$_3$ to USn_3. In the vicinity of USn_3, i.e. for $d_{U-U}>4.55$ Å, an additional mechanism appears. Dependent on the degree of hybridization and the position of the *local* f-electron energy relative to the Fermi energy, the Kondo clouds emerge (single-ion effect).

This speculation is supported by the interpretation of the strongly enhanced γ coefficient in $U(Sn_{0.6}In_{0.4})_3$ in Ref. [5], where the authors argue that this high

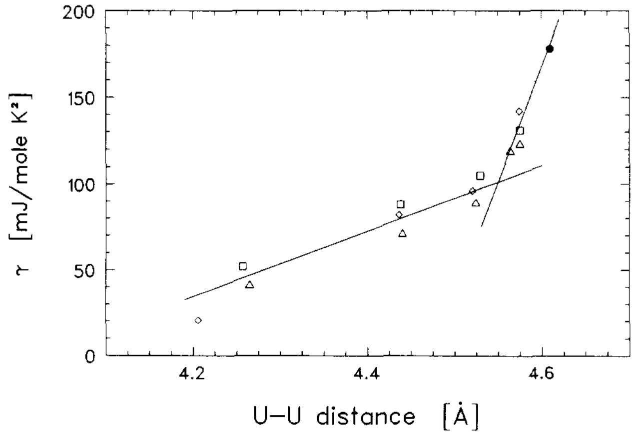

Fig. 3. The extrapolated γ values of $U(Sn_{1-x}M_x)_3$ (M = Al, △; Ga, □; Ge, ◇) are plotted against the U–U distance (USn_3: ●). There are two different slopes in the linear increase of γ with increasing Sn concentration, which is discussed in the text. (The solid lines are a guide for the eye.)

value is due to the formation of a Kondo lattice. Thus, the change in the slope of C/T vs. d_{U-U} (Fig. 3) reflects the beginning formation of single Kondo clouds. In USn_3 the contribution of the single-ion effect to the high γ value is about 40%, resulting from the difference of the measured value 178 mJ mole^{-1} K^{-2} and the extrapolated value of about 110 mJ mole^{-1} K^{-2}. This result is consistent with former assumptions [1].

In conclusion, our investigations are a strong hint that the enhanced γ coefficient of USn_3 in comparison with the neighboring compounds U(Al, Ga, Si, Ge)$_3$ is due to both f-ligand hybridization and single-ion effect.

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