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Substitution experiments in $U_3Cu_3Sn_4$ and $U_3Au_3Sn_4$

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Abstract

The results of specific heat and magnetic measurements on samples of the solid solution series $U_3(Cu_3Au_{1-x})_3Sn_4$ with $0 \leq x \leq 1$ are presented. For all samples, except $U_3Au_3Sn_4$, the susceptibility shows a peak similar to that seen in antiferromagnets. $U_3Au_3Sn_4$ shows no indication of a magnetic transition either in the specific heat or susceptibility data. Below 1 K c/T increases very rapidly, which is typical for heavy fermion systems. However, only the specific heat for $U_3Cu_3Sn_4$ shows a sharp transition. Samples with Au substitution into the Cu sites in $U_3Cu_3Sn_4$ exhibit no long range order in the specific heat. Even a small amount of Au (10%) destroys the peak in the specific heat of $U_3Cu_3Sn_4$, due to antiferromagnetic order.

Keywords: $U_3(Cu_xAu_{1-x})_3Sn_4$; Gold substitution; Specific heat; Magnetic measurements

1. Introduction

It is well known that many heavy fermion (HF) systems are near to antiferromagnetism. For example, doping of some non-ordering HF-compounds like UPt_3 with Pd [1], $CeCu_6$ with Au [2] or Ag [3] results in an antiferromagnetic ordering compound. However, the antiferromagnetic transition of other HF-compounds can be suppressed via doping, for instance U_2Zn_{17} [4] doped with Cu. For nearly all HF-systems the Sommerfeld coefficient, which represents the electronic part of the specific heat, depends on doping.

Takabatake and co-workers [5,6] reported measurements of the magnetic properties and the specific heat of the non-ordering HF-compound $U_3Au_3Sn_4$ ($\gamma =$ 380 mJ (U-mol)$^{-1}$ K^{-2}) and the antiferromagnetic ordering HF-compound ($\gamma = 280$ mJ (U-mol)$^{-1}$ K^{-2}), $T_{Néel} = 12$ K). Both compounds occur in the same cubic $Y_3Au_3Sb_4$-structure, space group $I\bar{4}3d$ [7]. The shortest U–U distance is 0.444–0.458 nm, which is well above the Hill limit. XPS, BIS [8] and UPS [9] of $U_3Cu_3Sn_4$ show that no direct exchange exists between the 5f electrons of U. The d-electrons of Cu are nearly localized and there is no strong hybridization between Cu and Sn. Also the 5f electrons of U are nearly localized. However, NMR studies of $U_3Cu_3Sn_4$ [10] show that the conduction electrons have d-like character and that the system is an exchange coupled system with antiferromagnetic order. NMR measurements on $U_3Au_3Sn_4$ indicate no magnetic order down to 1.5 K [11].

Replacement experiments of $U_3Cu_3Sn_4$ and $U_3Au_3Sn_4$ on the Cu and Sn sites were performed by Takabatake and co-workers [5,6] and Endstra et al. [12]. $U_3Cu_3Sb_4$ orders ferromagnetic. Non-isoelectronic replacement of Cu in $U_3Cu_3Sn_4$ by Pt, Ni or Pd [5,6], results for Pt and Ni in a non-ordering compound with a γ value of approximately 90 mJ (U-mol)$^{-1}$ K^{-2}. The compound with Pd is multiphased.

In view of the result that non-isoelectronic replacement of Cu or Sn changes the magnetism and the HF-behavior very drastically, we have chosen the isoelectronic replacement of Cu in $U_3Cu_3Sn_4$ to examine the formation of the HF-state and the antiferromagnetism simultaneously. The isoelectronic substitution of Ag for Cu or Au in $U_3Cu_3Sn_4$ or $U_3Au_3Sn_4$ was not successful, because even 10% Ag destroys the $Y_3Au_3Sb_4$-structure; $U_3Ag_3Sn_4$ does not form this crystal structure. Knowing that $U_3Cu_3Sn_4$ and $U_3Au_3Sn_4$ occur in the same crystal structure we had the opportunity to prepare the solid solution series of $U_3(Cu_xAu_{1-x})_3Sn_4$ with $0 \leq x \leq 1$.

2. Sample preparation

We prepared several samples with $0 \leq x \leq 1$ (see Table 1) by arc melting in a zirconium-gettered

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Table 1
Physical properties of the $U_3(Cu_xAu_{1-x})_3Sn_4$ system: x is the Cu concentration, a the lattice parameter, T_{max} is the maximum temperature of the peak in the susceptibility, Θ_{CW} is the Curie–Weiß temperature, μ_{eff} and $\chi(T_{max})$ are determined from the susceptibility; γ corresponds to the linear extrapolation of c/T vs. T^2 to $T \rightarrow 0$ K with $T \geq 1.4$ K; only for $U_3Au_3Sn_4$ and $U_3Cu_3Sn_4$ is $T \leq 0.35$ K

	x	a (nm)	T_{max} (K)	$\chi(T_{max})$ (memu(U − mol)$^{-1}$)	Θ_{CW} (K)	μ_{eff} (μ_B)	γ (mJ(U − mol)$^{-1}$ K^{-2})	γ(1.5 K) (mJ(U − mol)$^{-1}$ K^{-2})
Au	0	0.9818	—	—	−90	3.2	850	255
	0.05	0.9805	1.7	24.0	−115	3.4	—	—
	0.1	0.9792	2.5	28.0	−105	3.4	390	355
	0.2	0.9766	4.5	32.0	−105	3.4	275	275
	0.3	0.9735	6.0	35.0	−85	3.3	220	225
	0.4	0.9707	7.0	41.0	−90	3.4	—	—
	0.5	0.9677	8.0	42.5	−60	3.2	180	185
	0.7	0.9610	10.5	46.0	−60	3.2	—	—
	0.9	0.9542	11.0	38.5	−55	3.2	250	255
	0.95	0.9524	11.2	37.5	−55	3.4	310	310
	0.98	0.9513	11.7	34.0	−50	3.3	350	350
Cu	1	0.9505	12.5	29.5	−50	3.3	375	405

purified argon atmosphere. The starting elements were stoichiometrically weighed and had a purity of 99.99% for Au, 99.9995% for Cu, 99.999% for Sn and 99.95% for U. After remelting three times for homogenization the weight loss was less than 0.05%. Wrapped in tantalum foil and sealed in evacuated quartz glass tubes the samples were annealed for 5 weeks at 800°C according to Ref. [12]. The crystal structure and the phase purity of each sample were checked by X-ray powder diffraction. All samples show the expected $Y_3Au_3Sb_4$-structure with no indications of further phases.

The lattice constant increases linearly with the Au concentration $(1-x)$ from $U_3Cu_3Sn_4$ ($x=0$) 0.9505 nm to $U_3Au_3Sn_4$ ($x=1$) 0.9818 nm (see Table 1). This indicates that neither Au nor Cu will be accommodated in the lattice preferentially. For $U_3Au_3Sn_4$, the lattice constant agrees very well with Ref. [11]. Compared with Ref. [6] the lattice constants for $U_3Cu_3Sn_4$ and $U_3Au_3Sn_4$ are smaller.

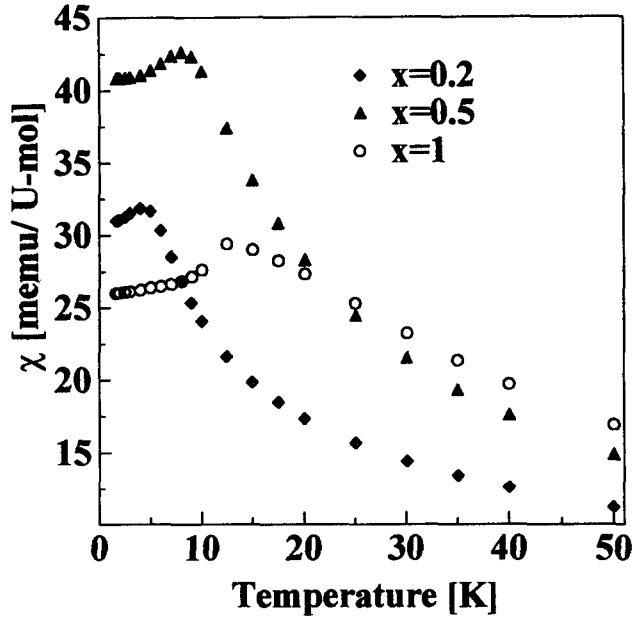

Fig. 1. Low temperature results of the d.c.-susceptibility of $U_3(Cu_xAu_{1-x})_3Sn_4$ with $x = 1$, 0.5 and 0.2 in 5 kG. The temperature of the maximum is T_{max}.

3. Susceptibility

The magnetic d.c.-susceptibility was measured with a Quantum Design SQUID magnetometer in a field of 5 kG, between 1.7 and 400 K. For all samples the susceptibility follows a Curie–Weiß law above 100 K. The paramagnetic Curie-temperature Θ_{CW} is between −115 and −50 K, μ_{eff} varies between 3.2 and 3.4 μ_B (see Table 1). The value of μ_{eff} corresponds nearly with the theoretical expected $5f^2$ ($\mu_{eff} = 3.58$ μ_B) or $5f^3$ ($\mu_{eff} = 3.62$ μ_B) state of uranium.

Below 20 K in $U_3(Cu_xAu_{1-x})_3Sn_4$, for all samples except $U_3Au_3Sn_4$, $\chi(T)$ goes through a maximum at T_{max} and for $1 \leq x \leq 0.2$ the susceptibility is constant ($=\chi_0$) well below T_{max} (see Table 1 and Fig. 1). For $U_3Au_3Sn_4$ (not shown) $\chi(T)$ increases with decreasing temperature; no maximum is visible.

With decreasing Cu concentration T_{max} shifts from 12.5 K ($x = 1$) to lower temperatures. It is approximately 1.7 K for $x = 0.05$. $\chi(T_{max})$ and χ_0 reach their highest value for $x = 0.7$. The results for $U_3Cu_3Sn_4$ agree with the measurement of Takabatake and coworkers [5,6], and for $U_3Au_3Sn_4$ with the results of Takagi et al. [11].

Additional $\chi(T)$ measurements up to 50 kG for the sample with $x = 0.3$ were performed. The maximum broadens with increasing magnetic field, while T_{max}, $\chi(T_{max})$ and χ_0 decrease (not shown). At 50 kG no clear maximum is visible. This behavior indicates an

antiferromagnetic transition with $T_{Néel} = T_{max}$ for all samples with $x \geq 0.05$.

4. Magnetization

Magnetization measurements at 2 K up to 70 kG indicate a weak metamagnetic transition for samples with $x \geq 0.2$ (see Fig. 2). The turning point of the curves, which marks the metamagnetic transition increases monotonously to higher magnetic fields with increasing Cu concentration x ($x = 0.2$ $B_T \approx 1.5$ kG, $x = 1$ $B_T \approx 47$ kG). The magnetization of the samples with $x < 0.2$ show no metamagnetic transition and tend to saturate slightly in high fields (see Fig. 2). For the sample with $x = 0.3$ the turning point is $B_T \approx 7.5$ kG, so the additional susceptibility measurement in 50 kG is well above the metamagnetic transition and so no maximum is visible.

5. Specific heat

We have measured specific heat for selected samples (see Table 1) between 1.3 and 18 K with a standard relaxation method [13]. For $U_3Cu_3Sn_4$ and $U_3Au_3Sn_4$, additional measurements between 0.35 and 1.5 K were performed.

The results for $U_3Cu_3Sn_4$ ($x = 1$) agree with those of Takabatake and co-workers [5,6]. The specific heat of $U_3Cu_3Sn_4$ shows a sharp λ-peak at 11.7 K. (see Fig. 3) This peak corresponds with the hump of the

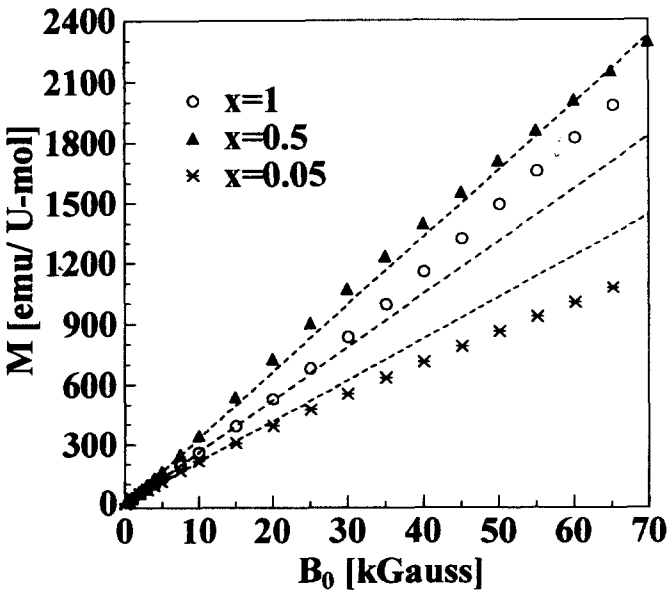

Fig. 2. Magnetization of $U_3(Cu_xAu_{1-x})_3Sn_4$ with $x = 0$, 0.5 and 1. The lines are the extrapolation of linear fits in the range of $B_0 \leq 10$ kG to make the metamagnetic transition visible for $x = 1$ and $x = 0.5$.

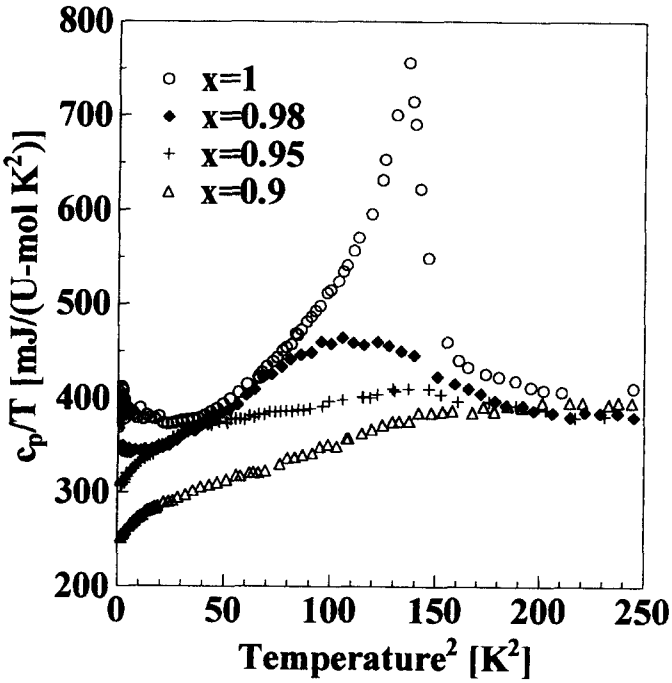

Fig. 3. Specific heat divided by T vs. T^2 for $U_3(Cu_xAu_{1-x})_3Sn_4$ with $x = 1$, 0.98, 0.95 and 0.9.

susceptibility (see Fig. 1) and so belongs to a long range antiferromagnetic transition. Below 6.5 K the specific heat decreases linearly. With decreasing temperature c/T increases between 6 and 1.25 K and reaches a maximum at 1.25 K and is nearly temperature independent below 0.7 K. The maximum c/T value is 410 ± 10 mJ (U-mol)$^{-1}$ K^{-2} and γ is 375 ± 10 mJ (U-mol)$^{-1}$ K^{-2}. If we only use the data down to 1.6 K for the linear extrapolation, as was the case in Refs. [5,6], we obtain good agreement.

With increasing Cu concentration the λ-peak broadens (see Fig. 3) and the maximum temperature T_{max} and the value of c/T for $T = T_{max}$ decrease. In the specific heat a very broad hump with a maximum exists only for $x = 0.98$. The curves of other samples show only a small bend with no maximum. In c/T for $x = 0.98$ the temperature of the maximum is approximately 10 K, and for $x = 0.95$ only a broad hump exists. For $x \geq 0.9$ the peak disappears further (see Fig. 3). For $x = 0.8$, no clear indication of a hump is visible. All samples with $x \leq 0.9$ show no indication in the specific heat for an antiferromagnetic transition.

For $x = 1$ and $x = 0.98$ we observe an upturn of c/T (not in c) well below the transition temperature. For $x = 0.98$ the upturn is smaller. For $0.95 \geq x \geq 0.3$, however, a downturn is seen. It might be that this effect is additive. One part of the sum is the normal linear behavior of a metal ($c/T = \gamma + \beta T^2$, with γ and β constant); the other part is the hump of the nearly disappeared transition.

The smallest γ is with 180 mJ (U-mol)$^{-1}$ K^{-2} found

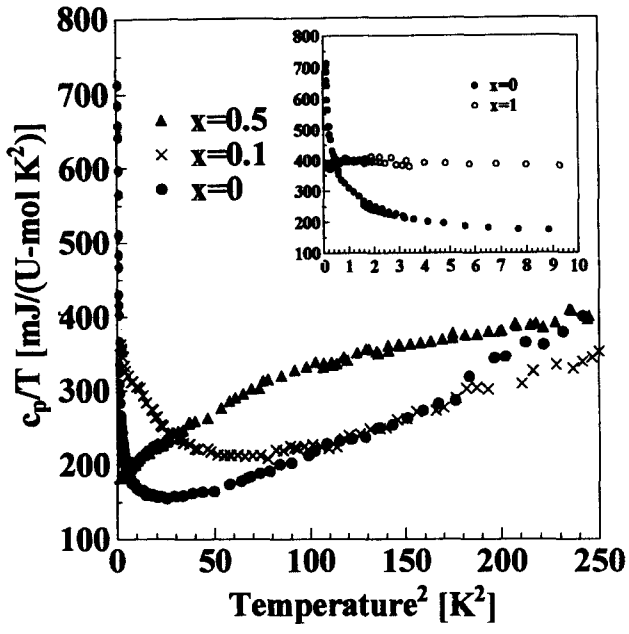

Fig. 4. Specific heat in a c/T vs. T^2 plot of $U_3(Cu_xAu_{1-x})_3Sn_4$ with $x = 0$, 0.1 and 0.5. The inset shows the low temperature behavior of c/T vs. T^2 for $U_3Au_3Sn_4$ and $U_3Cu_3Sn_4$.

for $x = 0.5$. For $x = 0.2$ c/T is constant below 12 K; γ is 275 mJ (U-mol)$^{-1}$ K^{-2}. For $x = 0.1$ and 0, c/T shows an upturn again (see Figs. 3 and 4).

The highest c/T ratio at 1.5 K is observed for $U_3Cu_3Sn_4$ (see Table 1). For $U_3Au_3Sn_4$ the measurement agrees with the results of Tagaki et al. [11]. Between 1.6 and 0.35 K, c/T increases very quickly and reaches $c/T = 715$ mJ (U-mol)$^{-1}$ K^{-2} at 0.35 K (Fig. 4). The extrapolation to $T \rightarrow 0$ is 850 ± 20 mJ (U-mol)$^{-1}$ K^{-2}. We have no indication of a transition, in agreement with the NMR results [11].

The integral of c/T vs. T, which is proportional to the entropy, becomes smaller with decreasing x. In the range the ordering part of the entropy disappears.

6. Conclusion and discussion

We have measured specific heat and d.c.-susceptibility for $U_3(Cu_xAu_{1-x})Sn_4$ with $0 \leq x \leq 1$. With increasing Au concentration, first the long range antiferromagnetic order disappears and changes to short range antiferromagnetism, then the antiferromagnetic order disappears completely. The long range order is marked by the peak in the specific heat, the short range order is marked by the metamagnetic transition in the magnetization. A similar behavior is known from of the doping experiments of UPt_3 with Pd [1].

One main influence of substitution is a change of the lattice constant. It increases linearly from Cu to Au. In this system we observe a change of the magnetic- and HF-behavior. None of the changes in, T_{max}, Θ_{CW}, μ_{eff}, χ_0, B_T, $\gamma(1.5\ K)$ or γ are linearly connected with the dopant concentration or with the lattice constant. So this indicates that the different behavior is not only dependent on the volume of the unit cell.

The U–U distance is well above the Hill limit and so too large for direct exchange. Hence the magnetism is probably due to an RKKY mechanism. The hybridization between the 5f states of U and the valence electron states of nearest neighbor T atoms (= Cu, Au, $d_{U-T} = 0.3006a$, a is the lattice constant) and/or the next neighbor Sn atoms ($d_{U-Sn} = 0.3349a$) is probably important.

However, it is doubtful whether the U–Sn hybridization is the decisive factor. When the interatomic spacing increases, the hybridization should decrease. According to the picture given by Doniach [14], the moment formation should increase. This is seen in doping experiments of $CeCu_6$ with Au [2] or Ag [3]. For $U_3(Cu_xAu_{1-x})_3Sn_4$ both the long range and short range magnetic order disappear with increasing lattice constant. Consequently, no simple argument can explain this effect. An explanation may be found in the difference between Cu and Au responsible for the change of the U–T hybridization. Cu and Au are isoelectronic, but their electronic configuration is different. The outer shells of Cu are 3d and 4s, for Au 5d and 6s. The 3d-electrons are more localized than the 5d-electrons. Therefore the hybridization may be different, as has also been found in UPt_4M with M = Au, Ag, Cu [15].

Another indication for the importance of the U–T hybridization is that $U_3(T_xAg_{1-x})_3Sn_4$ shows a different crystal structure, although Ag is isoelectronic with Cu and Au, and the atomic and ionic radii of Ag and Au are nearly similar.

The T–U distance becomes larger when replacing Cu by Au, but it seems that the hybridization of the U-5f states with the conduction electrons increases nevertheless. Therefore the U-5f electrons might become less localized in the Au-rich alloys.

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