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HYBRIDIZATION EFFECTS IN $UCu_{5-x}Au_x$ COMPOUNDS

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We review the results of bulk and neutron diffraction measurements on the $UCu_{5-x}Au_x$ system crystallizing in the cubic $AuBe_5$ -type structure. The observed properties may be understood in the light of competition between Kondo effect and RKKY exchange interactions. Effects of $5f$ -ligand hybridization between the U-atoms occupying the 4a-sites and the Au- or/and Cu-atoms placed at the 4c- and 16e-positions, respectively, are supposed to be different. We show that the preferential occupation of 4c-sites by Au has a marked effect on the magnetic properties of the investigated system.

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Among the $UT_{5-x}M_x$ alloys, where T is Ni, Cu and Pt and M is Cu, Ag, Au and Pd, the $UCu_{5-x}M_x$ phases attract much attention. One of the reasons is the fact that UCu_5 is a heavy-fermion antiferromagnet [1-4]. Moreover, this compound forms a gap in the electronic density of states below 1.2 K [1]. It has been interpreted that heavy fermions form a quasi-independent subsystem, which is associated with the weak magnetism or with spin-density-wave behaviour [4].

It has been recognized that the change of chemical composition in the $UCu_{5-x}M_x$ system strongly influences its low temperature properties. In the work of van Dall et al. [5] on $UCu_{5-x}Ni_x$, it was pointed out that replacing Cu by Ni leads to rapid disappearance of the antiferromagnetic ordering. A similar effect has been observed by us in the $UCu_{5-x}Pd_x$ alloys [6]. On the other hand, Ott et al. [1] have shown that when one Cu-atom in UCu_5 was replaced by the Ag-atom, then the linear coefficient of the specific heat, γ , extrapolated to $T = 0$ K rised from 86 mJ/mole K^2 to 310 mJ/mole K^2 and the Néel temperature increased from 15 K to 18 K. Replacement of Cu by Au in the $UCu_{5-x}Au_x$ system obviously should result in an analogous effect, because both the Ag and Au atoms have similar electronic configurations and atomic sizes. As expected, we have observed an increase in the Néel temperature from 15 K for UCu_5 to 27 K for UCu_4Au [7]. However, a

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further Au-substitution causes the decrease in the T_N value [7]. Therefore, what is of much interest here, is the answer on the question of the mechanism determining a change of the Néel temperature and the ordered uranium moment, μ_{ord} , in the $\text{UCu}_{5-x}\text{Au}_x$ system. From neutron diffraction experiments UCu_5 was identified to have an ordered moment 0.9 [2] or 1.3 μ_B [3] at 4.2 K and 1.55 μ_B at 10 mK [4]. UCu_4Au has been also studied by neutron diffraction measurements [8]. Surprisingly, despite the large value of T_N , μ_{ord} was found to be about 0.7 μ_B [8], thus lower than that of UCu_5 . Recently, a neutron diffraction study of UCu_3Au_2 has been performed at the LLB (CEN-Saclay, France). For this compound, a small magnetic peak (3/2, 1/2, 1/2) was observed at 1.3 K (Fig. 1), owing to a very small value of the magnetic moment, being probably less than 0.5 μ_B [9].

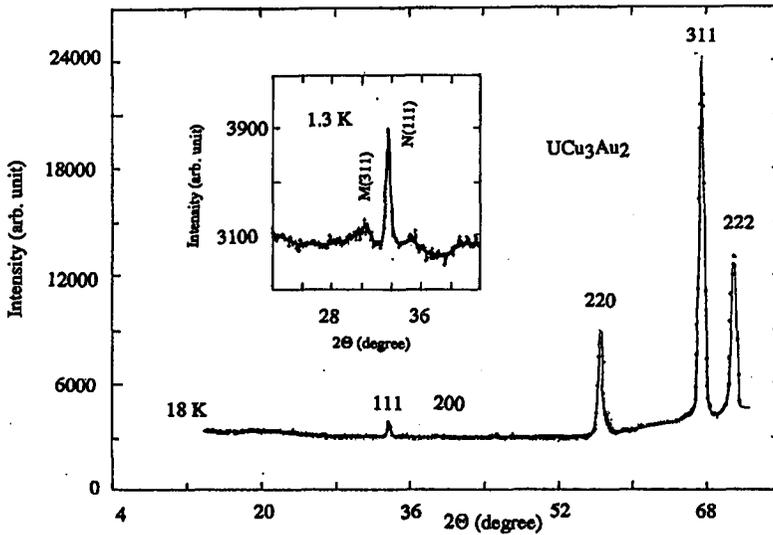


Fig. 1. Neutron diffraction patterns in UCu_3Au_2 ; diagram at 18 K and 1.3 K.

The investigated $\text{UCu}_{5-x}\text{Au}_x$ system crystallizes in the fcc AuBe_5 -type structure (space group $F\bar{4}3m$), in which the uranium atoms are situated at the 4a-positions, and the two inequivalent 4c- and 16e-sites, are occupied by Cu/Au atoms. Therefore, each uranium atom is surrounded by 12 Cu(Au) atoms as nearest ligands and by 4 Cu- or Au-atoms as the next nearest ligands (see below). In Table I we collect the lattice parameters and site occupancy found from the neutron diffraction measurements at low temperatures.

The results presented in Table I clearly show that Au-atoms as larger atoms have a strong preference to occupy the special 4c-sites in the AuBe_5 -type structure. These findings confirm earlier NMR investigations of similar systems by Umarji et al. [10].

TABLE I

Structural parameters for the $UCu_{5-x}Au_x$ system.

Compounds	a [Å] (± 0.001)	Crystallographic positions			Refs.
		4a (0,0,0)	4c (1/4, 1/4, 1/4)	16e (5/8, 5/8, 5/8)	
UCu_5	7.038	U	Cu	4Cu	[2, 3]
UCu_4Au	7.134	U	Au	4Cu	[8]
UCu_3Au_2	7.285	U	Au	3CuAu	[9]
UCu_2Au_3	7.425	-	-	-	-

The magnetic structure of $UCu_{5-x}Au_x$ compounds [2-4, 8, 9] displays a common feature: uranium moments align ferromagnetically in sheets parallel to the (111) plane and couple antiferromagnetically with the adjacent layers. The magnetic moments of uranium are then directed along the [111] axis and the magnetic unit cell is eight times larger than the chemical one with the wave vector $k = (1/2, 1/2, 1/2)$. This structure is labelled as AF II-type and is known as the MnO-type [11]. It should be noted here that the possible spin structures in the case of fcc lattice have been discussed on the basis of molecular field theory [12]. Denoting the nearest neighbour and next-nearest neighbour coupling by J_1 and J_2 , respectively, the AF II-type structure falls in the region lying between the $J_1 = -J_2$ and $J_1 = 2J_2$ lines in the diagram of Ref. [12]. On the other hand, the recent NMR data [13] for UCu_5 have suggested the occurrence of a quadrupole- q structure which below 1 K is supposed to be modified due to the formation of a spin excitation gap [13]. However, contrary to this result, the powder neutron diffraction experiments made down to 10 mK has shown no phase transition at $T = 1.2$ K [4]. In Table II, we present the most important parameters found for this system by means of the magnetic susceptibility, electrical resistivity, specific heat and neutron diffraction measurements.

TABLE II

Magnetic characteristics for the $UCu_{5-x}Au_x$ system.

Compounds	Θ_p	μ_{eff}	T_N	μ_{ord}	$\rho(300)$	$\gamma(0)$	Refs.
	[K]	[μ_B]	[K]	[μ_B]	$\rho(4.2)$	[mJ/mol K ²]	
UCu_5	-88	2.66	15	0.9-1.55	1.24	86	[1-4, 7]
UCu_4Au	-91	2.68	27	0.7	0.69	-	[7, 8]
UCu_3Au_2	-71	2.71	13	< 0.5	0.79	-	[7, 9]
UCu_2Au_3	-76	2.92	para-	-	0.71	-	[7]

As can be seen from this table, the uranium ordered moment decreases dramatically with increasing Au concentration, while T_N and Θ_p reach their maxima for UCu_4Au .

The different changes in T_N and μ_{ord} on composition for the $\text{UCu}_{5-x}\text{Au}_x$ system could be explained if one considers the interplay between the Kondo- and RKKY-type interactions. Due to the fact that the U-U distances, $d_{\text{U-U}}$, are in these compounds beyond 5 Å, the direct $5f-5f$ overlapping cannot be responsible for these changes. The magnetic properties of this system will be mainly dependent on the U- $5f$ and ligand- spd electron interaction parameter, J . In the Kondo-lattice model [14], this parameter is equivalent to the exchange integral J_{sf} involved in the hybridization matrix element, V_{sf} , and the position of the f -level with respect to the Fermi level, $E_F - E_f$, as illustrated by the following equation [15]:

$$J_{sf} \approx -|V_{sf}|^2 / (E_F - E_f).$$

Doniach [14] has shown that for a small J_{sf} value the ground state is always magnetic. In this picture, however, the Néel temperature is not a monotonic function of J_{sf} but passes through a maximum at a critical value of J'_{sf} and then falls to zero at J''_{sf} (see Fig. 2). For the $\text{UCu}_{5-x}\text{Au}_x$ system we have shown that the Kondo-like behaviour takes place in the overall composition range [7]. This

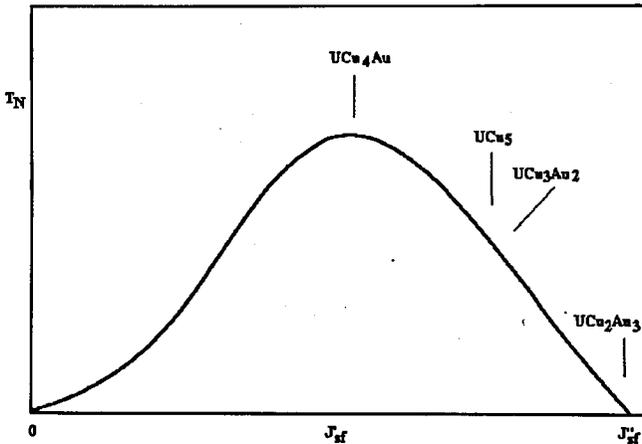


Fig. 2. Schematic dependence of the Néel temperature on the exchange parameter J_{sf} for $\text{UCu}_{5-x}\text{Au}_x$ system.

feature together with the diminishing of critical temperature in UCu_2Au_3 [7] indicates that the system lies in the region above J'_{sf} . In order to understand the observed behaviour one should distinguish two different exchange constants, i.e. $J_{ac} \approx |V_{ac}|^2$ and $J_{ae} \approx |V_{ae}|^2$. The $|V_{ae}|$ is the hybridization term between uranium at the 4a-position and the four ligands being at the 4c-position distanced by $R_{ac} = a\sqrt{3}/4$. The $|V_{ae}|$ stands for the hybridization term between uranium (4a) and the twelve ligands occupying the 16e-position with the uranium-ligand spacing equal to $R_{ae} = a\sqrt{11}/12$. According to the first principles one may expect

that the $|V_{ae}|$ -effect predominates, hence

$$J_{sf} \approx -|V_{ae}|^2 / (E_F - E_f).$$

On the other hand, the increase in the atomic volume should lead to a decrease in the J_{sf} value. This situation occurs in the case of substitution of Cu by one Au-atom. As we have shown above the gold atoms in UCu_4Au preferentially occupy the 4c-sites and the $|V_{ae}|$ should decrease only due to the lattice expansion. According to the discussion by Doniach [14] mentioned above, when J_{sf} decreases starting from a large value, the system will also show a magnetic ordering and then it will give rise to a maximum in the T_N value. This explains the change in T_N value of UCu_4Au . Moreover, we suggest heavy fermion behaviour in this compound because T_N is proportional to $J_{sf}^2 N(E_F)$. A further increase in the Au-content ($x = 2, 3$) in the system $UCu_{5-x}Au_x$ forces gold to occupy the 16e-sites. Assuming that the hybridization term V_{ae} is much larger for the U-Au(16e) pairs than that attributed to the U-Cu(16e) ones we can scale the observed behaviour in the $UCu_{5-x}Au_x$ system according to the Doniach relationship [14], as illustrated in Fig. 2.

As discussed above, it is reasonable to assume that the magnetic properties of $UCu_{5-x}Au_x$ are related to the preferential order of Au-atoms in the 4c-sites of the $AuBe_5$ -type structure which is crucial in the strength of 5f-ligand electrons hybridization. With the help of the above mechanism, we are also able to understand the increase in the γ value found, e.g., in case of UCu_4Ag [1] and UPt_4Au [16], both compounds belong to the heavy-fermion systems.

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