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Journal of Alloys and Compounds 317–318 (2001) 336–339

Journal of ALLOYS AND COMPOUNDS

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Magnetism of $U_4(Ru_{1-x}Os_x)_7Ge_6$ solid solutions

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Abstract

$U_4Ru_7Ge_6$ orders ferromagnetically at low temperature, displays a Kondo-like resistivity behaviour and has heavy-fermion properties, whereas $U_4Os_7Ge_6$ is a Pauli paramagnet. We measured the magnetisation and susceptibility of eleven $U_4(Ru_{1-x}Os_x)_7Ge_6$ compounds ($0 \leq x \leq 1$ with steps of 0.1) between 2 K and 300 K under external magnetic fields up to 6.5 T, using a SQUID magnetometer. For the solid solutions, we observe clearly a rapid loss of magnetism for increasing x: the ordering temperature decreases from 12 K for $x=0$ down to less than 2 K for $x=0.3$, whereas compounds with higher x are paramagnetic. The susceptibilities of all compounds follow a modified Curie–Weiss law. Values of Curie–Weiss parameters are discussed in the frame of the Doniach model.

Keywords: Uranium; Magnetic properties; Kondo lattice; Intermetallic compounds

1. Introduction

Uranium intermetallics have attracted considerable interest with the discovery of compounds exhibiting heavy fermion behaviour or superconductivity, sometimes even coexisting e.g. in the case of URu_2Si_2 [1] or UPd_2Al_3 [2]. A key role is played by f-elements intermetallics in the elucidation of particular magnetic and electronic properties. Since uranium is by far the most common 5f element and the easiest to handle, its compounds have been studied widely and constitute the main object of investigation of actinide compounds. In the frame of a better understanding of the magnetic and electronic properties of the actinides and the search for new compounds exhibiting interesting behaviour, we investigated the solid solutions $U_4(Ru_{1-x}Os_x)_7Ge_6$.

Since the discovery and first characterisation of the cubic $U_4Re_7Si_6$ 20 years ago [3], a number of isostructural $R_4T_7X_6$ (R=rare earth; T=Ru, Os, Rh, Ir; X=Si, Ge) have been synthesised [4,5]. More recently, isostructural uranium and neptunium compounds were obtained in this family and their magnetic and electronic properties investigated: $U_4Tc_7Si_6$, $U_4Tc_7Ge_6$, $Np_4Ru_7Ge_6$ [6], $U_4Ru_7Ge_6$ and $U_4Os_7Ge_6$ [7,8]. $U_4Ru_7Ge_6$ orders ferromagnetically at low temperature, displays a Kondo-like resistance behaviour, and heavy fermion-properties ($\gamma_0 \approx 109$ mJ/mol U K^2). On the contrary, $U_4Os_7Ge_6$ is a Pauli paramagnet, so that intermediate $U_4(Ru_{1-x}Os_x)_7Ge_6$ compounds should exhibit interesting properties as magnetic order is expected to be progressively destroyed by Kondo interactions. A similar situation occurs for URu_2Si_2 (heavy fermion, antiferromagnetic at 17.5 K) and UOs_2Si_2 (Pauli paramagnet) where the 5f–d hybridisation increases from the Ru 4d to Os 5d orbitals [7]. It should be mentioned that the neptunium counterpart $Np_4Ru_7Ge_6$, studied by Mössbauer spectroscopy, is close to a magnetic instability and has a non-magnetic ground state that may be understood within the Kondo lattice/RKKY model. Moreover, the observation of an enhanced susceptibility at low temperature may indicate heavy-fermion behaviour [9].

2. Experimental

The $U_4(Ru_{1-x}Os_x)_7Ge_6$ samples were prepared by arc melting the pure constituents in stoichiometric amounts under a purified argon atmosphere. The samples were characterised by X-ray powder diffraction. They all crystallise in the cubic $U_4Re_7Si_6$ structure (space group *Im3m*), derived from the $AuCu_3$ structure [3,4]: The uranium atoms are located on the gold sites, the germanium atoms occupy half the copper sites and the ruthenium or osmium atoms fill the other half of copper sites plus interstitial sites.

The magnetisation and susceptibility measurements were

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0925-8388/01/$ – see front matter
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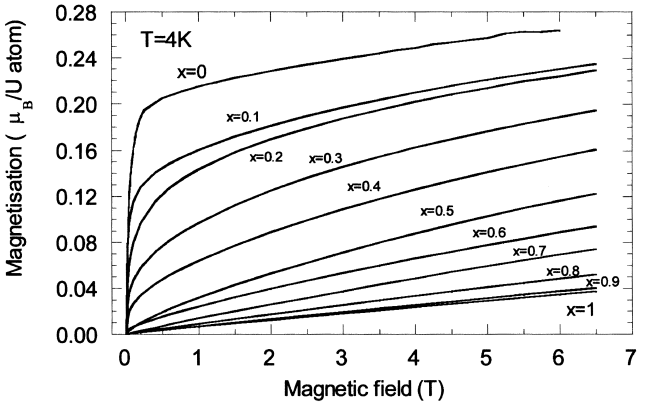

Fig. 1. Magnetisation of $U_4(Ru_{1-x}Os_x)_7Ge_6$ compounds at 4 K.

performed using a SQUID magnetometer on fixed powder samples. The experiments were carried out between 2 K and 300 K in magnetic fields up to 6.5 T.

3. Results and discussion

The magnetisation curves of $U_4(Ru_{1-x}Os_x)_7Ge_6$ show the occurrence of ferromagnetic order at low temperature for $x \leq 0.3$ whereas $U_4(Ru_{1-x}Os_x)_7Ge_6$ compounds with $x > 0.3$ remain paramagnetic down to 2 K (Fig. 1). Fig. 2 shows the magnetisation curves of $U_4(Ru_{0.9}Os_{0.1})_7Ge_6$ obtained for various temperatures, indicating the onset of ordering between 8 and 10 K. Curie temperatures were determined by performing Arrott plots, displayed in Fig. 3 for $U_4Ru_7Ge_6$ whose Curie temperature was claimed to be either 10–13 K [7] or 6.8 K [8].

Above ~50 K the susceptibility of all measured compounds follows a modified Curie–Weiss law: $\chi = C/(T-\theta_p)+\chi_0$ where the χ_0 term – mainly observed in actinide compounds – represents a contribution which may originate from various effects, but today's most accepted explanation seems to be the enhanced Pauli paramagnetism

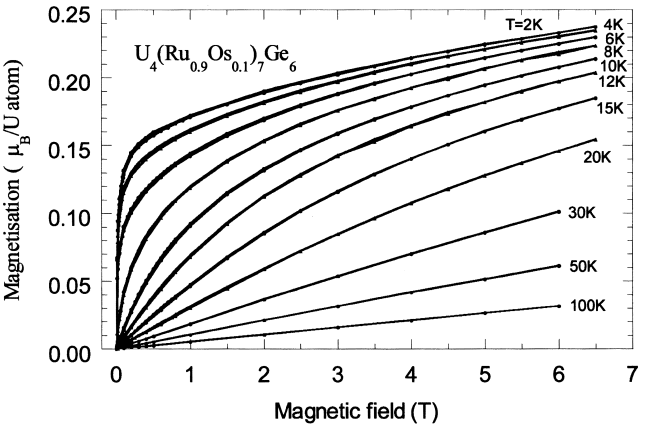

Fig. 2. Magnetisation of $U_4(Ru_{0.9}Os_{0.1})_7Ge_6$ at various temperatures.

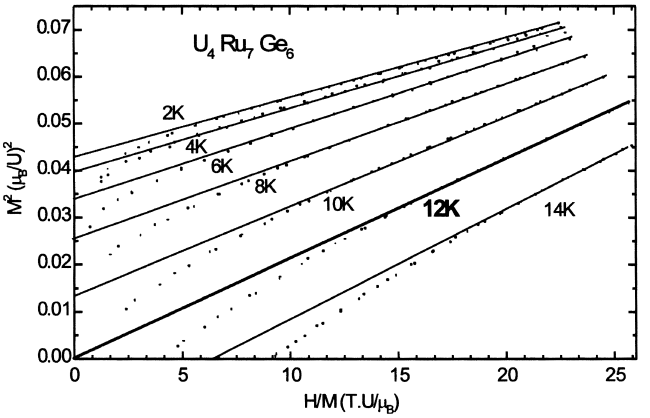

Fig. 3. Arrott plots of $U_4Ru_7Ge_6$ yielding $T_C = 12$ K.

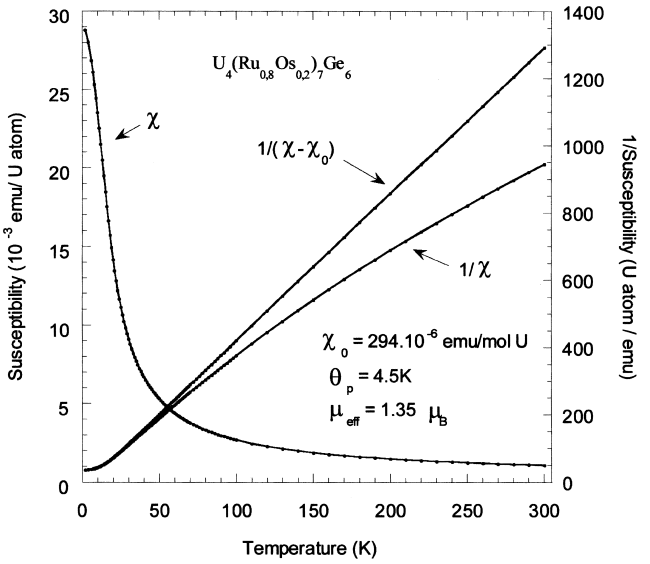

Fig. 4. Susceptibility and inverse susceptibility of $U_4(Ru_{0.8}Os_{0.2})_7Ge_6$. Plotting $1/(\chi-\chi_0)$ and checking that it represents a straight line validates the modified Curie–Weiss law used for the fit.

Table 1
Fitted parameters of the modified Curie–Weiss law $\chi = C/(T-\theta_p)+\chi_0$ and Curie temperature T_C of $U_4(Ru_{1-x}Os_x)_7Ge_6$ compounds. μ_{eff} and χ_0 are given per U atom

x	μ_{eff} (μ_B)	χ_0 (10^{-6} emu/mol)	θ_p (K)	T_C (K)
0	1.38(3)	279(15)	9(2)	12.0(5)
0.1	1.36(4)	455(26)	7(2)	9.0(5)
0.2	1.35(4)	294(23)	5(2)	7.0(5)
0.3	1.33(2)	344(10)	1(2)	~1.0[a]
0.4	1.34(2)	472(10)	−4(2)	–
0.5	1.32(9)	377(90)	−5(3)	–
0.6	1.29(2)	270(30)	−15(4)	–
0.7	1.26(7)	387(70)	−15(9)	–
0.8	1.28(2)	275(10)	−43(5)	–
0.9	1.24(2)	405(20)	−58(5)	–
1	1.24(5)	378(43)	−65(8)	–

[a] Estimated from extrapolation of Arrott plots.

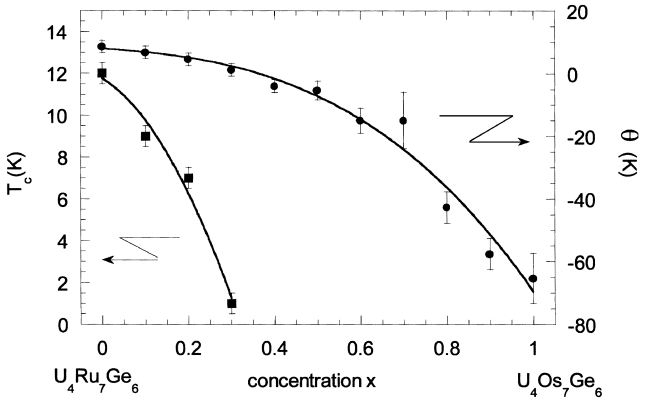

Fig. 5. Curie temperature T_C and paramagnetic Curie temperature θ_p of $U_4(Ru_{1-x}Os_x)_7Ge_6$ compounds as a function of the concentration x.

of unbound electrons [10–12]. The χ_0 term added to the Curie–Weiss susceptibility appears then to be related to the hybridisation of the 5f orbitals, via the concentration of 5f unbound electrons i.e. the delocalisation of 5f electrons. However it should be noted that χ_0 is very sensitive to eventual sample impurities or defects. Fig. 4 shows for example the typical susceptibility and inverse susceptibility of $U_4(Ru_{0.8}Os_{0.2})_7Ge_6$. The inverse of $(\chi-\chi_0)$ is also plotted and appears to be a straight line which shows self consistently that our modified Curie–Weiss fit with a constant χ_0 term is valid. The parameters obtained in the fits for all $U_4(Ru_{1-x}Os_x)_7Ge_6$ compounds are listed in Table 1. It is expected that the paramagnetic $U_4Os_7Ge_6$ compound exhibits more hybridisation and then a higher χ_0 value than the ferromagnetic $U_4Ru_7Ge_6$ but no clear trend can be extracted from our data.

The values of θ_p, relatively close to T_c, decrease from 9 K for $x=0$ down to 1 K for $x=0.3$ (ferromagnetism) and then become negative (non-magnetic Kondo lattice) down to -65 K for $x=1$ (Fig. 5).

The effective moment slightly decreases as x increases, from $\mu_{eff}\approx1.38\ \mu_B$ for $U_4Ru_7Ge_6$ to $\mu_{eff}\approx1.24\ \mu_B$ for $U_4Os_7Ge_6$. These values do not correspond to the free ion value, neither for U^{3+} ($5f^3$; $\mu_{eff}\approx3.62\ \mu_B$) nor for U^{4+} ($5f^2$; $\mu_{eff}\approx3.58\ \mu_B$). This is a common situation in actinide intermetallics. In addition, the relatively good agreement between T_c and θ_p does not suggest the occurrence of strong crystal–field effects. The approach of the modified Curie–Weiss law assuming crystal–field effects and using renormalised parameters [13] yields few difference for χ_0 and roughly the same value for μ_{eff}, which remains approximately constant. These results rather suggest a pronounced Kondo character increasing with x.

The $U_4(Ru_{1-x}Os_x)_7Ge_6$ system may be represented using the Doniach schematic diagram [14] illustrating the

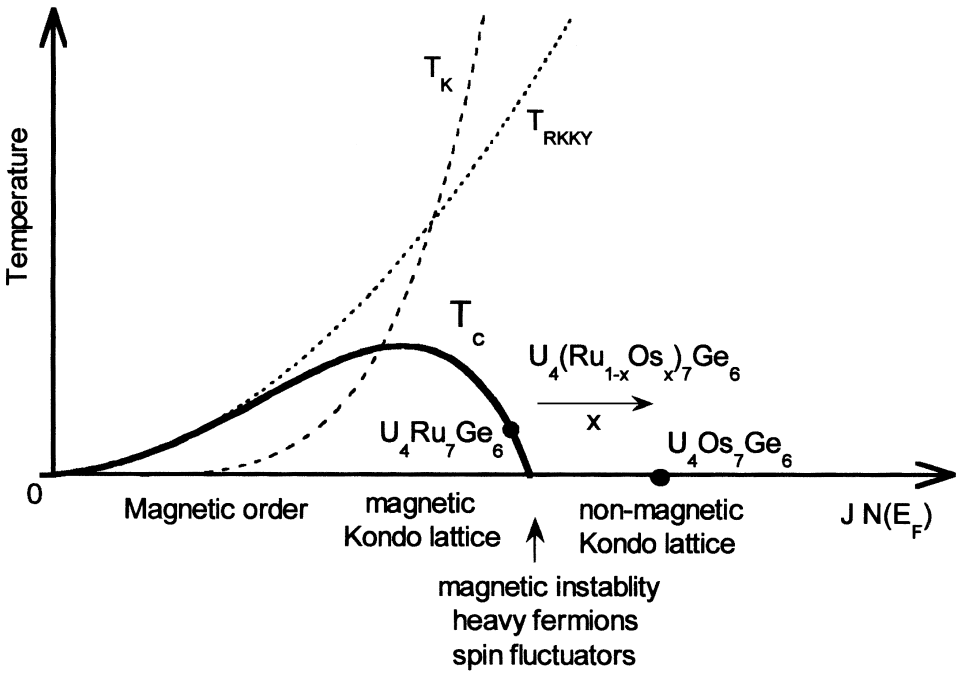

Fig. 6. Schematic plot (after [14]) featuring the magnetic properties resulting from the competition between the Kondo effect and the RKKY interaction. T_C represents the Curie temperature, T_K the Kondo temperature, T_{RKKY} the temperature associated with the Ruderman–Kittel–Kasuya–Yosida interaction, J the exchange coupling strength and $N(E_F)$ the density of states at the Fermi level. For low $J\,N(E_F)$ values, T_{RKKY} dominates and we observe a rare-earth like magnetism. Then, as $J\,N(E_F)$ increases, T_K increases more than T_{RKKY}, the magnetic ordering temperature T_C decreases, we now observe a Kondo lattice with magnetic order. Finally, T_K strongly dominates T_{RKKY} and a non-magnetic Kondo lattice takes place. It is worth noticing that the transition region where T_C goes to zero is a domain of magnetic instability where interesting phenomena such as heavy fermions and spin fluctuators may be observed. $U_4Ru_7Ge_6$ – which exhibits a rather low T_C decreasing rapidly to zero when Ru is replaced by Os – may be viewed as a magnetic Kondo lattice whereas $U_4Os_7Ge_6$ lies in the non-magnetic Kondo lattice domain. ($\theta_p<0$).

competition of the Kondo effect and the RKKY interaction (Fig. 6) and which was successfully applied e.g. to uranium monochalcogenides [15]: $U_4Ru_7Ge_6$ displays a rather weak Curie temperature which then rapidly decreases down to zero for $x>0.3$ in the $U_4(Ru_{1-x}Os_x)_7Ge_6$. Then for x increasing from 0.4 up to 1, the paramagnetic temperature θ_p and the effective moment μ_{eff} decrease while the χ_0 term – though not exhibiting a clear variation as mentioned above – globally seems to increase, suggesting a more and more pronounced Kondo system up to $U_4Os_7Ge_6$.

4. Conclusion

We investigated the $U_4(Ru_{1-x}Os_x)_7Ge_6$ system and followed the onset of magnetism from the paramagnet $U_4Os_7Ge_6$ ($x=1$) to the ferromagnet $U_4Ru_7Ge_6$ ($x=0$), which occurs for $x=0.3$. The susceptibility was successfully fitted using a modified Curie–Weiss law for the whole series. We interpret these results in terms of Kondo lattice systems where the RKKY interaction responsible for magnetic ordering is rapidly overwhelmed by Kondo interactions as x increases. Further examination of the compound at $x=0.3$, which might exhibit quantum critical effects with T_C~0 K, would seem worthwhile.

Acknowledgements

E. Colineau and E.J. Higgins acknowledge the European Commission for support given in the frame of the programme «Training and Mobility of Researchers».

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