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Thermopower studies of doped $CeAl_2$ and UAl_2

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Abstract. We have studied the thermopower of U doped $CeAl_2$ and Ce and La doped UAl_2. Despite different ground state properties of $CeAl_2$ and UAl_2, the former being an antiferromagnetic heavy-fermion compound and the latter non-magnetic, we have found that not only thermopower data for pure $CeAl_2$ and UAl_2 are similar but also the thermopower results of doped samples behave similarly. Although the similarity seen in pure systems is yet to be understood, we interpret the doping effects as the results of changes in energy dependent relaxation time with doping.

1. Introduction

Over years, many new compounds have been found to belong to a very exotic class of strongly correlated electron systems, the so called heavy-fermion compounds. Depending upon magnetic and electrical properties, there are four different sub-categories of this new materials; those with a non-magnetic ground state, the magnetic ones, the superconducting group and the low-density carrier systems [1].

Among them, $CeAl_2$ is a magnetic heavy-fermion compound with $\gamma = 135$ mJ mol^{-1} K^{-2} and $T_N = 3.87$ K [2]. Very near to the Néel temperature, the resistivity shows a marked drop which is often referred to as a signature of coherence, below which temperature, T_{coh}, every heavy electron takes part in the formation of a strongly correlated band, so that they are more conductive. The characteristic temperature, T_K, of this compound has been estimated to be 5 K. It is rather unusual to have T_K and T_{coh} very close to T_N. In fact, it is this closeness of the three characteristic energy scales that brings much attention to $CeAl_2$. Unlike other magnetic heavy-fermion compounds which have very small magnetic moments due to strong hybridization between f electrons and conduction electrons, $CeAl_2$ is one of a few magnetic heavy-fermion systems with a large ordered magnetic moment: $CeAl_2$ has $\mu_{ord} = 0.8\mu_B$ [3]. $CeAl_2$ is also unique in that it shows a rather well defined crystal field excitations in inelastic neutron scattering and has a dynamic Jahn–Teller distortion, unusual among rare earth compounds, splitting the excited otherwise quartet state into two doublets with $\Delta = 8.9$ and 15.7 meV [4]. Because of strong hybridization, most heavy-fermion compounds except for a few exceptions show at best very broad crystal field excitations. These properties undoubtedly suggest the existence of some localized 4f electrons coexisting with strongly hybridized 4f electrons as suggested for both UPd_2Al_3 [5] and UCu_5 [6].

On the other hand, UAl_2 is a heavy-fermion system without any phase transition at all. It is relatively heavy with $\gamma = 142$ mJ mol^{-1} K^{-2} [7]. It has a signature of spin Fermi liquid states at low temperatures, the $T^3 \ln T$ behaviour in heat capacity, which is rare among

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heavy-fermion systems. UPt_3 is only the other example showing such behaviour. Based on the heat capacity data, its characteristic temperature is estimated to be $T_{sf} = 26$ K [7]. What makes UAl_2 distinguishable from other heavy-fermion systems from our point of view, but seemingly less noticed since, is that it has very large $T = 0$ fluctuations which are seen in quasielastic neutron scattering experiments. According to quasielastic neutron scattering results [8], UAl_2 has a large line width of 25 meV at $T = 0$. It is a very large value considering that most heavy-fermion compounds have line widths one order of magnitude smaller. Thus it is a puzzle to us how UAl_2 alone can have such large $T = 0$ fluctuations if it is *heavy* only with the commonly believed strong spin fluctuations. Regarding the large value of quasielastic line width of UAl_2, it is interesting to note that those systems known to have comparable line width to that of UAl_2 are mixed valence compounds with strong charge fluctuations.

Despite the differences between $CeAl_2$ and UAl_2, they form in the same cubic Laves structure, $MgCu_2$. $CeAl_2$ has a lattice constant of 8.059 Å and it is 7.766 Å for UAl_2. With both systems having the same crystal structure, studies of alloying effects on $(Ce, U)Al_2$ are expected to provide an unique opportunity of examining evolution from an antiferromagnetic Kondo system with well localized magnetic moments to a non-magnetic Kondo compound with very energetic $T = 0$ quantum fluctuations.

In previous studies of U doped $CeAl_2$ using resistivity and susceptibility measurements [9], we have found that hybridization increases with U doping in $CeAl_2$ and the Néel temperature too; $(Ce_{0.8}U_{0.2})Al_2$ has an antiferromagnetic transition at 6 K. At the same time, it was also shown that the coherence temperature increases with U doping.

2. Experimental details

All samples have been made using an arc furnace under Ar atmosphere as described previously [9]. Since there is a miscibility gap from $x = 0.3$ to 0.7 for $(Ce_{1-x}U_x)Al_2$, we have only made $(Ce_{1-x}U_x)Al_2$ with $x = 0$, 0.05, 0.1, 0.2, 0.8, 0.9 and 1. A sample with $x = 0.3$ has been made too to see progressive changes in thermopower with further U doping on $CeAl_2$ despite the fact that this sample is known to have some second phases. We have also prepared $(U_{1-x}La_x)Al_2$ with $x = 0$, 0.1 and 0.2 for comparison on the UAl_2 side. Subsequently, they have been subjected to heat treatments. The Ce rich samples have been annealed at 800 °C for two days and at 873 °C for five days, while the U rich samples have been kept at 850 °C for five days as described before [9].

For thermopower measurements, we used a differential method. Below 70 K, measurements were made *in situ* against a high-T_c compound YBaCuO ($T_c = 82$ K). At high temperatures we have used pure lead as our reference material using Roberts' results [10] to get absolute values for thermopower.

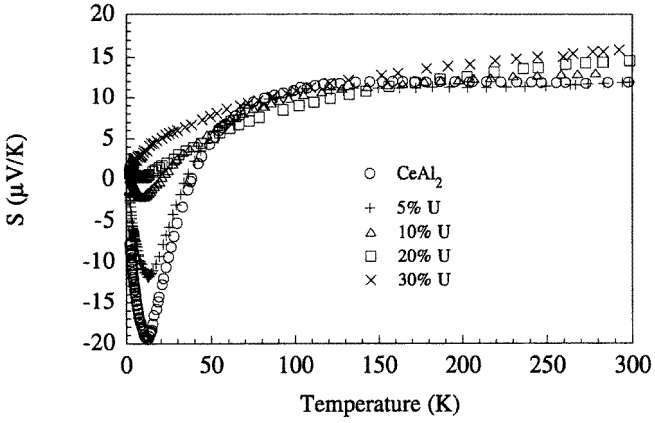
3. Data and analysis

We present results on the Ce rich side first and then on the U rich side as the two end materials have different ground states.

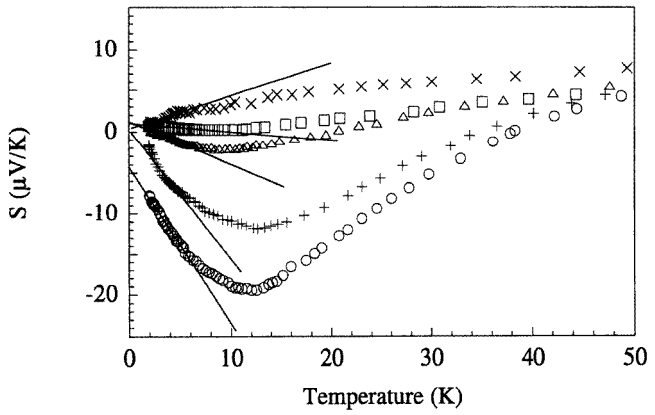
3.1. $(Ce_{1-x}U_x)Al_2$

Results on U doped $CeAl_2$ are given in figure 1. Our results for $CeAl_2$ are in good agreement with previously published data [11]. In $CeAl_2$, there are apparently two different temperature regions: one is a high-temperature region where thermopower seems to be

more or less temperature independent and then there is a low-temperature region where thermopower falls suddenly to form a negative maximum subsequently. Further down in temperatures, there appears a rather good temperature linear region from 2 to 6 K with a slope of $-1.9\ \mu V\ K^{-1}$. At the high-temperature side, we have found that above 80 K the thermopower can be described rather well by a phenomenological Hirst model [12]. We will discuss it in detail later.



(a)



(b)

Figure 1. (a) Thermopower data are presented for U doped $CeAl_2$ for 5%, 10%, 20%, 30% U along with data for pure $CeAl_2$. (b) Low-temperature blown-up picture for the same compositions. The lines are added to show linear temperature behaviours (see the text).

With increasing U concentrations, there appear a few changes to the thermopower data of $CeAl_2$. Firstly, the slope in the linear region at low temperatures becomes smaller, and by 20% U substitution it is almost zero. The lines in figure 1(b) are shown to illustrate this point, and they all except for the line drawn for the pure $CeAl_2$ lead to zero. With further doping of U to 30%, now the slope becomes positive. With the change in the low-temperature slope, the negative maximum becomes smaller all the time with U doping. In $(Ce_{0.8}U_{0.2})Al_2$, there is only a broad feature left reminiscent of the negative maximum. At 30% U substitution, there is no sign of such a feature; it should be recalled that the

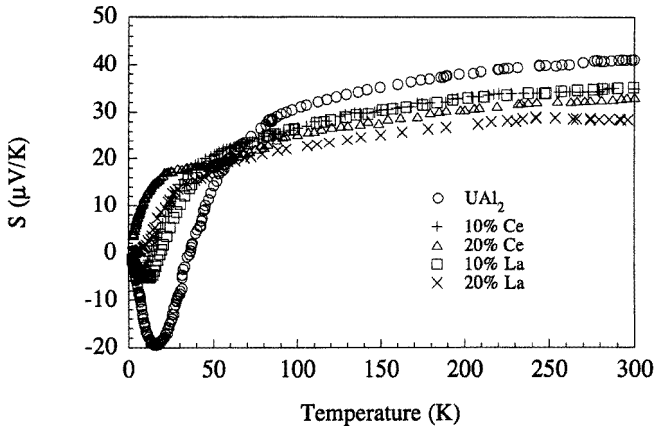
30% sample has some second phases. However, it can be said safely that the complete disappearance of the negative maximum would happen between 20 and 30% U doping if no miscibility gap existed. Apart from the fact that the negative maximum gets smaller with U doping, the centre of the maximum also moves towards lower temperatures. Despite the fact that $(Ce_{0.7}U_{0.3})Al_2$ does not have such a negative maximum, it is interesting to note that there is a change in slope around 5 K, which may well be suggestive of a similar feature. It is also interesting to note the temperatures where the thermopower changes sign; in the case of $CeAl_2$ it is around 38 K, decreasing systematically with doping of U.

Regarding the changes just mentioned, we would like to recall that a negative maximum in the thermopower of heavy-fermion systems has been considered as a signature of the presence of antiferromagnetic correlations. Such an interpretation is best justified in $Ce(Cu_{1-x}Au_x)_6$ [13]. $CeCu_6$ is itself a nonmagnetic heavy-fermion compound and has no negative maximum in low-temperature thermopower data. However with small doping of Ag or Au, doped $CeCu_6$ can be easily turned into a magnetic state, in this case antiferromagnetic. With this change in magnetic character, thermopower data for the doped $CeCu_6$ show a negative maximum. This interpretation also seems to be valid in the thermopower results of $(Ce_{1-x}U_x)Al_2$ as we have seen the opposite effects due to U doping on the antiferromagnetic ground state; with increasing U concentrations the antiferromagnetic transition gets weaker and the negative maximum becomes smaller though its transition temperature increases [9]. This observation has been corroborated by recent heat capacity measurements on similar compositions of $(Ce_{1-x}U_x)Al_2$ [14]. Therefore all the measurements agree in that antiferromagnetic correlations prevailing at low temperature in $CeAl_2$ are reduced by U doping. The reason for that may be found in the fact that the lattice constant of $CeAl_2$ is reduced by U doping which in turn produces chemical pressure effects on $CeAl_2$, so increasing hybridization between f and conduction electrons. The increase in the Néel temperature with U doping is unusual, but not entirely unexpected as Doniach's 1D necklace model [15] shows that in some regions of hybridization, J, magnetic transition temperatures can increase with J.

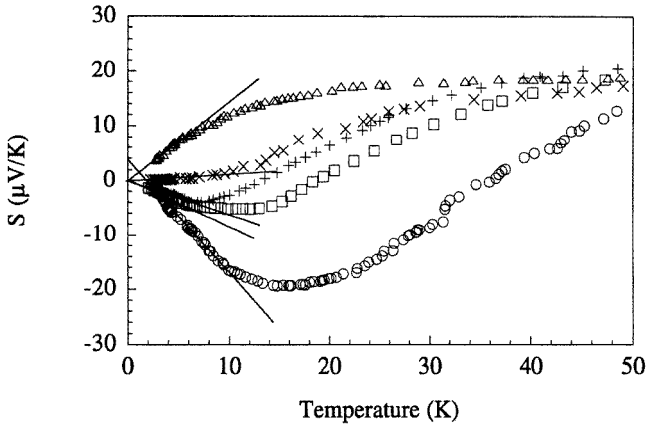
The high-temperature end of the thermopower shows that the slope becomes more evident with increasing U concentrations. It is noticeable too that room-temperature thermopower values increase steadily with U concentrations. These two changes apart, there are very few differences compared with $CeAl_2$ data at high temperatures.

3.2. $(U_{1-x}R_x)Al_2$ with $R = La$ and Ce

Our data for doped UAl_2 are shown in figure 2 together with data for pure UAl_2. The results for pure UAl_2 are in good agreement with published data [16]. Compared with the data for $CeAl_2$, similarities between the two are striking and little expected as they have very different ground state properties at low temperatures as we have noted in the introduction. In UAl_2, the thermopower becomes negative below around 35 K, almost the same temperature as in $CeAl_2$. Below that temperature, the thermopower forms again a narrow negative maximum centred at 16 K. Unlike the similar feature seen in $CeAl_2$, however, the negative maximum in UAl_2 cannot be understood in the same way as that in $CeAl_2$ since UAl_2 has no known magnetic transition. Slightly in favour of such an explanation with antiferromagnetic correlations for the negative maximum in UAl_2 may be the strong spin fluctuations present in UAl_2, which produce the $T^3 \ln T$ behaviour in heat capacity [7]. It then should be noted that μSR experiments [17] put the fluctuation rate of U 5f moments at 10^{13} Hz at least, which is very fast compared with that in any other systems near to a magnetic instability. Then the antiferromagnetic scenario may not work here. At



(a)



(b)

Figure 2. (a) Thermopower data are shown for Ce and La doped UAl_2 for 10% and 20% of each, together with data for pure UAl_2. (b) Low-temperature data are presented with lines added to show linear temperature behaviours.

the moment, we cannot think what else may give rise to the negative maximum in UAl_2. Apart from the negative maximum, there is a good temperature linear region between 2 and 10 K with a slope of $-2.13\ \mu V\ K^{-2}$ for UAl_2, a slightly larger value than that for $CeAl_2$.

At high temperatures, the thermopower for UAl_2 is more temperature dependent than in $CeAl_2$. It increases without a signature of saturation at high temperatures. Further analysis of the high-temperature thermopower will be made in the discussion.

Substitutions of either Ce or La make the negative maximum smaller and at the same time the centre of the peak moves towards lower temperatures. Along with these changes, the low-temperature slope also becomes smaller with doping and is eventually positive for $(U_{0.8}Ce_{0.2})Al_2$. Lines in figure 2(b) are added to show this point more clearly. In general, Ce doping has produced more significant effects than La, when compared at the same amount of doping. At high temperatures, one notices a small, but gradual, decrease in thermopower with Ce and La doping, which is opposite to the increase seen in high-temperature data for U doped $CeAl_2$. In $(U_{0.8}Ce_{0.2})Al_2$, there is another feature at 60 K showing some sort of

flattening, whose origin is not clear to us yet. It is noticeable that the negative maximum is destroyed by both Ce and La doping despite the fact that $CeAl_2$ is magnetic while $LaAl_2$ is non-magnetic.

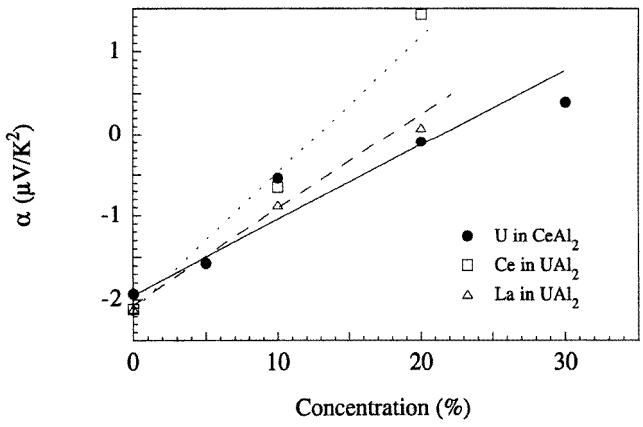


Figure 3. Coefficients of the low-temperature slope, $S(T) = \alpha T$, are given as a function of doping concentrations of U in $CeAl_2$ and Ce and La in UAl_2. Lines are guides to the eyes.

4. Discussion

Here we would like to discuss further similarities between $CeAl_2$ and UAl_2. First of all, we present figure 3 showing the concentration dependence of the low-temperature slope, $S(T) = \alpha T$, for both $CeAl_2$ and UAl_2. As we have pointed out in the previous sections, the low-temperature slope for doped $CeAl_2$ and UAl_2 indeed show similar concentration dependences. With increasing concentrations, all three sets of data show the slope to increase by more or less the same amount. For the analysis of the low-temperature slope, we use a free electron formula of thermopower as follows

$$S(T) = -\frac{\pi^2}{3}\frac{k_B}{|e|}k_B T\left[\frac{N(\varepsilon_F)}{n} + \frac{1}{\tau(\varepsilon_F)}\frac{\mathrm{d}\tau}{\mathrm{d}\varepsilon_F}\right]$$

where $N(\varepsilon_F)$ is the density of states at the Fermi level, n the conduction electron density, and τ the relaxation time. Since the electronic specific heat is almost the same for $CeAl_2$ and UAl_2, we can assume that the first term in the formula would not change much due to doping. Therefore most contributions to low-temperature thermopower seem to come from the second term, the energy dependent relaxation time. This then suggests that, whatever the origins of the low-temperature behaviour in both $CeAl_2$ and UAl_2, the destruction of the Kondo lattice due to doping is responsible for the change in the low-temperature slope. It subsequently means that the disappearance of antiferromagnetic ordering in $CeAl_2$ with U doping may also be at least partly due to disorder in the Ce lattice. That both Ce and La doping in UAl_2 give similar effects on the low-temperature behaviour may also be understood in terms of destruction of periodicity more naturally.

Apart from the low-temperature behaviour, similarities between $CeAl_2$ and UAl_2 extend in much the same way to high-temperature regions. Shown in figure 4 is a T/S versus T^2 plot for $CeAl_2$ and UAl_2. According to the phenomenological Hirst model used in [12], high-

temperature thermopower results of strongly correlated electron systems can be described using the following formula:

$$S(T) = \frac{AT}{B^2 + T^2} \qquad \text{with } A = \frac{2(\varepsilon_f - \varepsilon_F)}{|e|} \text{ and } B^2 = \frac{3[(\varepsilon_f - \varepsilon_F)^2 + \Gamma^2]}{(\pi k_B)^2}$$

where ε_f is the f electron level, ε_F the Fermi level, and Γ the width of Lorentzian shape excitations at the Fermi level. For temperatures higher than about 80 K, there are two linear regions in both $CeAl_2$ and UAl_2 data (see figure 4). Crossover from one to another occurs around 180 K for $CeAl_2$ and 150 K for UAl_2. The crossover temperature for $CeAl_2$ seems to be quite comparable to the width of crystal field excitations spanning about 185 K [4]. Then UAl_2 does not have any crystal field excitation to our best knowledge. From the line fitting to high-temperature data, we can estimate the f electron level with respect to the Fermi level, $\varepsilon_f - \varepsilon_F$, and the width of the Lorentzian, Γ. In the case of $CeAl_2$, data above 180 K can be described by a Lorentzian shape excitation with $\varepsilon_f - \varepsilon_F$ at 3.2 meV and Γ of 40 meV and from 180 to 80 K by one with $\varepsilon_f - \varepsilon_F$ at 1.8 meV and Γ of 23 meV. For UAl_2, one needs a Lorentzian shape excitation with $\varepsilon_f - \varepsilon_F$ at 11 meV and Γ of 42 meV to explain data above 150 K and one with $\varepsilon_f - \varepsilon_F$ at 5.6 meV and Γ of 25 meV for data from 150 to 80 K. Although the actual values should not be given too much attention, we believe that the trend is quite suggestive of how low-energy excitations may develop with temperatures in both samples. At least in the case of $CeAl_2$, the reduction in the Γ value can be linked to thermal depopulation of second excited doublets 15.7 meV above the ground state.

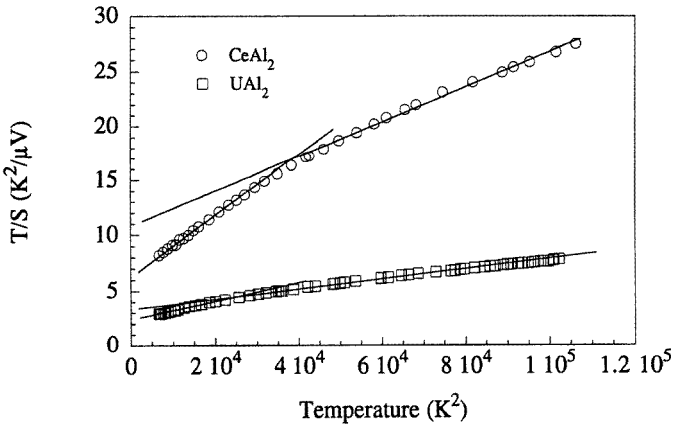


Figure 4. T/S versus T^2 plots are given for $CeAl_2$ and UAl_2 above 80 K. Lines are drawn to show linear behaviours in different temperature ranges.

In conclusion, our studies of alloying effects in the thermopower of $CeAl_2$ and UAl_2 have shown that despite the different ground states of the two systems thermopower results show striking similarities. Most features seen in thermopower data of $CeAl_2$ can be understood within the context of the antiferromagnetic fluctuations at low temperatures and crystal field excitations at high temperatures. In both low- and high-temperature regions, however, UAl_2 shows very similar behaviours in the thermopower to $CeAl_2$ despite the different ground states, which is puzzling to us.

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