Heavy Fermion Behavior in the System $EuCu_2(Si_xGe_{1-x})_2$

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In compounds based on ***f***-elements with an unstable ***f***-shell like Ce, Yb or U, the interaction between the unstable ***f***-electrons and the conduction electrons can lead at low temperatures to the formation of heavy fermions (quasi particles with an effective mass 100 or 1000 times larger than that of normal electrons). Many heavy fermion systems have already been observed among Ce- and U-based compounds, much less among Yb-based compounds. In contrast, no example for an Eu-based heavy fermion system has yet been found. It is surprising, since Eu also presents an unstable ***f***-shell, it can switch between the divalent, magnetic (J = 7/2) configuration and the trivalent, non magnetic (J = 0) configuration. The absence of heavy fermion systems is likely connected to the fact that the magnetic phase diagram observed in Eu based systems upon tuning the hybridization g between ***f***- and conduction electrons is very different from that found in Ce- and U-based systems. Starting from stable divalent Eu-systems, one never observes a decrease of the magnetic ordering temperature T_m with increasing g, as usually found in Ce- or U-systems. Instead, in Eu-systems T_m seems to be independent of g or even increases with g until the system makes a pronounced first order transition to a valence fluctuating regime with a valence close to 3 at a critical value g_c [1]. Since at $g \geq g_c$ the characteristic energy associated with the valence fluctuation is quite high, the mass enhancement of the conduction electron is comparatively small preventing the observation of heavy fermions. Accordingly, whereas Kondo behavior in transport properties (i.e., a pronounced increase of the magnetic scattering with decreasing temperature) is ubiquitous in Ce and U-based systems, no such behavior has yet been observed in Eu-based systems, with only one exception: the alloy $EuCu_2(Si_xGe_{1-x})_2$. In this alloy, exchanging Ge by Si induces a transition from a divalent, antiferromagnetically ordered state in pure $EuCu_2Ge_2$ to a valence fluctuating state in pure $EuCu_2Si_2$. In a preliminary investigation of this system, Levin et al. [2] observed Kondo-like behavior in the temperature dependence of the resistivity and of the thermopower for $0.5 < x < 0.7$. However, they presented only limited data. There are no specific heat results and the evolution of the magnetic ordered state in the alloy has not been investigated. In order to have a more precise view of this unusual Eu-system and to look for possible heavy fermion behavior we started a detailed investigation of this alloy by means of resistivity $\rho(T)$, magnetic susceptibility $\chi(T)$, thermopower $S(T)$ and specific heat $C(T)$ measurements. In addition, preliminary electron spectroscopy were performed in cooperation with Dr. Molodtsov at the Technical University Dresden.

Our first point of interest was to investigate the evolution of the magnetic order. Our susceptibility, resistivity and specific heat results demonstrate that the antiferromagnetic order is rather stable

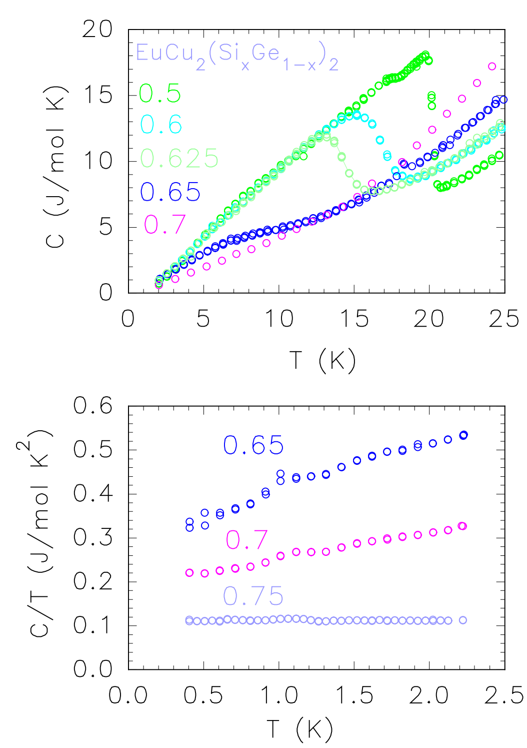

***Fig. 1:** Upper part: specific heat versus T for samples with $x \leq x_c$. The sharp step in C(T) corresponds to the transition into the antiferromagnetic state. Lower part: C/T versus T for samples with $x \geq x_c$, demonstrating the large linear electronic contribution to the specific heat.*

until $x = 0.65$. This is best seen in the specific heat data (Fig. 1). The sharp and sizeable step in $C(T)$ at T_N evidences a well defined collective long range order in the whole concentration range $0 \leq x \leq 0.625$, despite the disorder introduced by the alloying. With increasing Si content the transition temperature into the antiferromagnetic state first increases quite significantly from $T_N = 15$ K in pure $EuCu_2Ge_2$ to $T_N = 20$ K at $x = 0.5$, then decreases to $T_N = 14$ K at $x = 0.625$ and eventually drops very sharply and disappears near $x_c = 0.65$. It is the first Eu-system where a significant decrease of T_N can be observed before the disappearance of the magnetic order. The significant decrease of T_N as well as the decrease of the size of the anomaly in $C(T)$ at T_N between $x = 0.5$ and $x = 0.625$ suggest that the disappearance of the magnetic order occurs continuously in the $EuCu_2(Si_xGe_{1-x})_2$ alloy, in contrast to the first-order transition observed in other Eu-systems. For Ge concentration at or slightly above the critical value $x_c = 0.65$, $C(T)$ at low temperatures (< 2 K) is dominated by a large linear term corresponding to a large Sommerfeld coefficient γ, which decreases from $\gamma = 300$ mJ/K^{2}mol at x_c to $g = 200$ mJ/K^{2}mol at $x = 0.7$ and eventually $\gamma = 100$ mJ/K^{2}mol at $x = 0.75$. This is the first observation of heavy fermion behavior in an Eu-System. The highest Sommerfeld coefficient previously reported for Eu-compounds, $\gamma = 100$ mJ/K^{2}mol, was recently observed in $EuNi_2P_2$ [3].

Further hallmarks for heavy fermion behavior are a very large magnetic contribution to the resistivity with a negative temperature coefficient, as well as a large thermopower, both being related to the strong scattering between conduction- and f-electrons. Therefore, we investigated both properties in detail (Fig. 2 and Fig. 3). A first interesting result was the observation of an increase of $\rho(T)$ below T_N in pure $EuCu_2Ge_2$ as well as in Si-doped samples. This point to the opening of a gap on part of the Fermi surface at T_N which might indicate some SDW-character of the antiferromagnetic order. For $x \geq 0.5$, a Kondo-like increase of $\rho(T)$ with decreasing T is observed above T_N, becoming more and more pronounced when approaching the critical concentration g_c. At $x = 0.6$ this increase amounts to 50% of the resistivity value at the minimum. This increase ends at the onset of the antiferromagnetic order leading to a sharp maximum near T_N. Our results clearly show that this maximum is related to the magnetic order and not to the

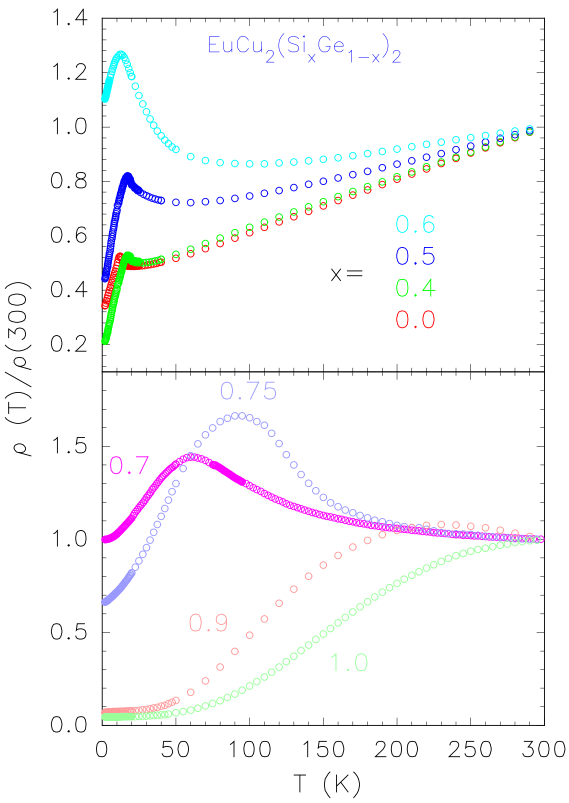

***Fig. 2:** Temperature dependence of the resistivity. Upper part: samples with $x < x_c$, where antiferromagnetic order is observed. Lower part: samples with $x > x_c$, where antiferromagnetic order has disappeared.*

Kondo temperature T_K as suggested by Levin et al. For $x > x_c$, the $\rho(T)$ curves look very similar to those observed in canonical Kondo-lattices: $\rho(T)$ increases with decreasing T below room temperature, passes through a broad maximum at a temperature $T_{\rho max}$ related to the Kondo temperature T_K and decreases at lower temperature due to the onset of coherence. Tr_{max} increases strongly from 60 K at $x = 0.7$ K to 300 K in pure $EuCu_2Si_2$.

This Kondo-like behavior is also observed in the thermopower (Fig. 3). In pure $EuCu_2Si_2$, $S(T)$ is very small in the whole temperature range between 5 K and 300 K. With increasing Si content, $S(T)$ becomes larger and shows a characteristic temperature dependence. From room temperature, where it is negative, it increases with decreasing temperature, changes sign (at $T = 50$ K for $x = 0.5$), increases further strongly, before showing a pronounced positive peak at T_N. Then the onset of magnetic order leads to a strong decrease. For $x > x_c$, the peak at T_N is replaced by a broad maximum at T_{Smax}. Both the temperature of this maximum as well as

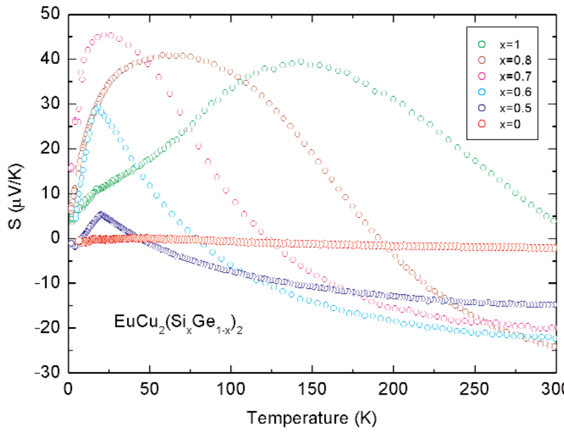

Fig. 3: Temperature dependence of the thermopower for selected samples.

the temperature where the change of sign occurs shift to higher energies with increasing $\boldsymbol{x}$ and scale with the temperature $\boldsymbol{T}_{\rho max}$. Obviously, these three temperatures are related to $\boldsymbol{T}_K$. We are presently analyzing this thermopower in cooperation with the theory group of Dr. Zlatic in Zagreb (Croatia). It seems that the observed behavior of the thermopower is in accordance with theoretical predictions of a Kondo model for Eu-systems. The observance of pronounced Kondo-like behavior even in samples showing magnetic order (at $\boldsymbol{x}$ = 0.5 and $\boldsymbol{x}$ = 0.6) is interesting, since it indicates that the antiferromagnetic order forms out of a paramagnetic state with significant valence fluctuations. The presence of valence fluctuations seems to be confirmed by preliminary electronic spectroscopy measurements.

In summary, we have investigated the alloy $EuCu_2(Si_{\boldsymbol{x}}Ge_{1-\boldsymbol{x}})_2$ by means of resistivity, susceptibility, specific heat and thermopower measurements. We established the magnetic phase diagram which shows the disappearance of antiferromagnetic order near $\boldsymbol{x}_c = 0.65$. A significant decrease of $\boldsymbol{T}_N$ for $\boldsymbol{g} < \boldsymbol{g}_c$ suggests that this disappearance is a continuous process, not a first-order transition. At $\boldsymbol{g}_c$, we found the first example of heavy fermion behavior in an Eu-based system with γ up to 300 mJ/K^{2}mol. Our data confirm the pronounced Kondo-like behavior in $\rho(\boldsymbol{T})$ and $\boldsymbol{S}(\boldsymbol{T})$ first observed by Levin et al.. Further on, our results suggest that for $\boldsymbol{g} < \boldsymbol{g}_c$, the antiferromagnetic state forms out of a paramagnetic state with significant valence fluctuation. The reason why this alloys is the only Eu-system showing heavy fermion and Kondo-like behavior is not clear to us and shall be the subject of further investigations.

References

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