Thermoelectricity of EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$ intermetallics

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Abstract

Analyzing the heat and charge transport in a thermoelectric by transport equations, and assuming a simple scaling between the current and the heat current densities, we evaluate $Q/S$ and $Q/\gamma T$ and find at low temperatures the 'universal law' $q = N_A/N$. The deviations from the simple scaling law are also discussed and the results are used to analyze the effects of chemical pressure on $q(x)$ in the EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$ and YbIn$_{1-x}$Ag$_x$Cu$_4$ intermetallic compounds. The characteristic temperatures of these compounds is greatly affected by doping, such that the ground state at $x = 0$ and $x = 1$ is completely different. A qualitative description of $q(x)$ can be obtained from the scaling law but the quantitative features require microscopic modeling. We use for EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$ and YbIn$_{1-x}$Ag$_x$Cu$_4$ the Anderson and the Falicov-Kimball model, respectively.

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This paper explains the thermopower $S(T)$ of EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$ intermetallic compounds. We discuss, first, the systematics which emerges from the experimental results as Ge concentration is varied from zero to one[1,2], and show that the properties of the paramagnetic phase follow from Kondo scattering on Eu ions, which fluctuate between two Hund’s rule configurations. Assuming that Si-Ge substitution gives rise to chemical pressure effect, which modifies the width and the position of an effective f-level representing the Eu ions, we show that the NCA solution of the Anderson model gives the same features as seen in the data. (For details on the modeling of the rare earth intermetallics, and on our method of solution, see Ref. [3].)

The thermopower of EuCu$_2$(Ge$_{1-x}$Si$_x$)$_2$ is characterized for $x \geq 0.8$ by a large peak centered at temperature $T_{\text{max}} \geq 150$ K. The value of $S(T)$ at $T_{\text{max}}$ is large, $S_{\text{max}} > 50 \mu V/K$, and above $T_{\text{max}}$ the thermopower falls-off slowly. At low temperatures $S(T)$ assumes a linear form and the slope $S(T)/T$ is small. The specific heat is featureless and $\gamma = C_V/T$ also is small. For $0.80 \geq x \geq 0.65$ the width of the thermopower peak is reduced and $T_{\text{max}}$ shifts rapidly to lower values as $x$ is reduced. Here, $S(T)$ changes sign for $T > T_{\text{max}}$. Since $S_{\text{max}}$ remains large, $S(T)/T$ is enhanced with respect to the $x \geq 0.8$ data. In this concentration range $\gamma$ changes rapidly with $x$ and for $x < 0.7$ assumes very large values. The electrical resistance $\rho(T)$ has a broad maximum which is shifted to lower temperatures as $x$ is reduced. The resistivity maximum occurs at $T \gg T_{\text{max}}$ but $\rho(T)$ drops off slowly and is quite large at $T_{\text{max}}$. The ground state is a Fermi liquid (FL) up to $x_c \approx 0.65$ and then becomes magnetic. The specific heat and the electrical resistance show at $T_N$ a clear-cut anomaly but the AFM transition can be seen in the $S(T)$ data only for $x < 0.6$. For $0.60 \leq x \leq 0.5$ the thermopower has a sharp cusp at $T_N$, i.e the overall shape of $S(T)$ in these samples appears to be quite different from the shape seen in non-magnetic samples. However, if we assume $T_0 < T_N$ in this concentration range, we see that...

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The magnetic samples exhibit above $T_N$ the same features as the non-magnetic samples well above $T_0$. The size of the specific heat anomaly and the value of $T_N$ increase rapidly with $x$ up to about $x = 0.5$[1]. Similarly, the electrical resistance also changes shape across the magnetic boundary. (See Fig. 6 in Ref.[2]) That is, for $0.50 \leq x \leq 1$, the transport properties of the paramagnetic phase follow the same pattern and seem to be due to the same scattering mechanism, regardless of the nature of the ground state which develops at low temperatures. For $x \leq 0.25$ the size of $S(T)$ becomes very small and is not affected by the AFM transition, which leads to a sharp anomaly in $C_V$ and also shows up clearly in the electrical resistance. (See Figs. 4 and 7 in Ref. [2])

The initial thermopower slope of the paramagnetic samples changes by more than one order of magnitude.

The Eu doping reduces the unit-cell volume and leads to the mixing of the Eu$^{2+}$ and Eu$^{3+}$ configurations, as indicated by the photoemission data.

The Si doping reduces the unit-cell volume and leads to a partial screening of the magnetic entropy, such that $\theta_N$ increases continuously with $x$, and $T_N/T_K$ changes from $T_N/T_K \approx 1$ for $x \approx 0$ to $T_N/T_K \ll 1$ for $x \approx 0.6$. For $T_N/T_K < 1$ and temperatures around $T_N$, the entropy has a large SDW contribution, such that $\tilde{q} < 1$ but for $T \to 0$ the universal behavior, $\tilde{q} \approx 1$, should be recovered. (Does one get $\lim_{T \to 0} q = 1$ in CeAl$_2$, CeB$_6$, and other Kondo systems with $T_K > T_N$?)

The low-temperature specific heat and the thermopower change from $Q/T \simeq 12$ and $\gamma \simeq 450$ for $x \geq 0.68$ to $Q/T \approx 1$ and $\gamma \simeq 30$ for $x = 1$, giving $q \approx 1.5$ and $q \approx 3$, respectively[1,2]. Thus, an increase in $T_K$ by more than one order of magnitude, and the complete change in the character of the ground state, has little effect on the low-temperature value of $q$. The slight increase of $q$ with the Si doping is most likely due to a reduction of the $f$-charge, which accompanies the enhanced mixed-valence character of the Si-rich samples and can be accounted for by Eq. ??.

The sharp drop of $\tilde{q}$ above $T_K$ indicates the crossover to weak coupling limit and the localization of the $f$-electrons, i.e., the change in $V_F$.

The size of the $C_V$-discontinuity is roughly independent of Si-concentration for $x \leq 0.55$ but $Q(T_N)$ increases rapidly with $x$. For $x \geq 0.55$ the $T_N$ starts to decrease, the discontinuity of $C_V$ becomes weaker, and the cusp in $Q(T)$ is gradually transformed into a rounded maximum. Thus, while $T_N$ shows a non-monotonic behavior, $T_0$ and $T_K$ increase continuously with $x$, and $T_N/T_K$ changes from $T_N/T_K \gg 1$ for $x \approx 0$ to $T_N/T_K \ll 1$ for $x \approx 0.6$. For $T_N/T_K < 1$ and temperatures around $T_N$, the entropy has a large SDW contribution, such that $\tilde{q} < 1$ but for $T \to 0$ the universal behavior, $\tilde{q} \approx 1$, should be recovered. (Does one get $\lim_{T \to 0} q = 1$ in CeAl$_2$, CeB$_6$, and other Kondo systems with $T_K > T_N$?)

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Fig. 1. The NCA result for the thermopower plotted versus temperature for $E_f=-0.12$ and for various hybridization widths $\Gamma$, as indicated in the figure.

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