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Thermoelectricity of $EuCu_2(Ge_{1-x}Si_x)_2$ intermetallics

Veljko Zlatić[a,*], R. Monnier[b], J. Freericks[c]

[a]Institute of Physics, Bijenička cesta 46, P.O. Box 304, 10001 Zagreb, Croatia
[b]ETH Hönggerberg, Laboratorium für Festkörperphysik, Zürich, Switzerland
[c]Georgetown University, Washington DC, USA

Abstract

The evolution of the thermopower $S(T)$ of $EuCu_2(Ge_{1-x}Si_x)_2$ intermetallics, which is induced by the Si–Ge substitution, is explained by the Kondo scattering of conduction electrons on the Eu ions which fluctuate between the magnetic 2+ and non-magnetic 3+ Hund's rule configurations. The Si–Ge substitution is equivalent to chemical pressure which modifies the coupling and the relative occupation of the f and conduction states.

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This paper explains the evolution of the thermopower $S(T)$ of $EuCu_2(Ge_{1-x}Si_x)_2$ intermetallic compounds induced by the Si–Ge substitution. We discuss the systematics which emerges as Si is replaced by Ge [1,2] and show that the NCA solution of the Anderson impurity model captures all the qualitative features of the experiments.

In Si-rich samples, $x>0.9$, the thermopower is positive below room temperature (RT). It attains large values, $S_{max}>40\,\mu V/K$ at $T^S_{max}\geqslant 125\,K$, and for $T\geqslant T^S_{max}$ it falls off slowly. The low-temperature slope $\alpha = S(T)/T$ is also small. For $0.90\geqslant x\geqslant 0.65$ the maximum value of the thermopower peak remains large but its width is reduced and T^S_{max} is shifted to lower values, such that α gets enhanced. In this concentration range $S(T)$ changes sign at $T_0\gg T^S_{max}$, which is still much below RT. The XPS data indicate a significant mixture of Eu^{2+} and Eu^{3+} ions [1,2]. The electrical resistance $\rho(T)$ is high and has a maximum at $T>T^S_{max}$. $\rho(T)$ drops off quite slowly as the temperature is lowered, and at T^S_{max}, it is still high, so that the electron propagation is incoherent. The ground state of the compound for $x\geqslant x_c\simeq 0.65$ is a Fermi liquid (FL).

For $x<x_c$ the long-range magnetic order sets in, as indicated by an anomaly in $C_P(T)$ and the discontinuity of the slope of $\rho(T)$ at T_N. The AFM transition does not show up in $S(T)$ for $x>0.6$ or $x<0.3$ but for $0.60\leqslant x\leqslant 0.3$ a cusp appears at T_N, making the overall shape of $S(T)$ quite different from what one finds in the non-magnetic samples. However, the shape of $S(T)$ above T_N still looks much the same as in the non-magnetic samples well above T^S_{max}. That is, the transport properties of the paramagnetic phase exhibit the same pattern for all x (see Fig. 6 of Ref. [2]). The XPS data indicate for $0.3<x<x_c$ the presence of Eu^{2+} and Eu^{3+} ions [1,2] but the Eu^{3+} component is less pronounced than for $x\geqslant x_c$. In Ge-rich samples, $x\leqslant 0.25$, the anomalies in C_P and $\rho(T)$ are well defined but $S(T)$ is very small and does not indicate an AFM transition. (See Figs. 4 and 7 in Ref. [2].) Here, only Eu^{2+} ions are detected in the XPS experiments.

The experimental results are explained by assuming that Si–Ge substitution is equivalent to chemical pressure, which changes the coupling and the relative occupation of the f and conduction states. To describe the Eu ions, which are allowed to fluctuate between the non-degenerate Hund's rule ground state of the $4f^6$ configuration and the 8-fold degenerate $4f^7$ configuration by exchanging

*Corresponding author. Fax: +385 1 4680 399.
E-mail address: zlatic@ifs.hr (V. Zlatić).

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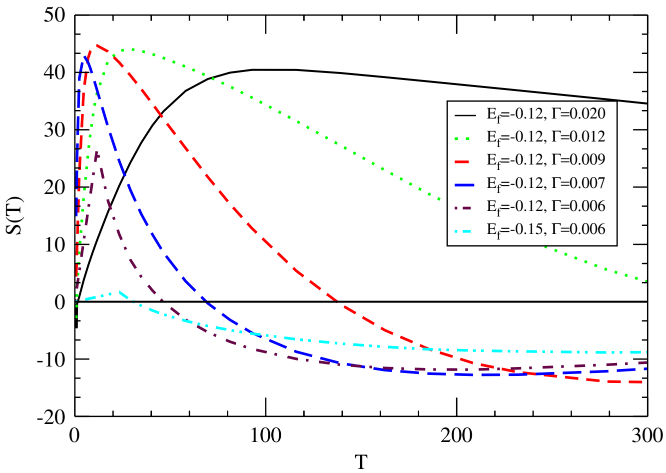

Fig. 1. The NCA result for the thermopower plotted versus temperature for various couplings $g = \Gamma/\pi|E_f|$. The values of E_f and Γ are indicated in the figure.

electrons with the conduction band, we use the single-impurity Anderson model. The energy difference between the two states is $|E_f|$, the configurational mixing is characterized by the matrix element V, and the density of conduction states is $N(\omega)$. The $4f^5$ configuration as well as excited multiplets of the $4f^6$ configuration are excluded. The conduction states and the f states have a common chemical potential μ, which is taken as the origin of the energy axis. The charge-neutrality constraint is imposed on the local scattering problem at each temperature and pressure but any other lattice effects are neglected. The properties of the model depend in an essential way on the coupling constant $g = \Gamma/\pi|E_f|$, where $\Gamma = \pi V^2 N(\mu)$. The effect of pressure is represented by changing Γ and/or the bare f-level position. (For details see Ref. [3].) The NCA results for $S(T)$ obtained in such a way are shown in Fig. 1 for several values of g. The low-temperature behavior is universal but the overall shape is parameter dependent.

For large coupling $S(T)$ is always positive and has a broad peak at T^S_{max}. For smaller g the widths of $S(T)$ is reduced and T^S_{max} is pushed to lower temperatures but S_{max} is unchanged. Estimating the Kondo scale of the model from the low-energy peak in the spectral function we find $T^S_{max} \simeq T_K$ [3]. For small enough coupling $S(T)$ is negative at high temperatures, changes sign at T_0, and then continues to increase up to S_{max}. T_0 is a monotonic function of T_K but the relationship is not universal; for T_K between 5 and 20 K we find $T_0 \simeq 20\,T_K$. (Note, the experimental result for T_0 is very sensitive to any additional contribution to $S(T)$.) The sign-change and the subsequent low-temperature increase of $S(T)$ is a typical feature of Kondo systems in which the conduction electrons scatter on the f-ions which fluctuate between two configurations. The Kondo resonance grows as the temperature is reduced, and the maximum of $S(T)$ occurs when the Kondo resonance is fully developed, and its center is within the Fermi window, $T \simeq T_K$. For $T \ll T_K$, where the NCA breaks down, the properties of the Anderson model can be described by the FL laws, which give $S \simeq T/T_K$. However, for $T \ll T^S_{max}$ the interaction between the f-ions set in, making our model inadequate. None-the-less, the above results explain the thermoelectric properties of $EuCu_2(Ge_{1-x}Si_x)_2$ in the paramagnetic regime and can be used to discuss the overall behavior at various Si–Ge concentrations. The high-pressure state which evolves for high Si content is described by a moderate g. Here, the Eu^{2+} moment is fully screened below T_K and $S(T)$ develops a Kondo maximum. The interaction effects set in below T^S_{max} but the ground state is a FL and the single-site approximation captures all the main features of $S(T)$. The low-pressure state, due to high Ge-content, is described by a small g. Here, the magnetic entropy cannot be completely removed by the Kondo effect, because the Kondo scattering is cut off at T_N. The magnetic transition is driven by the terms which are not accounted for by the single-site approximation, but we know from general thermodynamic arguments that the thermopower of an AFM decreases linearly with temperature. Thus, in Kondo systems with an AFM ground state the slope of $S(T)$ at T_N is discontinuous. (Note, our calculations are not valid below T_N and the straight lines in Fig. 1 are obtained by interpolation.) For g such that $T_N \ll T_K$ the change of slope occurs well below T^S_{max}, where $S(T)$ is quasi-linear, and the discontinuity is difficult to observe. However, for g such that $T_N \geqslant T_K$ the Kondo maximum cannot develop and $S(T)$ exhibits a clear cusp at T_N [2]. For very small g the magnetic transition occurs at temperatures at which $S(T)$ is very small and the discontinuity might again be difficult to observe.

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