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

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- Motivation, introduction
- Description of the experimental data and problem setting
- Microscopic description
- Conclusions

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Motivation

- The nature of the ground state of EuCu$_2$(Si$_x$Ge$_{1-x}$)$_2$ depends on concentration. The QCP is located close to $x=0.68$.
- The overall features of the thermoelectric power $S(T)$ depend on Si concentration.
- $\alpha = \lim_{T \to 0} S/T$ and $\Upsilon = \lim_{T \to 0} C_V/T$ change rapidly with $x$ but $q = (N_A e)(\alpha/\Upsilon)$ is almost $x$-independent ($q \sim 1$).
- How does the change of the ground state affects $S(T)$?
- Can we explain $S(T)$ by Kondo effect?
Description of $\text{Eu}_2\text{Cu}_2(\text{Si}_x\text{Ge}_{1-x})_2$ data

**Thermopower**

**Specific heat**

Characteristic temperatures change with doping.

Chemical pressure favors $4f^6$ with respect to $4f^7$ configuration.
FL ground state for $x > 0.65$.

$S(T)$ broadens and the maximum shifts to lower $T$ with Ge-doping.

Maximum of $S(T)$ is at $T_K$. 
FL ground state for $x > 0.65$.

$S(T)$ broadens and the maximum shifts to lower $T$ with Ge-doping.

Maximum of $S(T)$ is at $T_K$

$S(T)=0$ at $T_0$

$T_0$ changes with doping.
FL ground state for \( x > 0.65 \).

\( C_V \) and \( S(T) \) have anomaly at \( T_N(x) \).

\( T_N(x) \) is a non-monotonic function of \( x \).

\( 0.65 < x < 0.65 \) – \( S(T) \) shows at \( T_N \) a break of slope.

\( x < 0.6 \) – \( S(T) \) shows a cusp at \( T_N \).
Large entropy change for $x < 0.5$

Small entropy change for $x > 0.5$
**Eu$_2$Cu$_2$(Si$_x$Ge$_{1-x}$)$_2$**

Z. HOSSAIN et al.

S. FUKUDA et al.
The valency of Eu ions changes with doping.

- \( 1 < x < 0.8 \)  Valence fluctuations (2+,3+)
- \( 0.8 < x < 0.7 \)  Kondo effect, FL ground state
- \( 0.7 < x < 0 \)  2+ and 3+ mixture, Kondo, AFM ground state
- \( x = 0 \)  2+ state, AFM, no Kondo effect
Universality of $S(T)/T$ and $C V/T$ at low temperatures

$$\frac{S}{\gamma T} = \frac{q}{eN_{Av}}$$

$q=1$ in EuCu$_2$(Si$_x$Ge$_{1-x}$)$_2$
Eu\textsubscript{2}Cu\textsubscript{2}(Si\textsubscript{x}Ge\textsubscript{1-x})\textsubscript{2}

Eu assumes 4f\textsuperscript{7} or 4f\textsuperscript{6} Hund’s rule configuration.

Configurational splitting is $E_f$

Configurational fluctuations give rise to Kondo effect
Modeling unstable 4f ions

Configurational splitting $E_f$.

Configurational mixing $V$ (hybridization).

Dimensionless coupling $g = \pi V^2 n(E_F)/E_f = \Gamma/E_f$.

Intra-configurational excited states are neglected.

Configurational mixing via conduction band.
Relevant parameters:

Only $4f^6$ and $4f^7$ states admitted: $U_{ff} \gg W$

Configurational splitting: $E_f < W$

f-d mixing: $\Gamma \ll E_f$

Properties depend on: $g = \Gamma/\pi l_E_f l$

and relative occupation:

$n_c(T)$ and $n_f(T)$
Anderson lattice model

\[ H_d = \sum_{i,j,\sigma} (t_{ij} - \mu \delta_{ij}) d_{i\sigma}^\dagger d_{j\sigma} \]

\[ H_f = \sum_{l,\eta} (\epsilon_{f\eta} - \mu) f_{l\eta}^\dagger f_{l\eta} - U \sum_{l,\sigma>\eta} f_{l\sigma}^\dagger f_{l\sigma} f_{l\eta}^\dagger f_{l\eta} \]

\[ H_{fd} = \frac{1}{\sqrt{N}} \sum_{k,l,\sigma} (V_k c_{k\sigma}^\dagger f_{l\sigma} + \text{h. c.}) \]

\[ U \rightarrow \infty \quad \text{Infinite correlation} \]

Fixed points of the periodic model not well understood.
**Poor man’s solution**

- Neglect coherent scattering on 4f ions.
- Impose local charge conservation at each f-site.

\[ n_{tot} = n_c(T) + c_i n_f(T) \]

Thermoelectric properties depend on \( g = \Gamma / \pi |E_f| \)
What is needed?

**Green’s function**

\[ G_f(z) = \frac{1}{z - (\epsilon_f - \mu) - \Gamma(z) - \Sigma(z)} \]

**Spectral function**

\[ A(\omega) = -\frac{1}{\pi} \text{Im } G_f(\omega + i0^+) \]

**Transport relaxation time**

\[ \tau(\omega) = cN\pi V^2 A(\omega) \]

**Transport integrals**

\[ L_{ij} = \sigma_0 \int_{-\infty}^{\infty} d\omega \left( -\frac{df(\omega)}{d\omega} \right) \tau(\omega) \omega^{i+j-2} \]
NCA calculations for CeEu$_2$(Si$_x$Ge$_{1-x}$)
(initial parameters for $x=0$)

- Semielliptic conduction band of $W=4$ eV
- Initial f-level at $E_f = -0.12$ eV
- Initial hybridization width $\Gamma=0.006$ eV
- 0.93 particles per effective ‘spin’ channel
Assume that Si doping increase hybridization $\Gamma$.
Fine-tuning: change the f-level position and consider the excited states of 3+ configuration.
Thermopower of Eu$_2$(Si$_{1-x}$Ge$_{1-x}$)$_2$: comparison with experiment
Thermopower - changing the f-level position.

Universal behavior is restricted to $T \leq T_{\text{max}} \sim T_0$.

Temperature of the sign-change $T_x$ is not simply related to $T_0$ and does not provide a physical characterization of the system.
Eu summary of calculations:

Ge doping shifts $E_f$ and reduces $n_f$ but $\Gamma$ is unchanged.

For each $E_f$ we shift $\mu$ so as to conserve $n_{tot}$.

Thus $E_0$, $E_f$, and $E_f - E_0$ change with pressure for Yb ions.

This procedure makes Yb more magnetic under pressure.
Electrical resistance

Transport and thermodynamics should be related to the fixed points of the model!
Spectrum of elementary excitation

$E_f = -0.12, \quad \Gamma = 0.20$

$T_0 = 2000$ K

$T = 2$ K

$T = 92$ K

$T = 400$ K
Spectrum of elementary excitation

$E_f = -0.12, \quad \Gamma = 0.012$
Spectrum of elementary excitation

\[ E_f = -0.12, \quad \Gamma = 0.006 \]
Spectrum of elementary excitation

\[ E_f = -0.15, \quad \Gamma = 0.006 \]

Temperature dependence:
- \( T = 2 \text{ K} \)
- \( T = 92 \text{ K} \)
- \( T = 400 \text{ K} \)

Temperature \( T_0 = 7 \text{ K} \)
Summary of NCA thermopower calculations

• Thermopower in Ce, Eu, and Yb intermetallics can be understood from the fixed point analysis of the effective single impurity Anderson model.

• Properties depend on the number of electrons and the relative magnitude of $\Gamma/E_f$.

• Shape of $S(T)$ follows the redistribution of the spectral weight within the Fermi window.

• Pressure changes $E_f$ and $\Gamma$.

• Combining the NCA and the Fermi liquid approximations provides the solution for any $T$. 
Conclusions

- Above the coherence temperature \( T_c \sim T_0 \), we do not see any effects due to the proximity of the QCP.
- Single ion Kondo effect does all the work. Effective f-degeneracy changes with temperature. Local environment is important (CF splitting, ligands).
- Pressure, chemical pressure or temperature change \( n_f \) and \( S(T) \), which strongly depends on \( n_f \).
- High-concentration data and low-concentration data are not related by a simple scaling law. Shape of \( S(T) \) changes with concentration (chemical pressure).
Thermopower ($\alpha$) versus entropy ($s_N$)

\[ j = \frac{\langle e^{-\beta H} j \rangle}{\langle e^{-\beta H} \rangle} \]  \text{current}

\[ q = \frac{\langle e^{-\beta H} q \rangle}{\langle e^{-\beta H} \rangle} \]  \text{heat current}

Gradient expansion leads to transport equations (Luttinger)

\[ j = -\sigma \nabla \varphi - \sigma \alpha \nabla T \]

\[ q = (\varphi + \Pi)j - \kappa \nabla T \]  \text{Rightarrow}  \quad eN_A (\alpha / s_N) = N_A / N
Seebeck effect: current generation

\[ \alpha = \frac{\Delta V}{\Delta T} \]

Seebeck coefficient: transport eq. for \( j = 0 \)
Peltier effect: thermoelectric cooling

Onsager: $\alpha = \frac{\Pi}{T}$

Peltier coefficient: transport eq. for $\nabla T = 0$

$\Pi(T) = \frac{q}{j}$
Stationary state in isothermal condition:

\[ \frac{dQ}{dt} = -\text{div } q = 0 \]

\[ \text{div } q = T j \nabla \alpha \]

Integrating over the interface:

\[ g_s - g_l = (\Pi_s - \Pi_l) j \]

Interface leads to the discontinuity in the heat current.

Stationary flow: \[ j = nev \]
Analysis of transport equation

\[ q_{exp} = N_A \frac{e\alpha(T)}{S(T)} = \frac{N_A}{N} \frac{1}{1 + S_M(T)/S_N(T)}, \]

\( N/N_A \) is proportional to the Fermi volume of charge carriers

- Free electrons: \( q=1 \)
- Anderson model: \( q=1 \)
- Falicov-Kimball model: \( q=1 \)
- Periodic Anderson model (NFL): \( \alpha \sim S_N \)
Additional self-consistent loop for spectral functions:

<table>
<thead>
<tr>
<th>Spectral Function</th>
<th>Equation</th>
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<tr>
<td><strong>B-spectral function</strong></td>
<td>[ b(\epsilon) = \frac{e^{-\beta(\epsilon-\omega_0)}}{\pi Z} \text{Im} G_0(\epsilon) ]</td>
</tr>
<tr>
<td><strong>F-spectral function</strong></td>
<td>[ a_\Delta(\epsilon) = \frac{e^{-\beta(\epsilon-\omega_0)}}{\pi Z} \text{Im} G_\Delta(\epsilon) ]</td>
</tr>
</tbody>
</table>

**Self-consistency eqns.**

\[ b(\omega) = |G_0|^2 \int d\epsilon \ a_\Delta(\omega + \epsilon) \Gamma(-\epsilon)f(\epsilon) \]

\[ a_\Delta(\omega) = |G_\Delta|^2 \int d\epsilon \ b(\omega + \epsilon) \Gamma(\epsilon)f(\epsilon) \]

**Partition function**

\[ Z = e^{-\beta \omega_0} \int d\omega [b(\omega) + \sum_\Delta a_\Delta(\omega)] \]
Self-consistent NCA solution:

Hybridization parameter

\[ \Gamma(\omega) = \int V^2(\epsilon) \rho_c(\epsilon - \omega) \]

Bosonic Green’s function

\[ G_0(\omega) = \frac{1}{\omega - \epsilon_0 - \Pi(\omega)} \]

Fermionic Green’s function

\[ G_f^\Delta(\omega) = \frac{1}{\omega - \epsilon_f^\Delta - \Sigma(\omega)} \]

Fermionic self energy

\[ \Sigma(\omega) = \int d\epsilon \ G_0(\omega + \epsilon) \Gamma(-\epsilon) f(\epsilon) \]

Bosonic self energy

\[ \Pi(\omega) = \sum_{\Delta} n_f^\Delta \int d\epsilon \ G_f^\Delta(\omega + \epsilon) \Gamma(\epsilon) f(\epsilon) \]