SCES'05 Vienna:

Thermoelectricity $EuCu_2(Si_xGe_{1-x})_2$ intermetallics

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

Work at Institute of Physics, Zagreb, and Georgetown University, supported by the NSF.

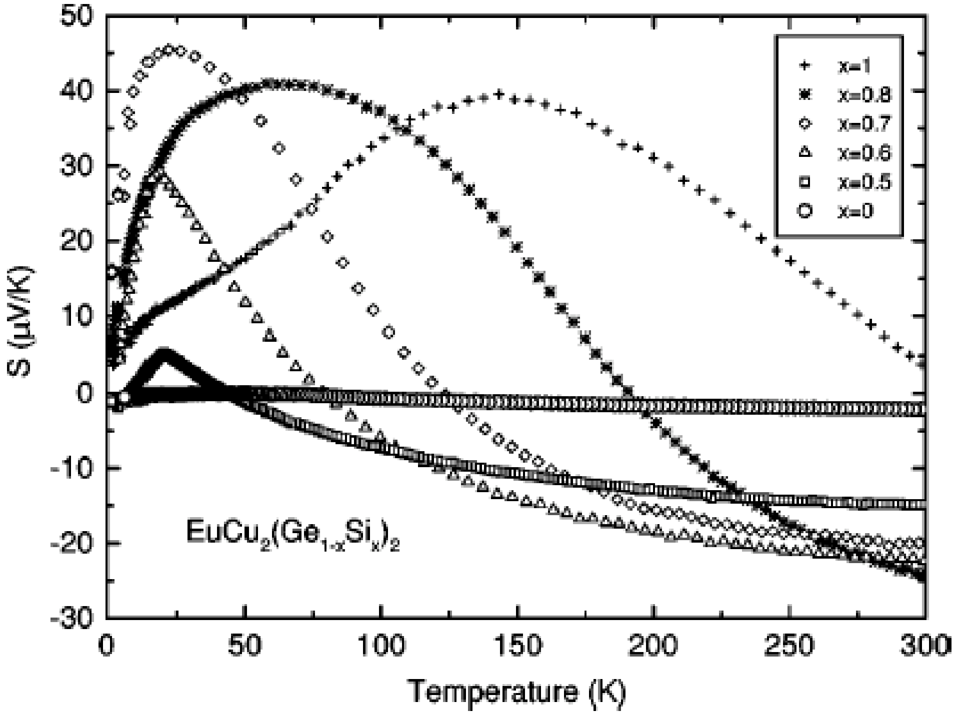
Motivation

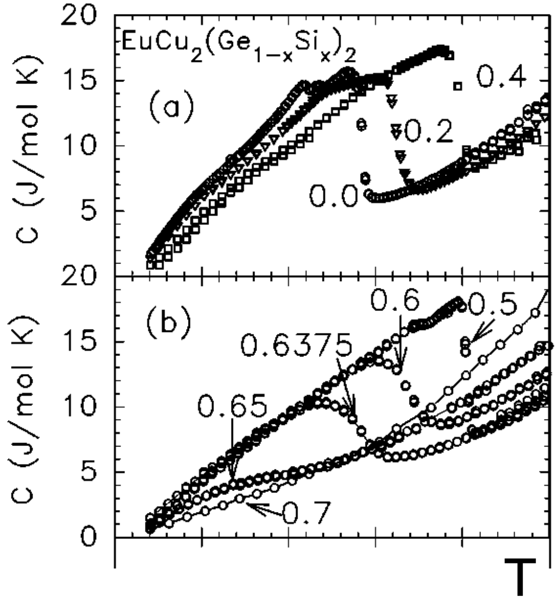
- The nature of the ground state of $EuCu_2(Si_xGe_{1-x})_2$ depends on concentration. The QCP is located close to x=0.68.
- The overall features of the thermoelectric power S(T) depend on Si concentration.
- $\alpha = \lim_{T \to 0} S/T$ and $\gamma = \lim_{T \to 0} C_V/T$ change rapidly with x but $q = (N_A e)(\alpha/\gamma)$ 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 $Eu_2Cu_2(Si_xGe_{1-x})_2$ data

Thermopower

Specifiec heat



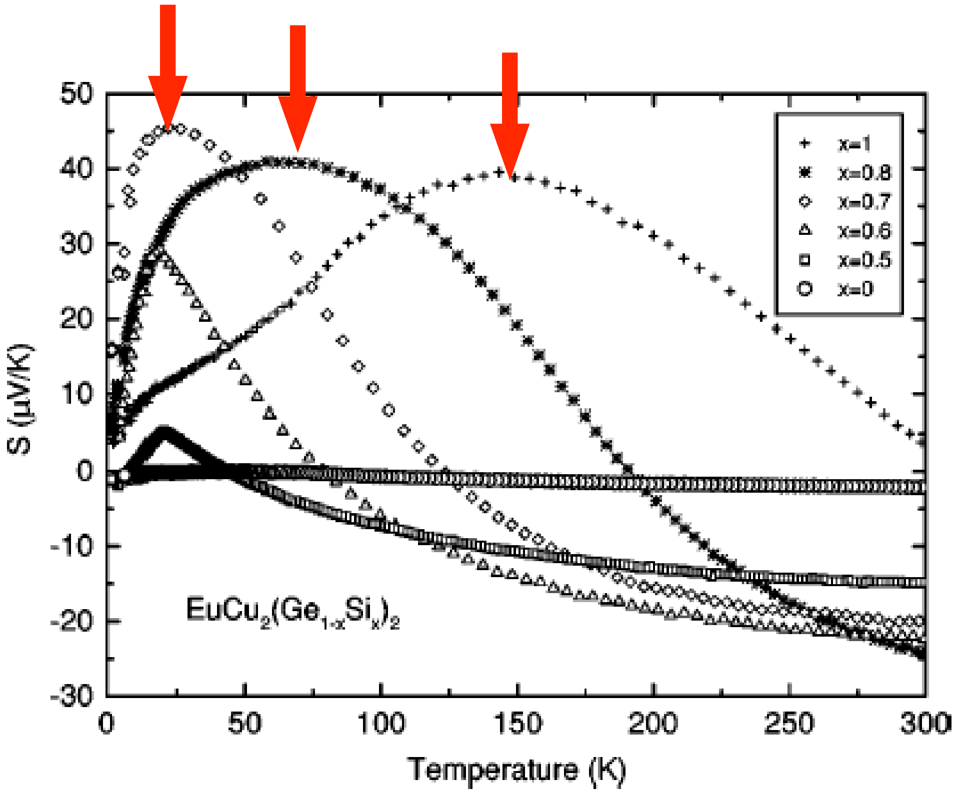


Characteristic temperatures change with doping.

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.

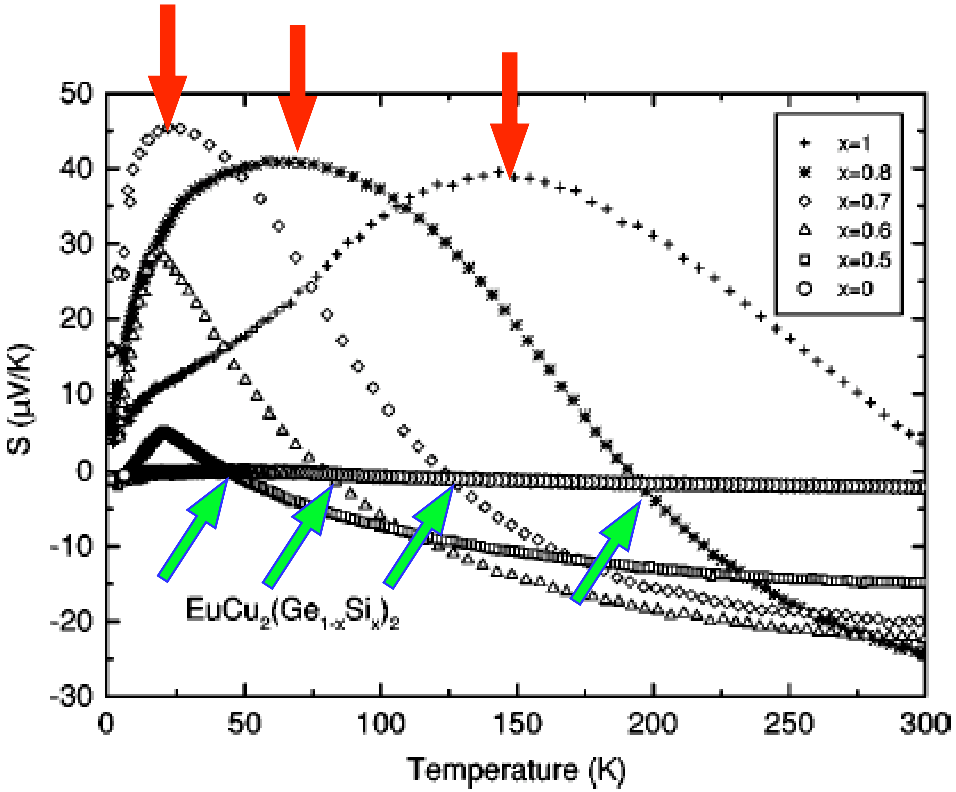


Maximum of S(T) is at T_K

T

FL ground state for x > 0.65.

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



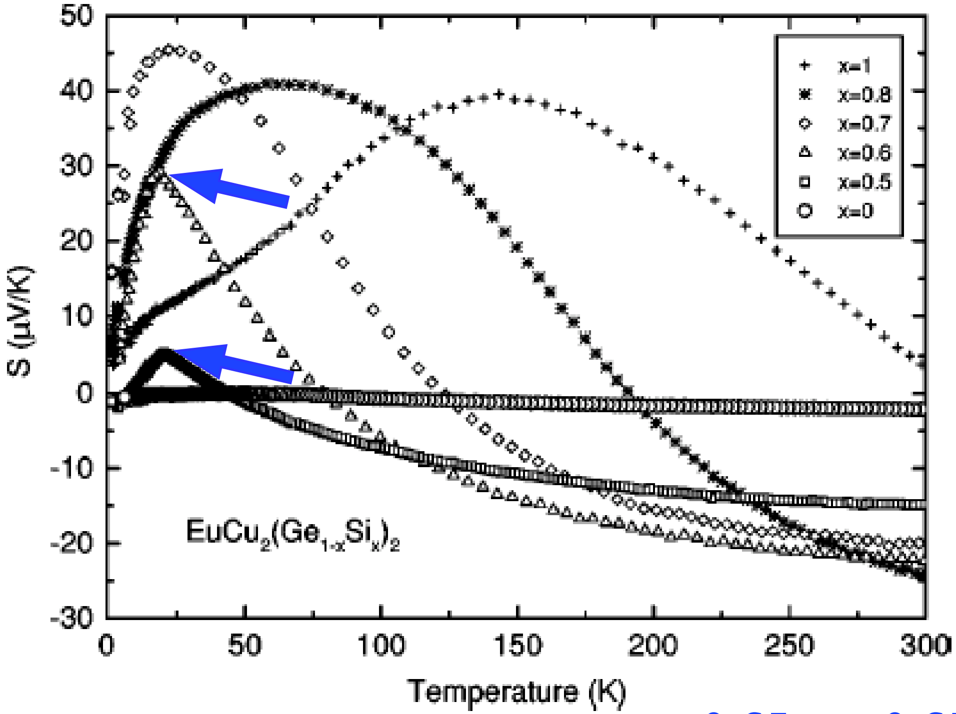
Maximum of S(T) is at T_K

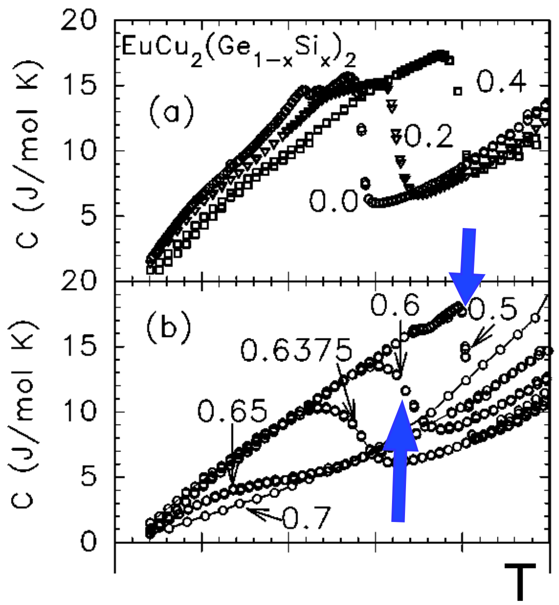
S(T)=0 at T_0

T_0 changes with doping.

FL ground state for x > 0.65.

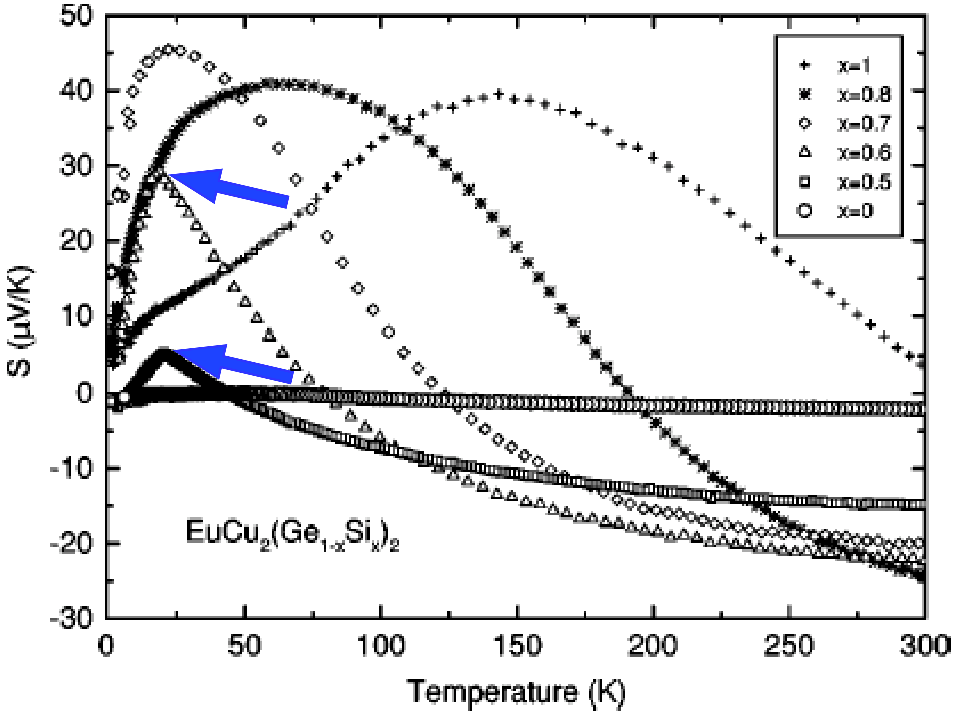
C_V and S(T) have anomaly at $T_N(x)$.
$T_N(x)$ is a non-monotonic function of x.



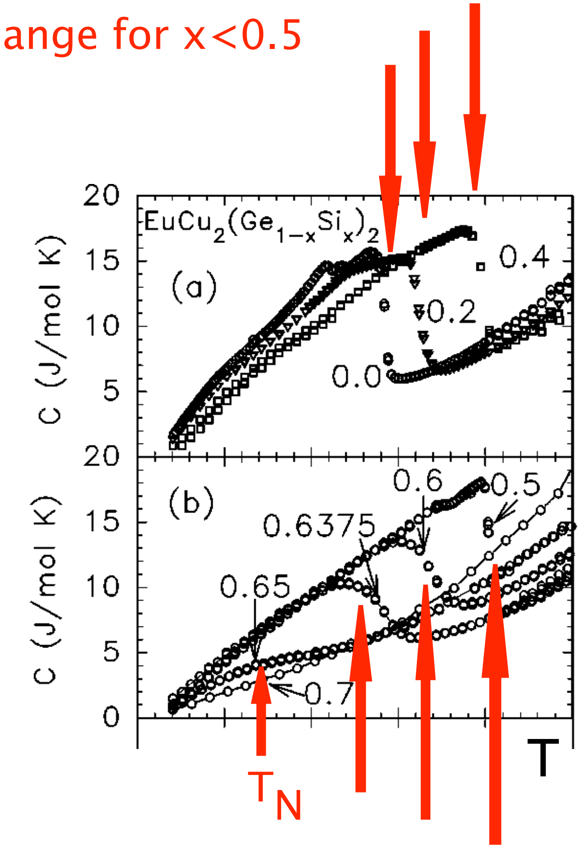


0.65<x<0.65 – S(T) shows at T_N a break of slope.
x<0.6 – S(T) shows a cusp at T_N.

FL ground state for x > 0.65.



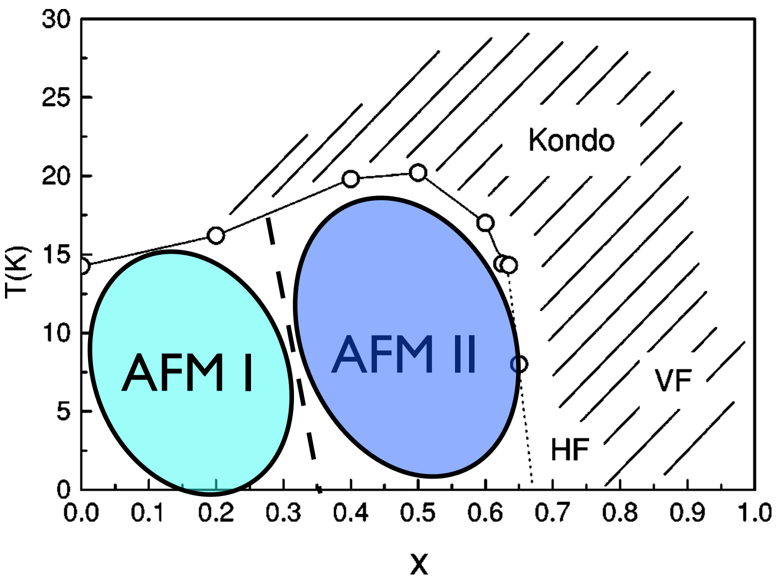
Large entropy change for x<0.5



Small entropy change for x>0.5

$Eu_2Cu_2(Si_xGe_{1-x})_2$

Z. HOSSAIN *et al.*



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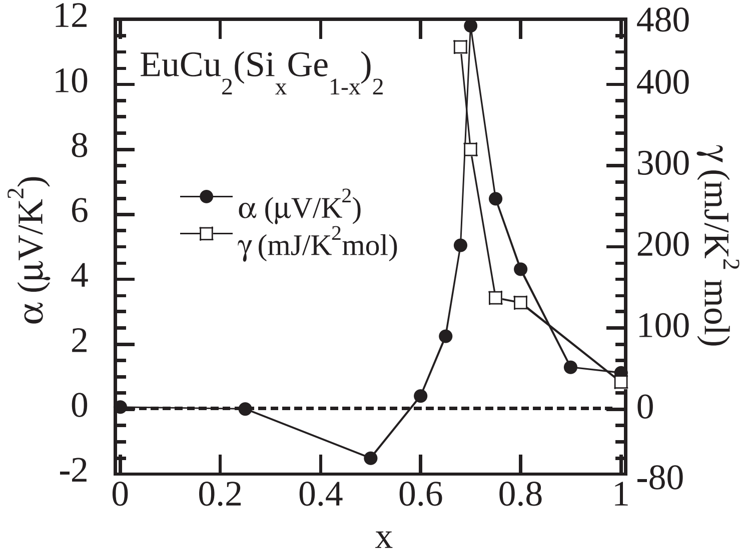
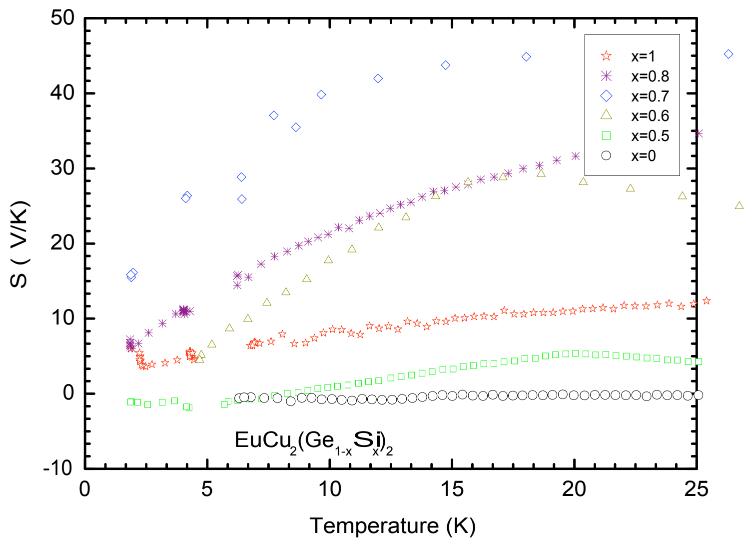
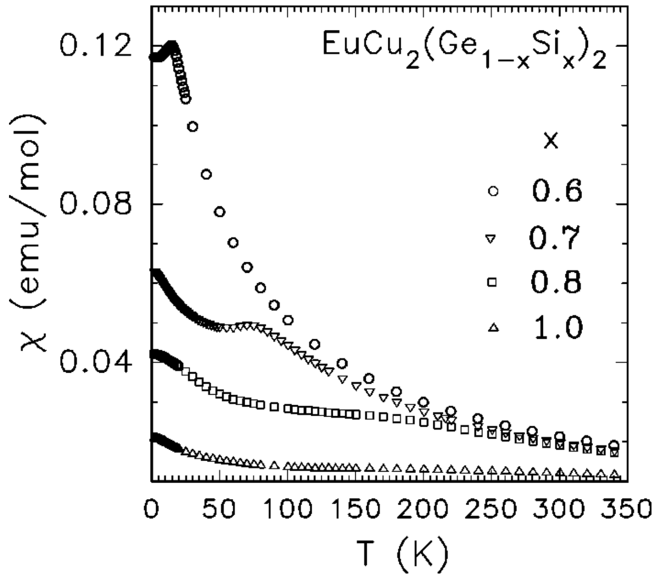
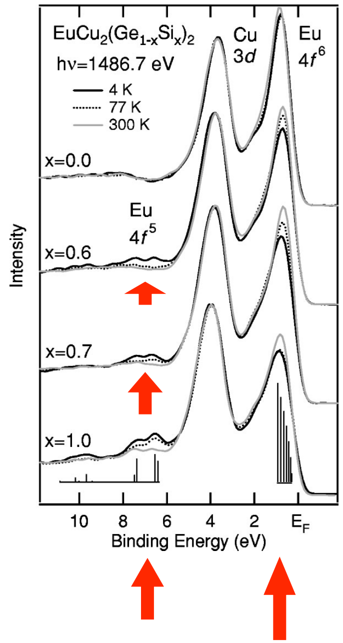








The valency of Eu ions changes with doping.

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

$$\frac{S}{\gamma T} = \frac{q}{e N_{Av}}$$

q=1 in $EuCu_2(Si_xGe_{1-x})_2$

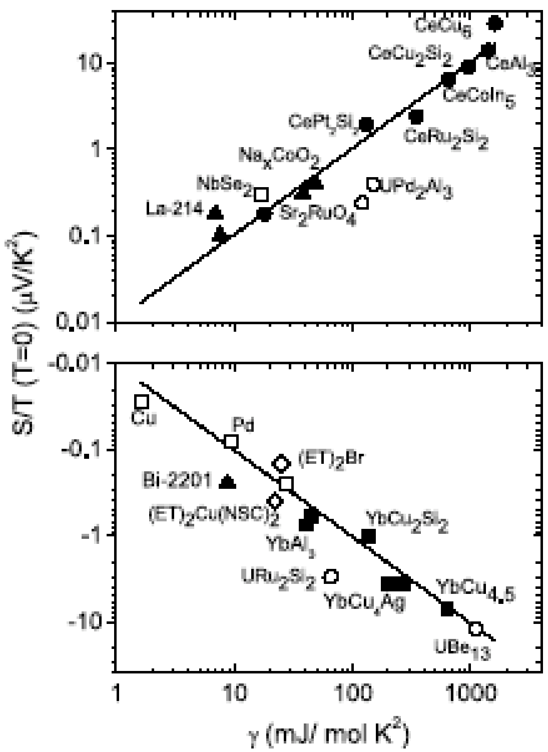


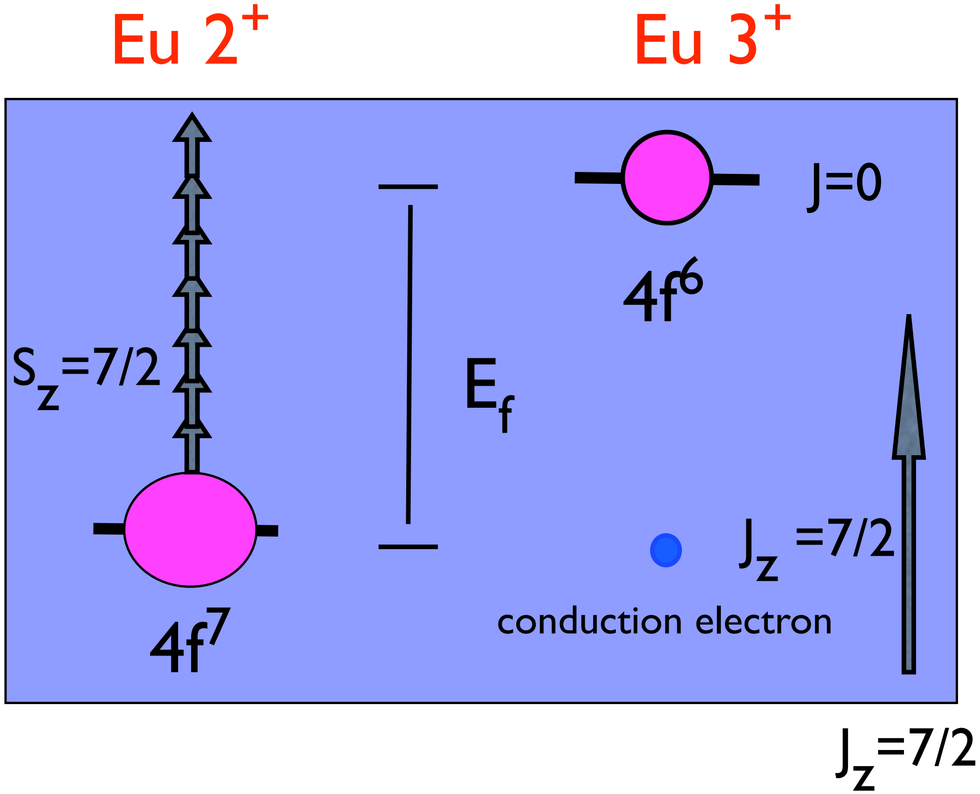
Figure 2. S/T versus γ for the compounds listed in table 1. Solid circles (squares) represent Ce (Yb) heavy-fermion systems. Uranium-based compounds are represented by open circles, metallic oxides by solid triangles, organic conductors by open diamonds, and common metals by open

$Eu_2Cu_2(Si_xGe_{1-x})_2$

Eu assumes $4f^7$ or $4f^6$ Hund's rule configuration.

Configurational splitting is E_f

Configurational fluctuations give rise to Kondo effect



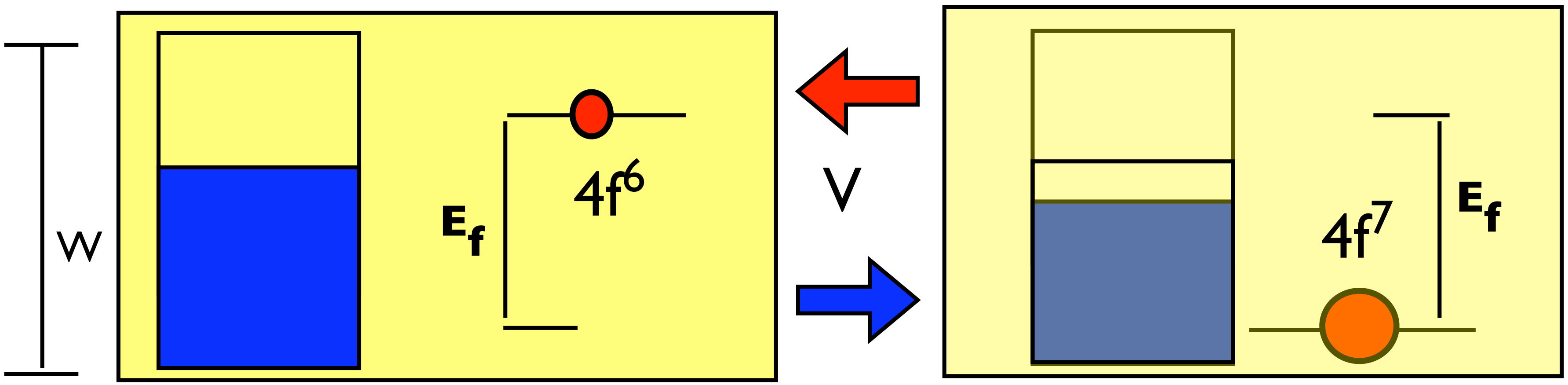
Modeling unstable 4f ions

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: $U_{ff} >> W$

Configurational splitting: $E_f < W$

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

Properties depend on: $g = \Gamma/\pi|E_f|$

and
relative occupation:

$n_c(T)$ *and* $n_f(T)$

Anderson lattice model

$$H_d = \Sigma_{ij,\sigma}(t_{ij} - \mu\delta_{ij})d^\dagger_{i\sigma}d_{j\sigma}$$

$$H_f = \Sigma_{l,\eta}(\epsilon_{f\eta} - \mu)f^\dagger_{l\eta}f_{l\eta} - U\Sigma_{l,\sigma>\eta}f^\dagger_{l\sigma}f_{l\sigma}f^\dagger_{l\eta}f_{l\eta}$$

$$H_{fd} = \frac{1}{\sqrt{N}}\Sigma_{\mathbf{k},l,\sigma}(V_{\mathbf{k}}c^\dagger_{\mathbf{k}\sigma}f_{l\sigma} + \mathrm{h.\ c.})$$

$U \rightarrow \infty$ 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.

$$n_{tot} = n_c(T) + c_i\, n_f(T) \qquad c_i = 1$$

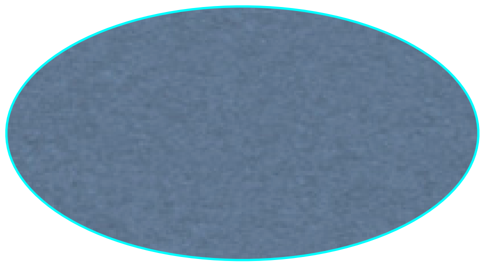
Thermoelectric properties depend on $g = \Gamma/\pi|E_f|$

What is needed?

Green's function $$G_f(z) = \frac{1}{z - (\epsilon_f - \mu) - \Gamma(z) - \Sigma(z)}$$

Spectral function $$A(\omega) = -\frac{1}{\pi} \mathrm{Im}\, G_f(\omega + i0^+)$$

Transport relaxition time



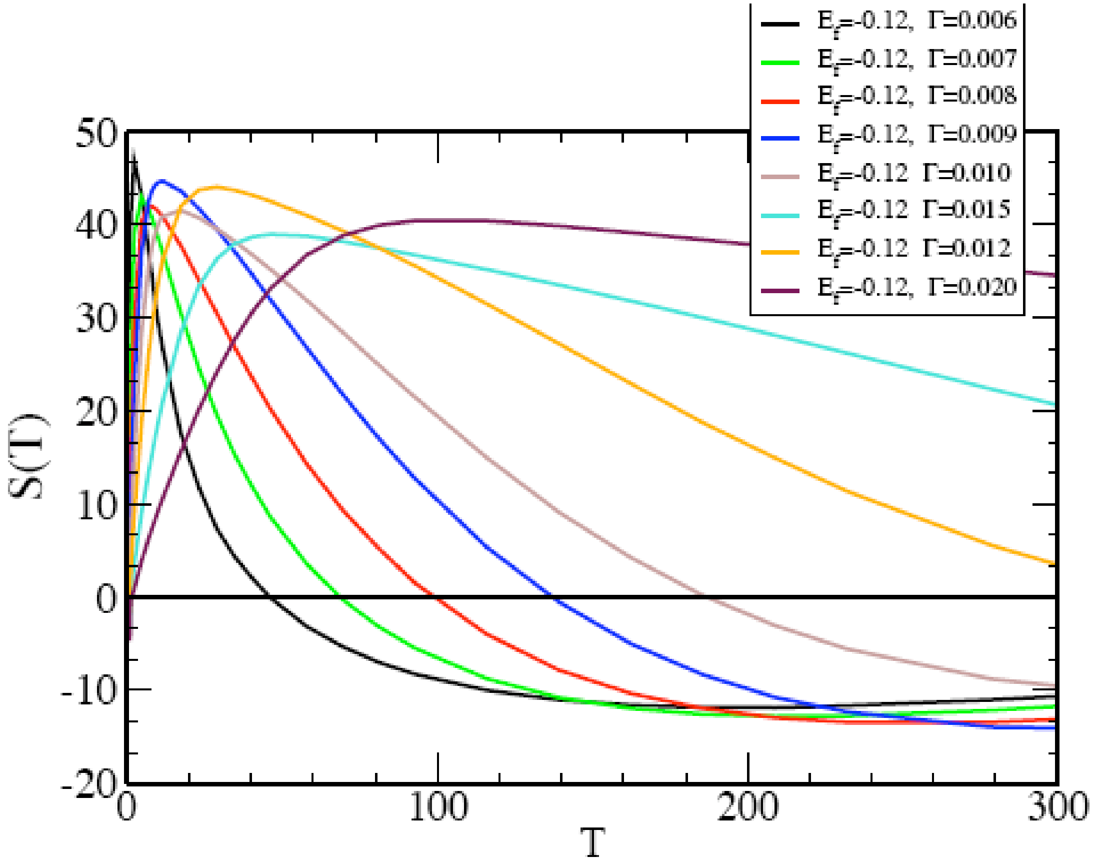
Transport integrals $$L_{ij} = \sigma_0 \int_{-\infty}^{\infty} d\omega \left(-\frac{df(\omega)}{d\omega} \right) \tau(\omega) \omega^{i+j-2}$$

NCA calculations for $CeEu_2(Si_xGe_{1-x})$ (initial parameters for $x=0$)

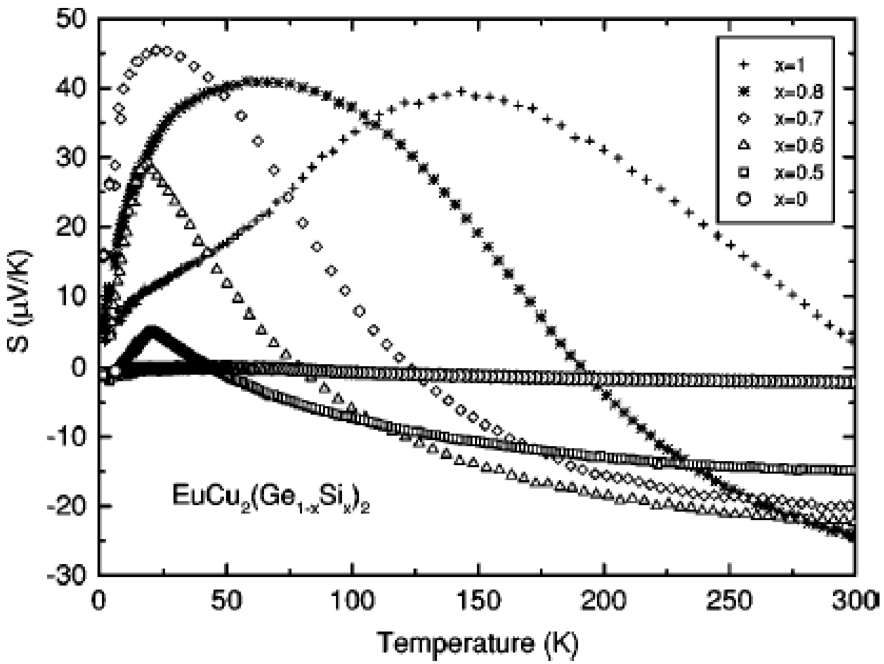
- Semielliptic conduction band of W=4 eV
- Initial f-level at E_f = - 0.12 eV
- Initial hibridization width Γ=0.006 eV
- 0.93 particles per effective 'spin' channel

Assume that Si doping increase hybridization Γ.

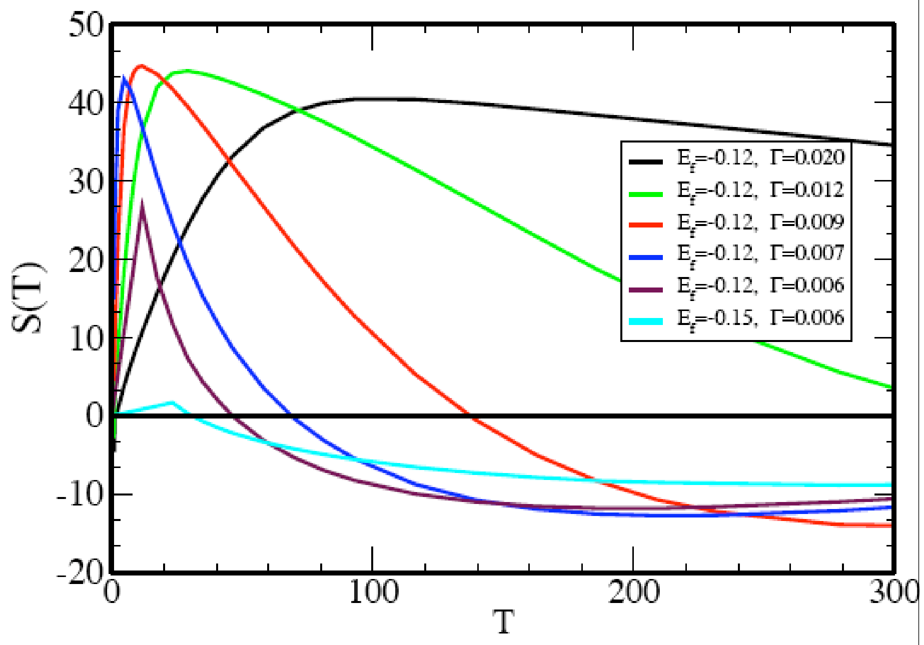
Fine-tuning: change the f-level position and
consider the excited states of 3+ configuration.



Thermopower of $Eu_2(Si_{1x}Ge_{1-x})_2$: comparison with experiment

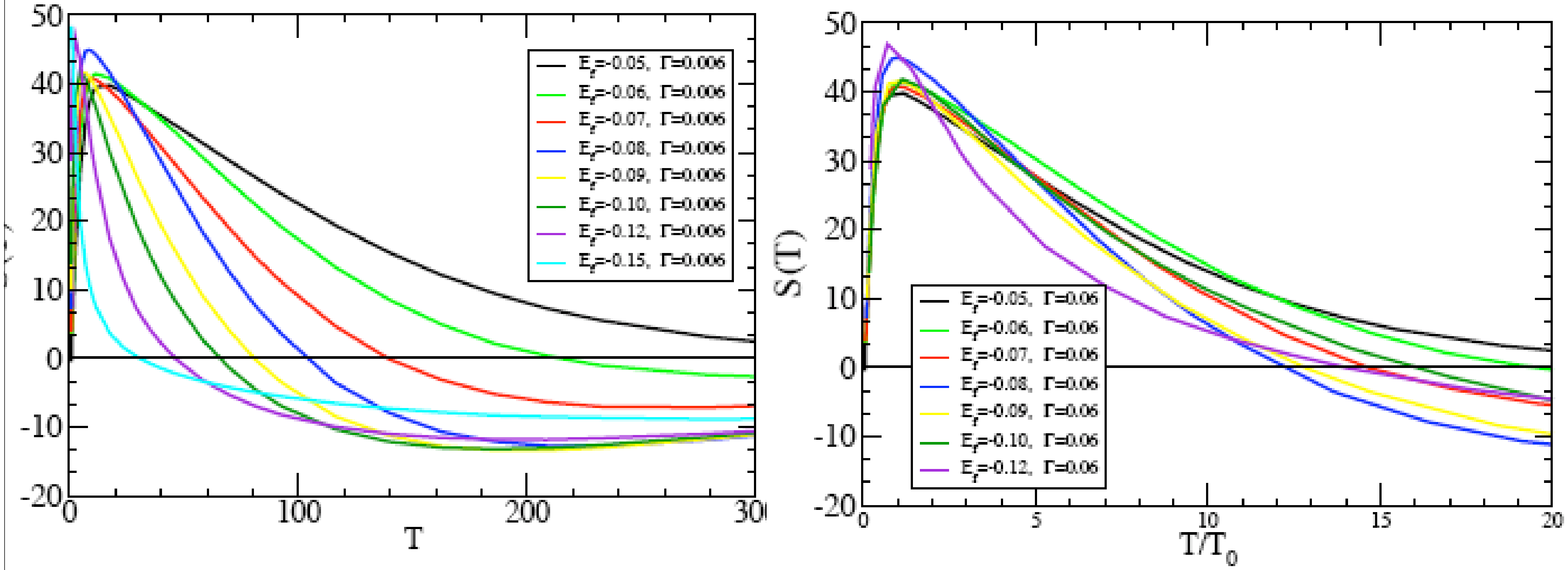


Experiment



Theory

Thermopower - changing the f-level position.

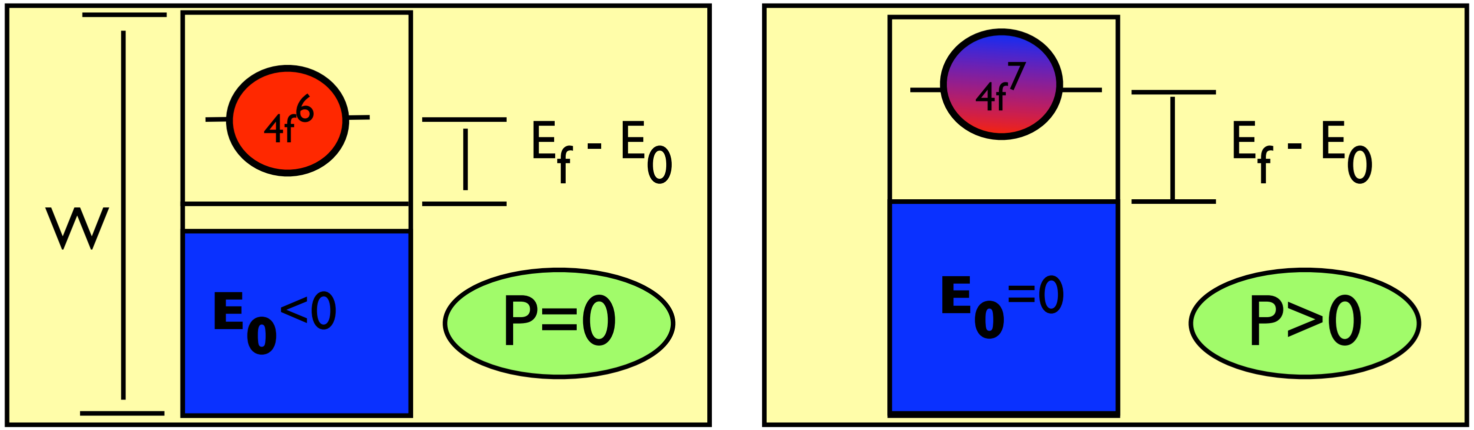


Universal behavior is restricted to $T \leq T_{max} \sim T_0$

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 Γ is unchanged.



For each E_f we shift μ 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

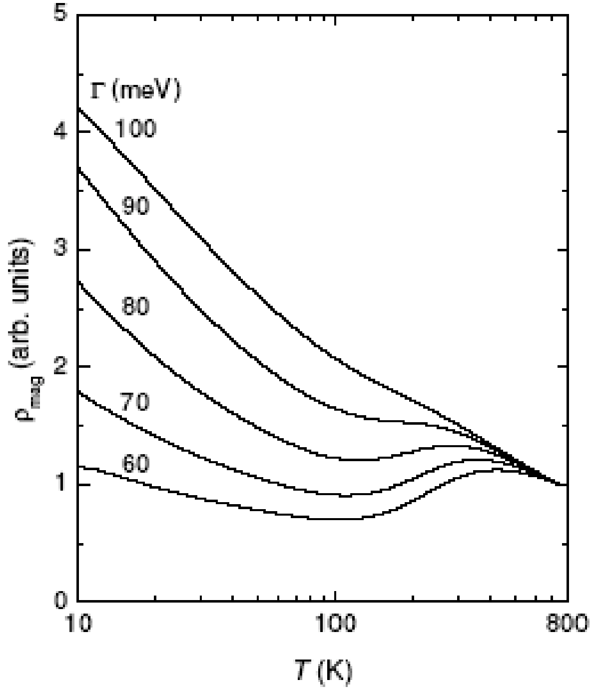


Figure 5: Electrical resistivity vs. temperature calculated by the NCA for the CF splitting $\Delta = 0.07$ eV and for several values of the hybridization strength Γ, as indicated in the figure.

f-particle number:

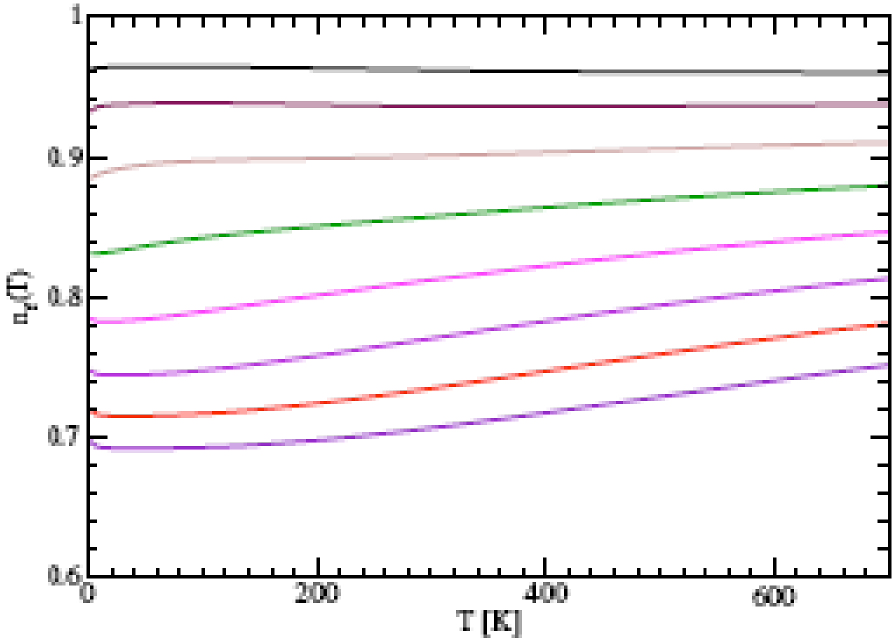
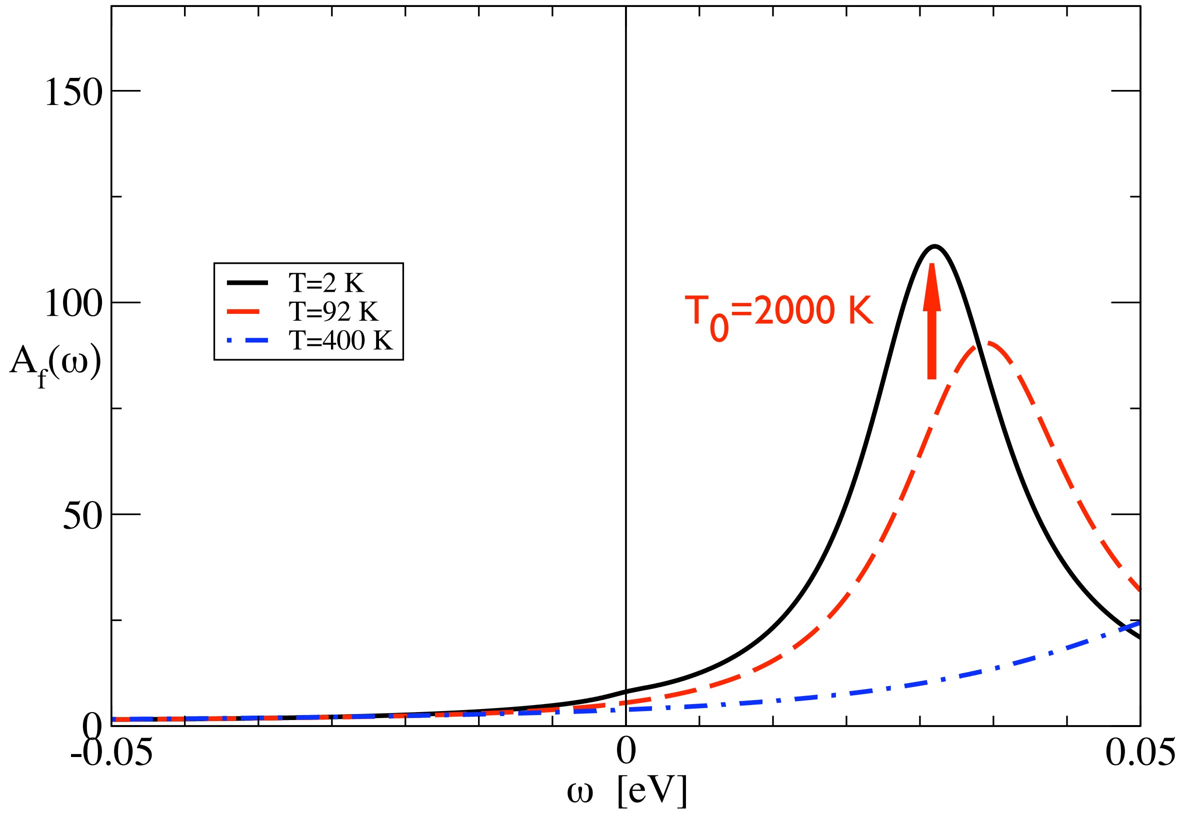


Figure 4: f-electron number, n_f, calculated by the NCA for the CF splitting $\Delta = 0.07$ eV is plotted as a function of temperature for several values of the hybridisation strength Γ. For the uppermost curve Γ=0.06 eV and then it increases in steps of 0.02 eV. At the bottom curve Γ=0.20 eV.

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

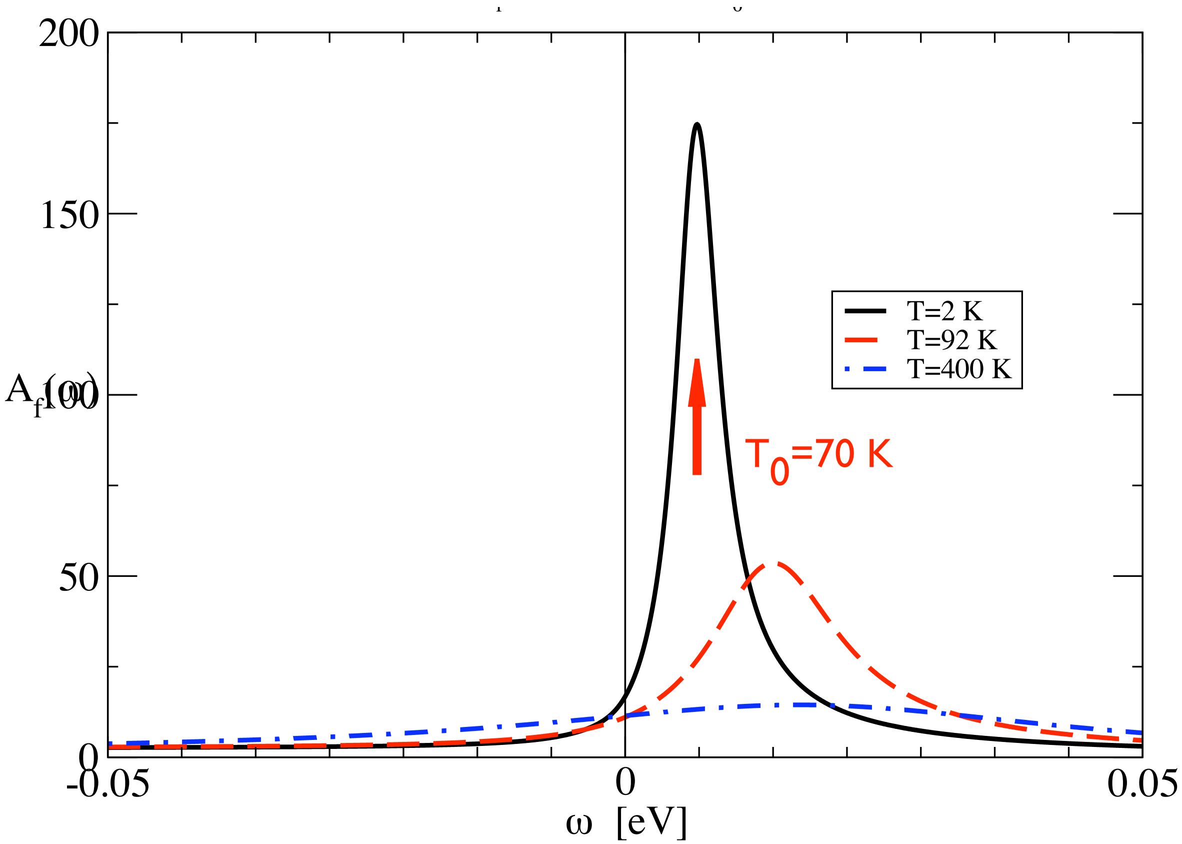
Spectrum of elementary excitation

E_f=-0.12,   Γ=0.20



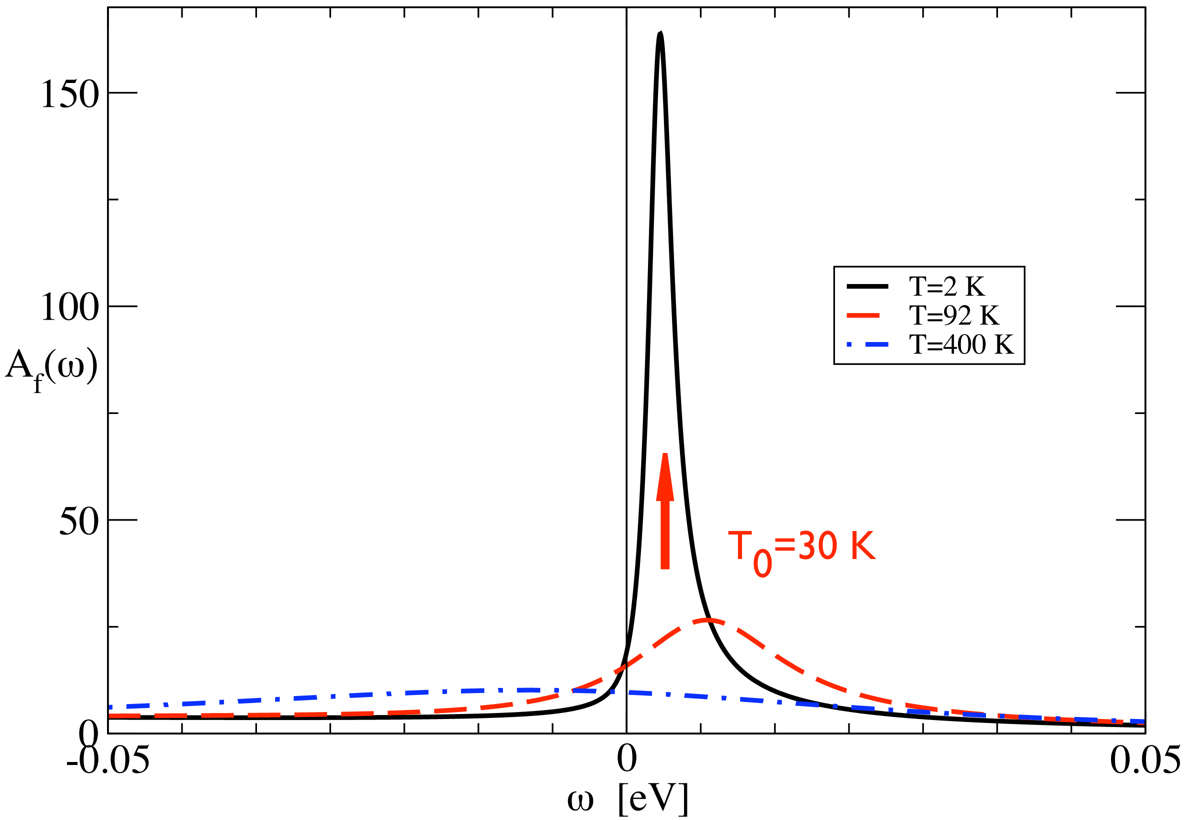
Spectrum of elementary excitation

E_f=-0.12, Γ=0.012



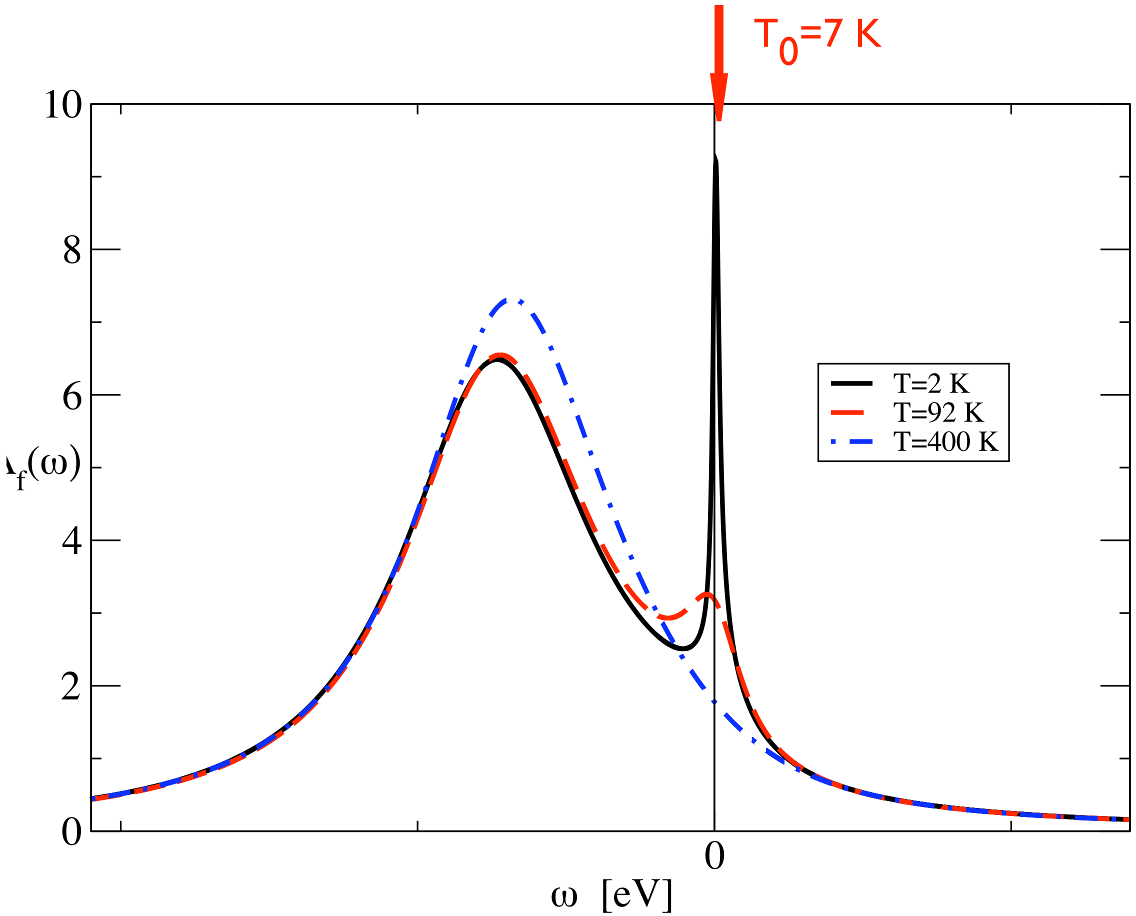
Spectrum of elementary excitation

E_f=-0.12, Γ=0.006



Spectrum of elementary excitation

E_f=-0.15, Γ=0.006



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 Γ/E_f.
- Shape of S(T) follows the redistribution of the spectral weight within the Fermi window.
- Pressure changes E_f and Γ.
- Combining the NCA and the Fermi liquid approximations provides the solution for any T.

Conclusions

- Above the coherence temperature (T_c~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 (α) versus entropy (s_N)

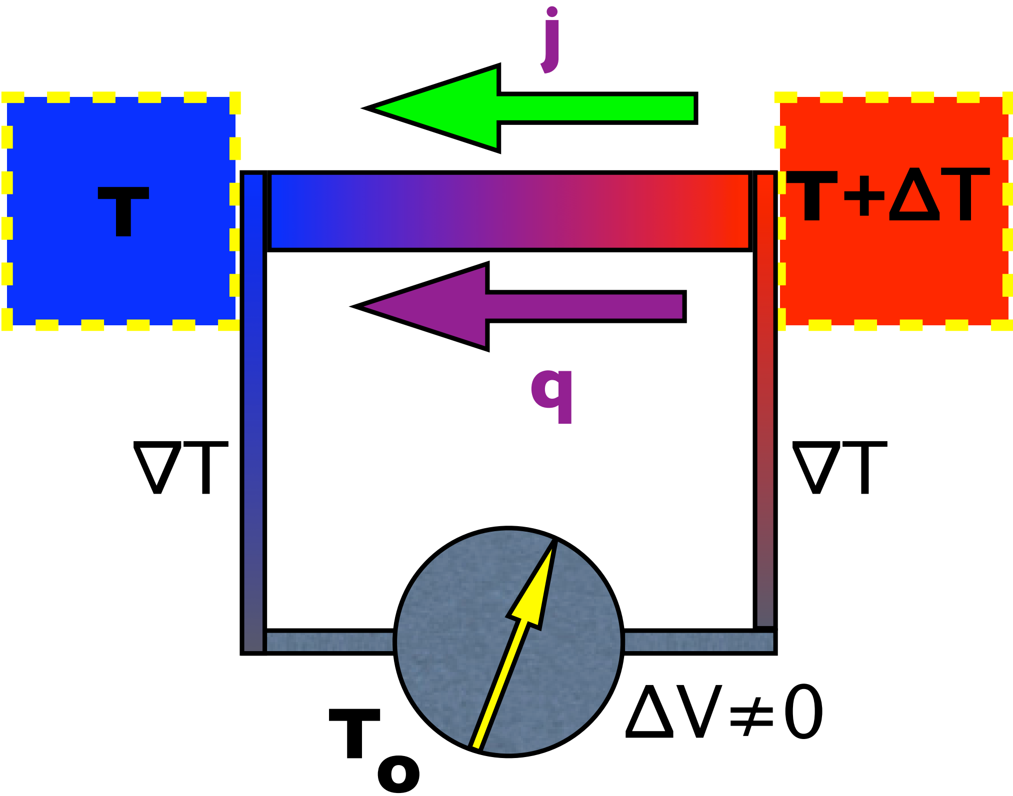
$$\mathbf{j} = \langle e^{-\beta H}\, \mathbf{j} \rangle / \langle e^{-\beta H} \rangle$$ current

$$\mathbf{q} = \langle e^{-\beta H}\, \mathbf{q} \rangle / \langle e^{-\beta H} \rangle$$ heat current

Gradient expansion leads to transport equations (Luttinger)

$$\left.\begin{aligned} \mathbf{j} &= -\sigma\nabla\varphi - \sigma\alpha\nabla T \\ \mathbf{q} &= (\varphi+\Pi)\mathbf{j} - \kappa\nabla T \end{aligned}\right\} \Rightarrow eN_A(\alpha/s_N) = N_A/N$$

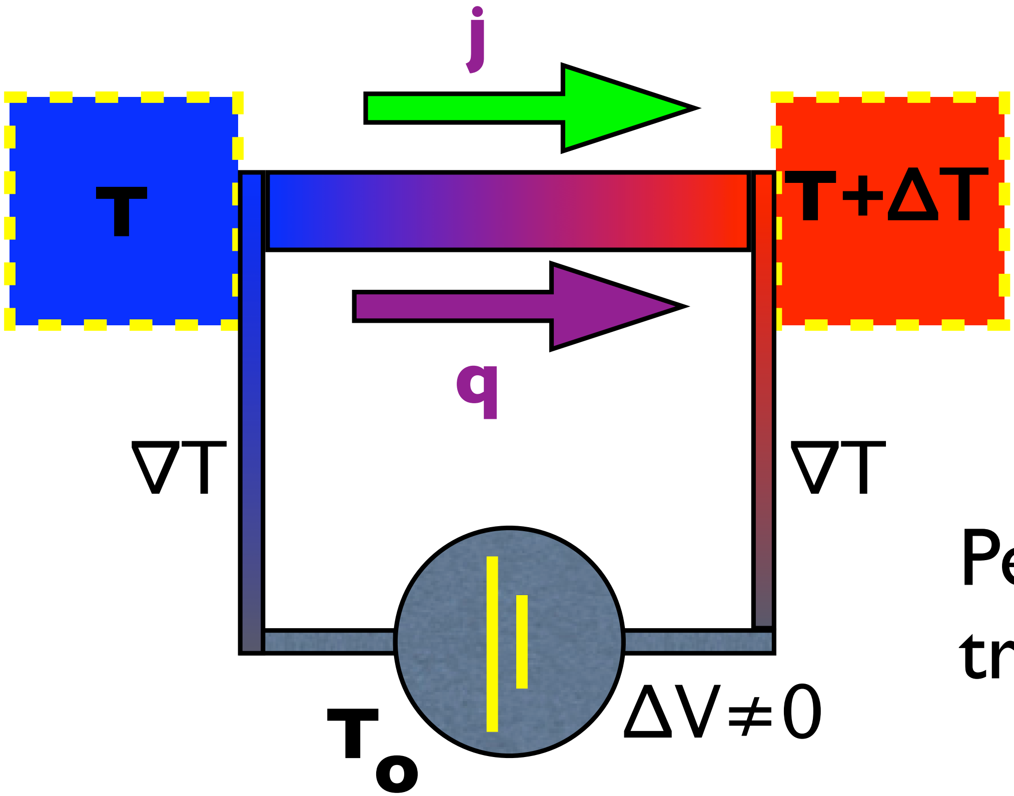
Seebeck effect: current generation



Seebeck coefficient:
transport eq. for j=0

$$\alpha = \Delta V / \Delta T$$

Peltier effect: thermoelectric cooling



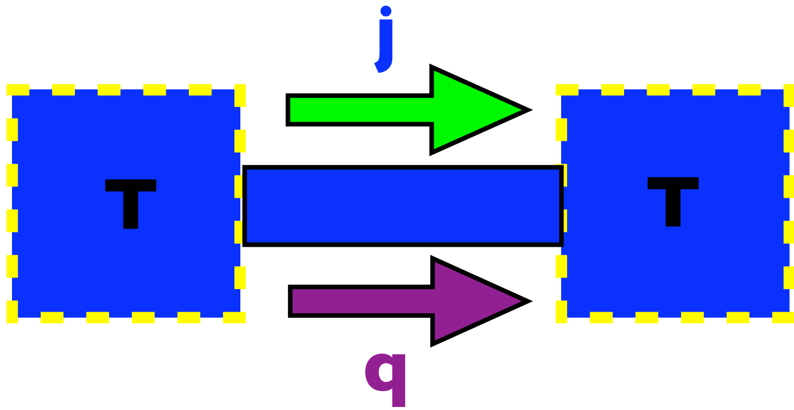
Peltier coefficient:
transport eq. for ∇T=0

$$\Pi(T) = \frac{q}{j}$$

Onsager: $\alpha = \Pi / T$

Stationary state in isothermal condition:

$$dQ/dt = -\mathrm{div}\, q = 0$$



$$\mathrm{div}\, q = Tj\nabla\alpha$$

Integrating over the interface:

$$g_s - g_l = (\Pi_s - \Pi_l)j$$

Interface leads to the discontinuity in the heat current.

$$\alpha/\gamma_N T = N_A/N$$

Stationary flow: $j = nev$

Analysis of transport equation

$$q_{exp} = N_A \frac{e\alpha(T)}{\mathcal{S}(T)} = \frac{N_A}{N} \frac{1}{1 + \mathcal{S}_M(T)/\mathcal{S}_N(T)},$$

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:

B-spectral function

$$b(\epsilon) = \frac{e^{-\beta(\epsilon-\omega_0)}}{\pi Z} \, \mathrm{Im} G_0(\epsilon)$$

F-spectral function

$$a_\Delta(\epsilon) = \frac{e^{-\beta(\epsilon-\omega_0)}}{\pi Z} \, \mathrm{Im} G_\Delta(\epsilon)$$

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

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