# The thermoelectric power and the thermal conductivity of Cerium Kondo compounds : Theoretical models.

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Summary :

-The Kondo effect.

- The case of Cerium or other anomalous rare-earth systems.

- The « high temperature » ($T>T_k$) description of the thermopower of Kondo systems.

- The « low temperature » ($T<T_k$) description of the thermopower of Kondo systems.

- The thermal conductivity of Kondo systems.

# Single-impurity Kondo model

Antiferromagnetic interaction between the local spin $S_f = \frac{1}{2}$ of the magnetic impurity and the local spin density $s_c$ of conduction electrons :

**Kondo Hamiltonian:** $H = H_{cond} + J_K\, s_c . S_f$

**Calculation of the magnetic resistivity:**

$$\rho_{mag} = A(J_K)^2 [1 + B\, J_K n(E_F)\, Log(T/D)]$$

**There is a minimum of the total resistivity for $J_K > 0$.**
**A good agreement is obtained for many resistivity curves at « high temperatures » above the Kondo temperature $T_k$ :**

$$T > T_k = D \exp(-1/ J_K n(E_F))$$

**The observed LogT behavior of the resistivity in many magnetic systems is really a « signature » of the Kondo effect.**

**Examples : $CeAl_2$, $CeAl_3$, $CeB_6$, LaCe, AuYb, TmS, $PrSn_3$ …**

At low temperatures ($T<T_k$), the Kondo impurities are well described by a Fermi liquid behavior :

- Electrical resistivity has a $T^2$ behavior
- Magnetic susceptibility tends to a huge constant $\chi_0$ which behaves as $1/T_k$.
- The electronic specific heat constant $\gamma$ has also a huge value which behaves as $1/T_k$.

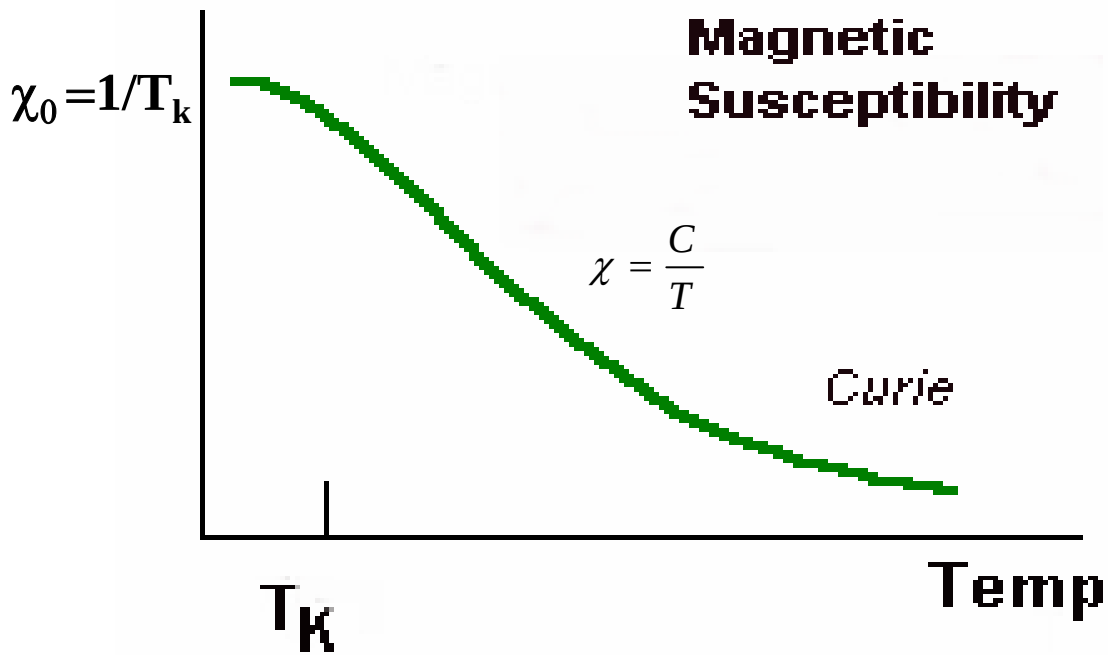
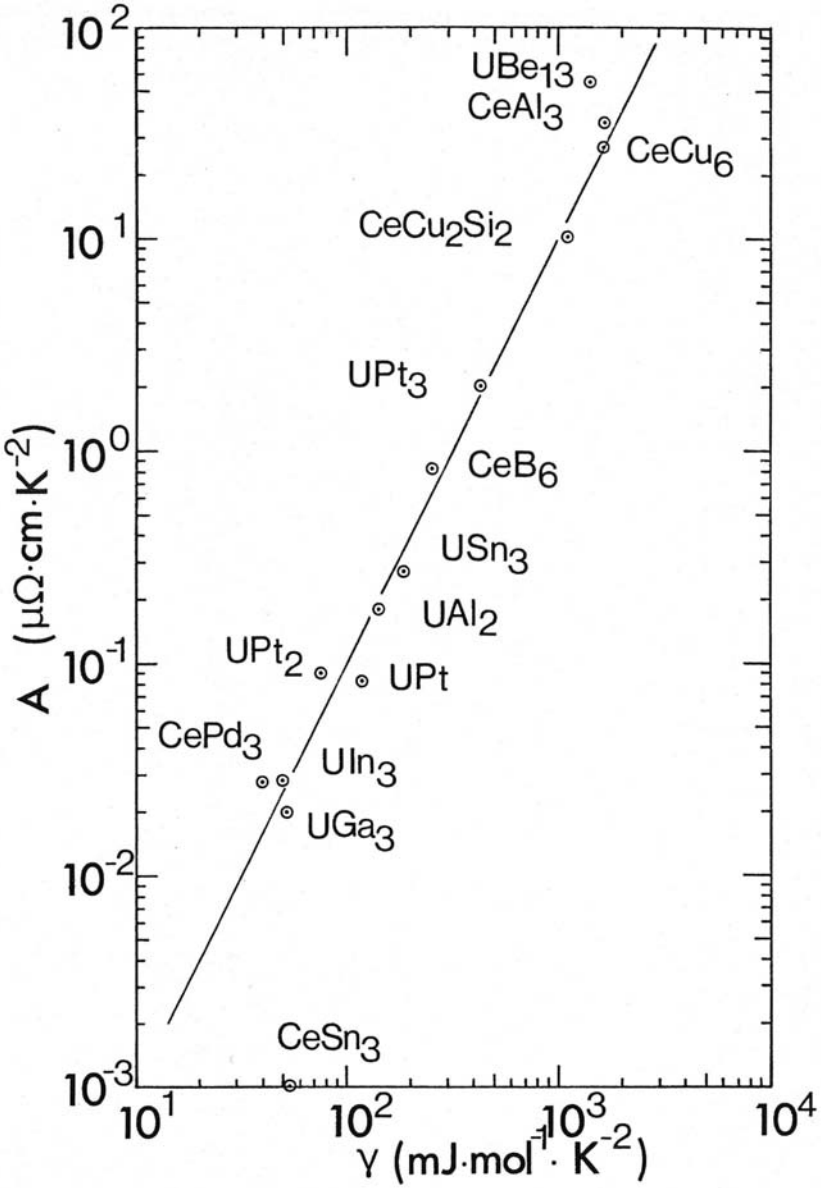


**TABLE 1.** Some examples of heavy fermion compounds

| **Compound** | **Crystal Structure** | **CF** (in K) | $\mathbf{T_N}$ (in K) | $\gamma(mJ/moleK^2)$ |
|---|---|---|---|---|
| $CeAl_3$ | Hexagonal | 60-90 | - | 1600 |
| $CeCu_2Si_2$ | Tetragonal | 140-360 | - | 1000 |
| $CeCu_6$ | Orthorhombic | 100-240 | - | 1500 |
| $CeRu_2Si_2$ | Tetragonal | 220 | - | 350 |
| $CeInCu_2$ | Cubic ($\Gamma_7$) | 90 | - | 1200 |
| $CeCu_4Ga$ | Hexagonal | 100 | - | 1800 |
| $CeAl_2$ | Cubic ($\Gamma_7$) | 100 | 3.85 | 135 |
| $CeB_6$ | Cubic ($\Gamma_8$) | 500 | 3.2 | 300 |
| $CeRh_2Si_2$ | Tetragonal | 150 | 36 | 23 |
| $Ce_3Al_{11}$ | Orthorhombic | 100 | 6.2* | 120 |
| $CeIn_3$ | Cubic ($\Gamma_7$) | 100 | 10 | 140 |
| $CeAl_2Ga_2$ | Tetragonal | 65-120 | 8.5 | 80 |
| $CeCu_2$ | Orthorhombic | 200 | 3.5 | 82 |
| $CeCu_2Ge_2$ | Tetragonal | 200 | 4.15 | 100 |
| $Ce_2Sn_5$ | Orthorhombic | 70-155 | 2.9 | 380 |
| $YbCu_4Ag$ | Cubic | 45 | - | 245 |
| $YbBiPt$ | Cubic | - | - | 8000 |
| $YbNi_2B_2C$ | Tetragonal | 40-200 | - | 530 |
| $YbCu_2Si_2$ | Tetragonal | 216 | - | 135 |
| $YbNiAl$ | Hexagonal | 35 | 2.9 | 350 |
| $U(Pt_{0.95}Pd_{0.05})_3$ | Hexagonal | - | 6 | 500 |
| $UPd_2Al_3$ | Hexagonal | - | 14.3 | 150 |
| $UNi_2Al_3$ | Hexagonal | - | 4.6 | 120 |
| $NpSn_3$ | Cubic | - | 9.5 | 240 |

* Ferromagnetic $T_c$




**Kadowaki-Woods diagram :**
**A (resistivity coefficient of the $T^2$ term) versus $\gamma$.**

# Cerium and Ytterbium compounds

- Cerium : $4f^0 – 4f^1$
- Ytterbium : $4f^{14} – 4f^{13}$
- Pr, Sm, Eu and Tm can be anomalous.

- Cerium → N(4f) < 1 : Intermediate valence.
  → N(4f) close to 1, almost $4f^1$ (S=1/2, L=3, J=5/2) and Magnetic : Kondo effect.

# The KONDO effect in Cerium (or Ytterbium) systems within the effective exchange (C.S.) Hamiltonian.

- - Ce : configuration $4f^1$ : l=3, s=1/2, j=5/2 (M=$j_z$ = -5/2, -3/2 … +5/2)
  (The j=7/2 multiplet is widely separated from the j=5/2 multiplet)

- - Only the conduction-electron partial-wave states with same l, s, j and M values are “mixed” with localized states.

- - The crystal-field effect splits the (2j+1)-degenerate 4f level into : either one doublet $\Gamma_7$ and one quartet $\Gamma_8$ or three doublets.

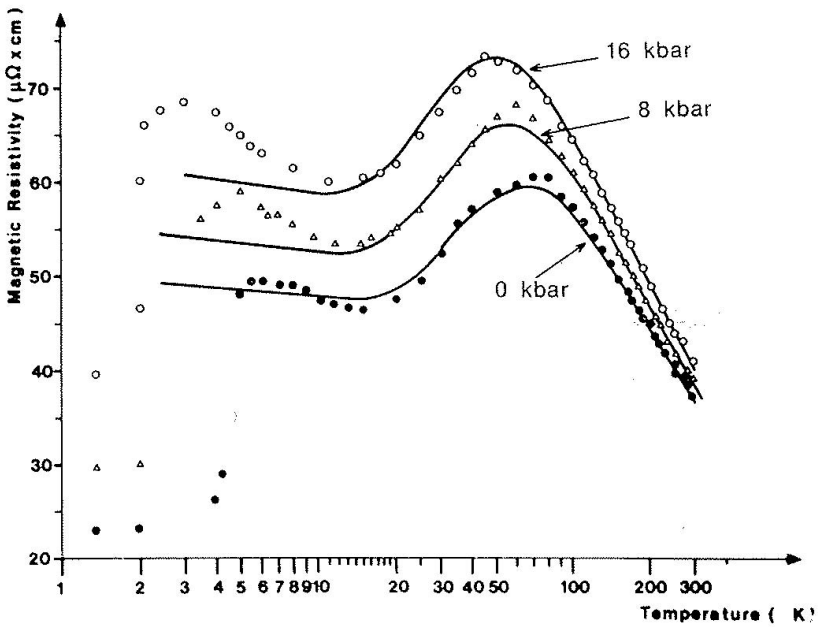
- - The exchange integral $J_K$ is given by :

$$J_K = |V_{kf}|^2/|E_0|$$

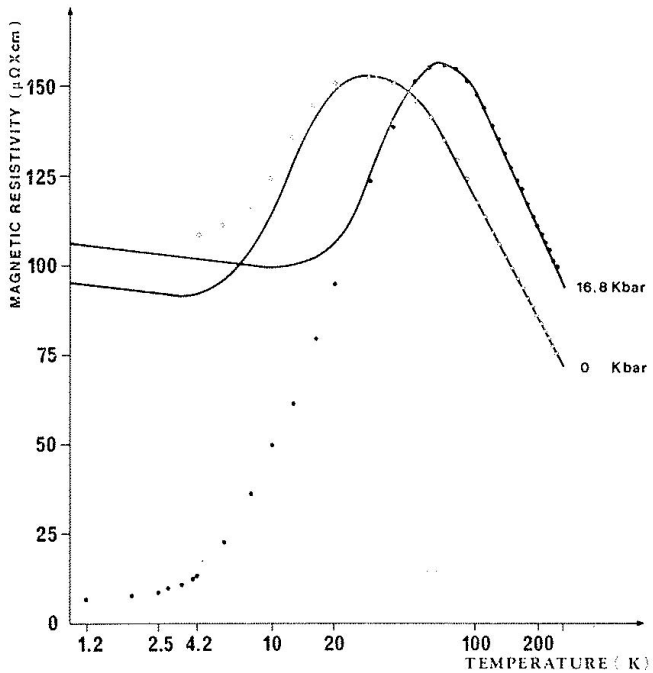
- - The parameters of the model are $J_K$ and the crystalline field (CF) splitting $\Delta$.

The electrical resistivity (B. Cornut and B. Coqblin, Phys. Rev. **B5**, 4541 (1972)), the thermoelectric power (A. K. Bhattacharjee and B. Coqblin, Phys. Rev. **B13**, 3441 (1976)) and the thermal conductivity (A. K. Bhattacharjee and B. Coqblin, Phys. Rev. **B38**, 338 (1988)) have been computed in the model which describes both the Kondo effect and the crystalline field effect, within the perturbation theory in third order in the exchange integral $J_K$, in the so-called "high temperature" limit, i.e. $T>T_k$, where $T_k$ is the Kondo temperature.

But, in many Kondo systems, $T_k$ can be very small, for example of order a fraction of 1K to some °K and the crystalline field splitting $\Delta$ is generally much larger than $T_k$.


Magnetic Resistivity (μΩ x cm)
70
60
50
40
30
20
16 kbar
8 kbar
0 kbar
1
2
3
4
5
6
7
8
9
10
20
30
40
50
100
200
300
Temperature ( K)

$CeAl_2$


MAGNETIC RESISTIVITY (μΩ x cm)
150
125
100
75
50
25
0
16.8 Kbar
0 Kbar
1.2
2.5
4.2
10
20
100
200
TEMPERATURE ( K)

$CeAl_3$

A.K Bhattacharjee and B. Coqblin,Phys. Rev B **13**, 3441 (1976).

**The thermoelectric power S is given by :**

$$S = -\frac{1}{eT}\left[\int_{-\infty}^{\infty} \epsilon_k \left(-\frac{\partial f_k}{\partial \epsilon_k}\right) \tau_k \, d\epsilon_k \Big/ \int_{-\infty}^{\infty} \left(-\frac{\partial f_k}{\partial \epsilon_k}\right) \tau_k \, d\epsilon_k\right]$$

**with $e > 0$.**

So, the total resistivity $\rho$ is given by:

$$\frac{1}{\rho} = \sigma = \frac{e^2}{3\pi^2 m} \int_0^{\infty} k^3 \left(-\frac{\partial f_k}{\partial \epsilon_k}\right) \tau_k \, d\epsilon_k$$

The value of $\tau_k$ is given by:

$$\frac{1}{\tau_k} = \frac{mkv_0 c}{\pi \hbar^3 (2j+1)} (R_k + S_k) \quad ,$$

$$R_k = \sum_M \left( |V_{MM}|^2 - 2V_{MM} J_{MM} \langle n_M \rangle \right)$$

$$+ \sum_{M,M'} \frac{|J_{MM'}|^2 \langle n_{M'} \rangle}{1 - f_k (1 - e^{\beta(E_M - E_{M'})})},$$

$$S_k = 2 \sum_{M,M'} \sum_m J_{MM'} J_{mM} J_{mM'} \langle n_{M'} \rangle$$

$$\times (1 - \delta_{mM} \delta_{mM'}) \frac{g(\epsilon_k + E_m - E_M)}{1 - f_k (1 - e^{\beta(E_M - E_{M'})})}$$

$$- 2 \sum_M \sum_m (1 - \delta_{mM}) V_{MM} |J_{MM}|^2$$

$$\times (\langle n_M \rangle - \langle n_m \rangle) g(\epsilon_k + E_m - E_M),$$

where $R_k$ is the second-order term, $S_k$ is the third-order term, $m$ is the mass of the conduction electrons, $k$ is their wave number, $v_0$ is the sample volume, $c$ is the impurity concentration

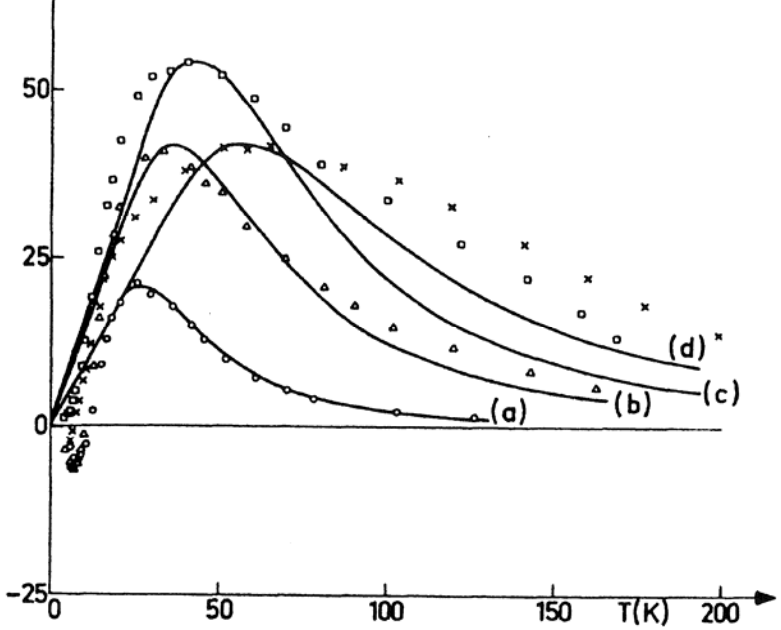
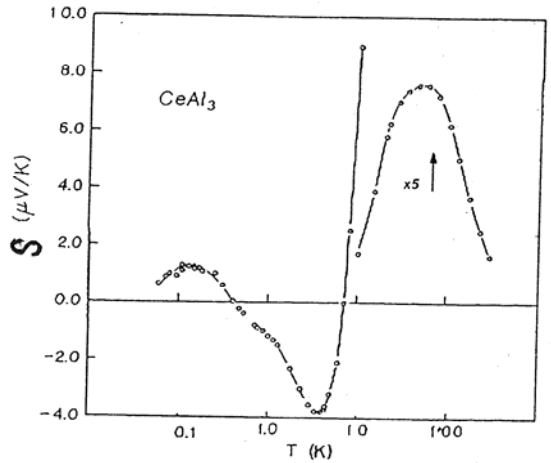
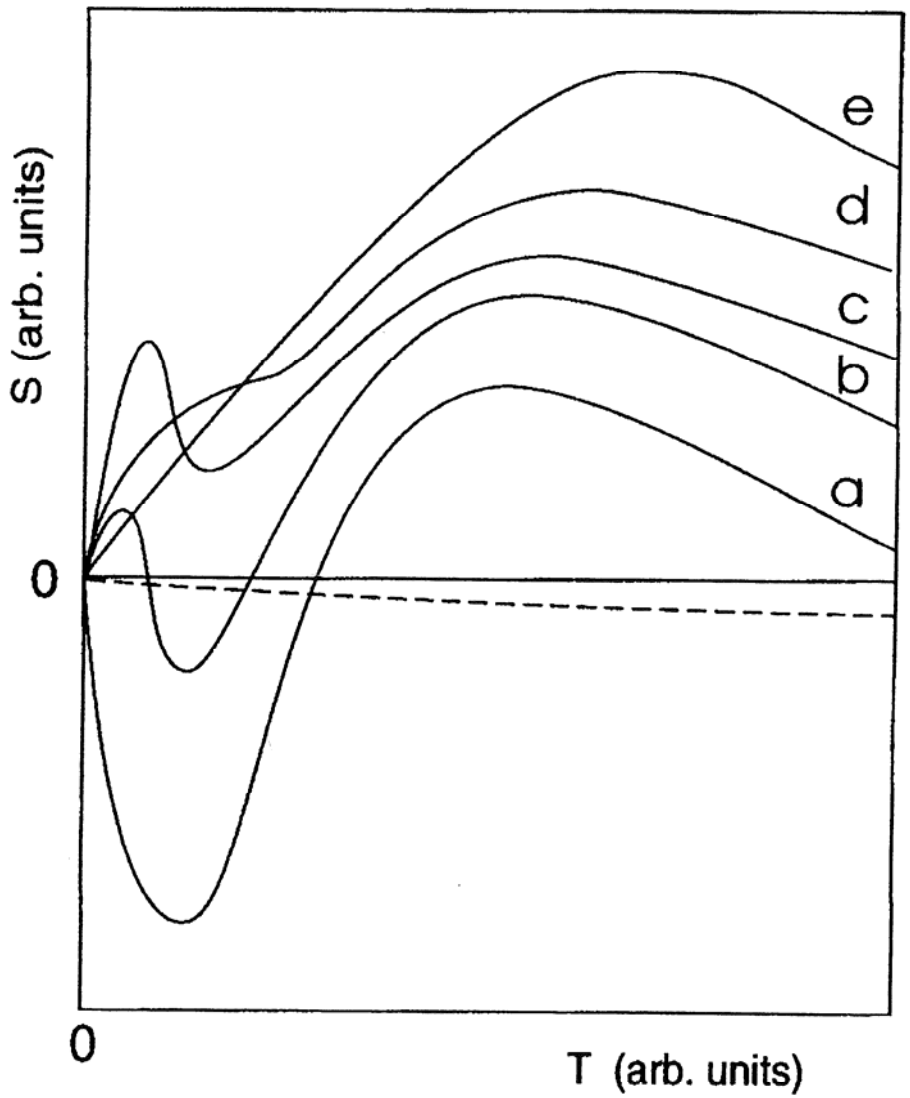



FIG. 6. Comparison between experiment and theory for $Ce_{1-x}La_xAl_3$. Experimental points show the differences between the Seebeck coefficients of $Ce_{1-x}La_xAl_3$ and of $LaAl_3$ for $x = 0.99$ (o), 0.90 (Δ), 0.50 (□), 0 (x).




Thermoelectric power Q of $CeAl_3$ over almost 4 decades of temperatures.




Characteristic thermopower behaviours of metallic Ce-based systems.

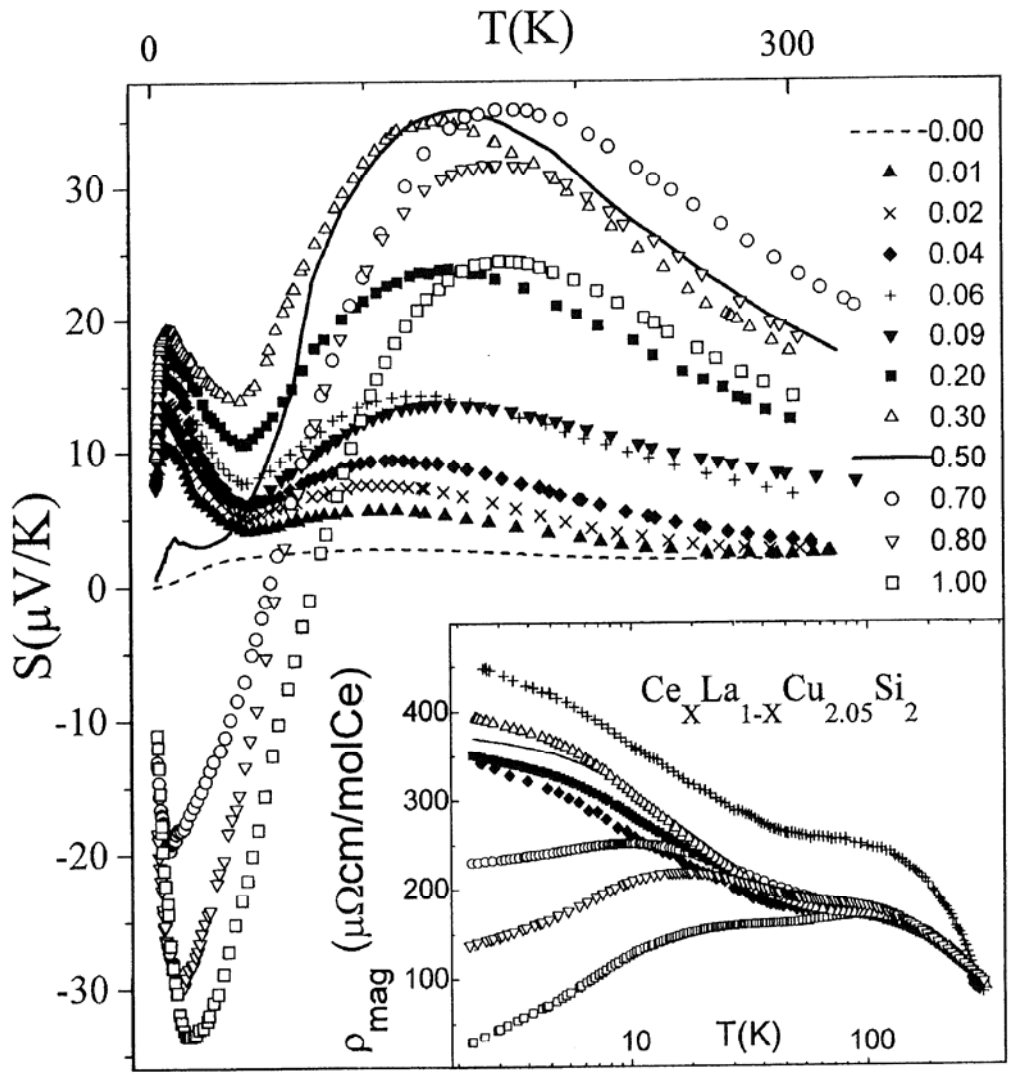



Fig. 1. Thermopower of the $Ce_xLa_{1-x}Cu_{2.05}Si_2$ alloy system. *Inset*: Magnetic contribution to the resistivity, $\rho_{mag}$.

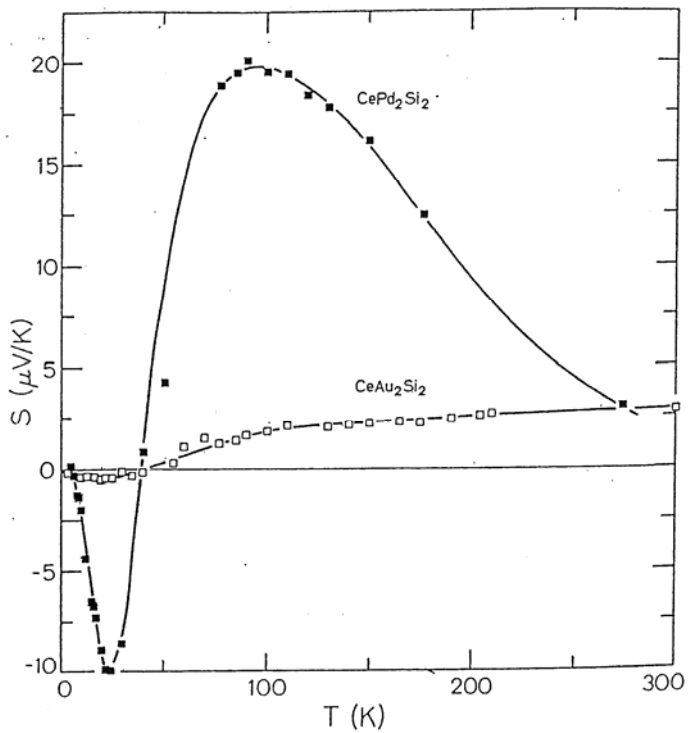



Fig. 1. Absolute thermopower of $CeAu_2Si_2$ and $CePd_2Si_2$

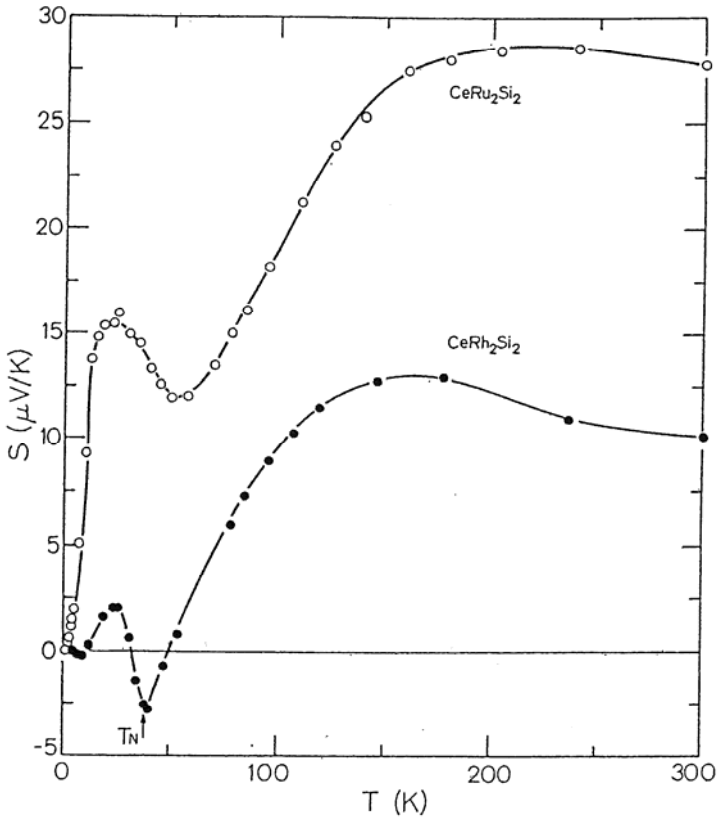
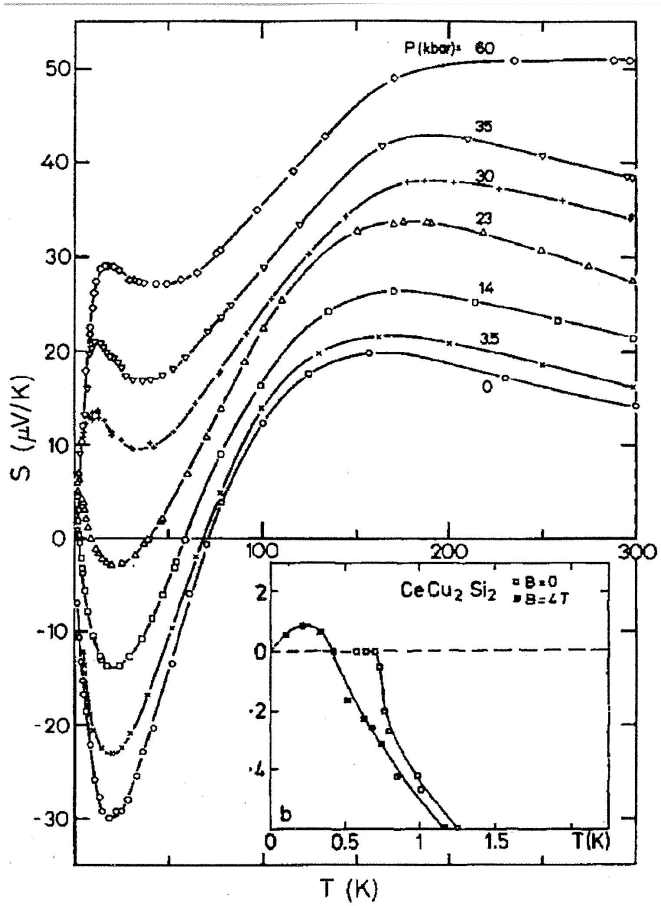



Fig. 2. Absolute thermopower of $CeRh_2Si_2$ and $CeRu_2Si_2$. The arrow indicated the ordering temperature $T_N$


P(kbar)= 60
35
30
23
14
35
0
S (μV/K)
T (K)
CeCu2 Si2 ▫ B=0 ▪ B=4T
b
T(K)

V. Zlatic, B. Horvatic, I. Milat, B. Coqblin, G. Czycholl and C. Grenzebach,
Phys. Rev B **68**, 104432 (2003).

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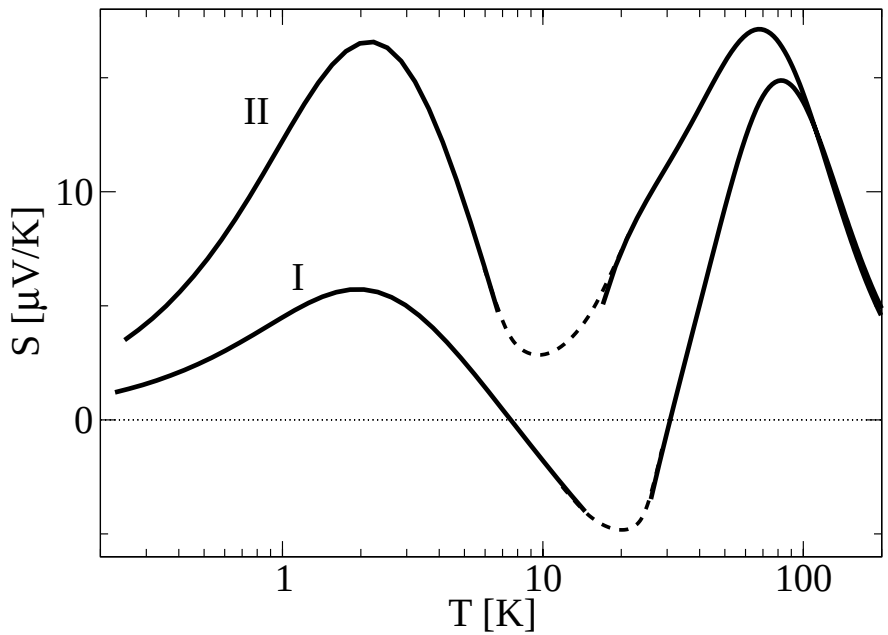
**At low temperatures ($T<T_k<\Delta$), the Cerium Kondo impurity is described by the Fermi liquid model for the doublet ground state . Within the Single-impurity Anderson model, the f-electron spectral function presents a peak at the Fermi energy (« Kondo resonance »), which depends on the c-f hybridization $V_{kf}$ and the Coulomb integral U. We use a modified perturbation theory which interpolates between the two limiting cases of $V_{kf}$ and U tending to zero and which allows to have a good description of the Kondo resonance. Then we compute the thermoelectric power which presents a positive (negative) peak at a temperature roughly equal to $T_k/2$ for Cerium (Ytterbium) compounds.**

**Increasing pressure : I → II**

**I : $n_f$=0.98, $V_0$=-0.2 eV**

**II : $n_f$=0.95, $V_0$=-0.35 eV**




**Maxima at $T_k/2$ and $\Delta/3$**

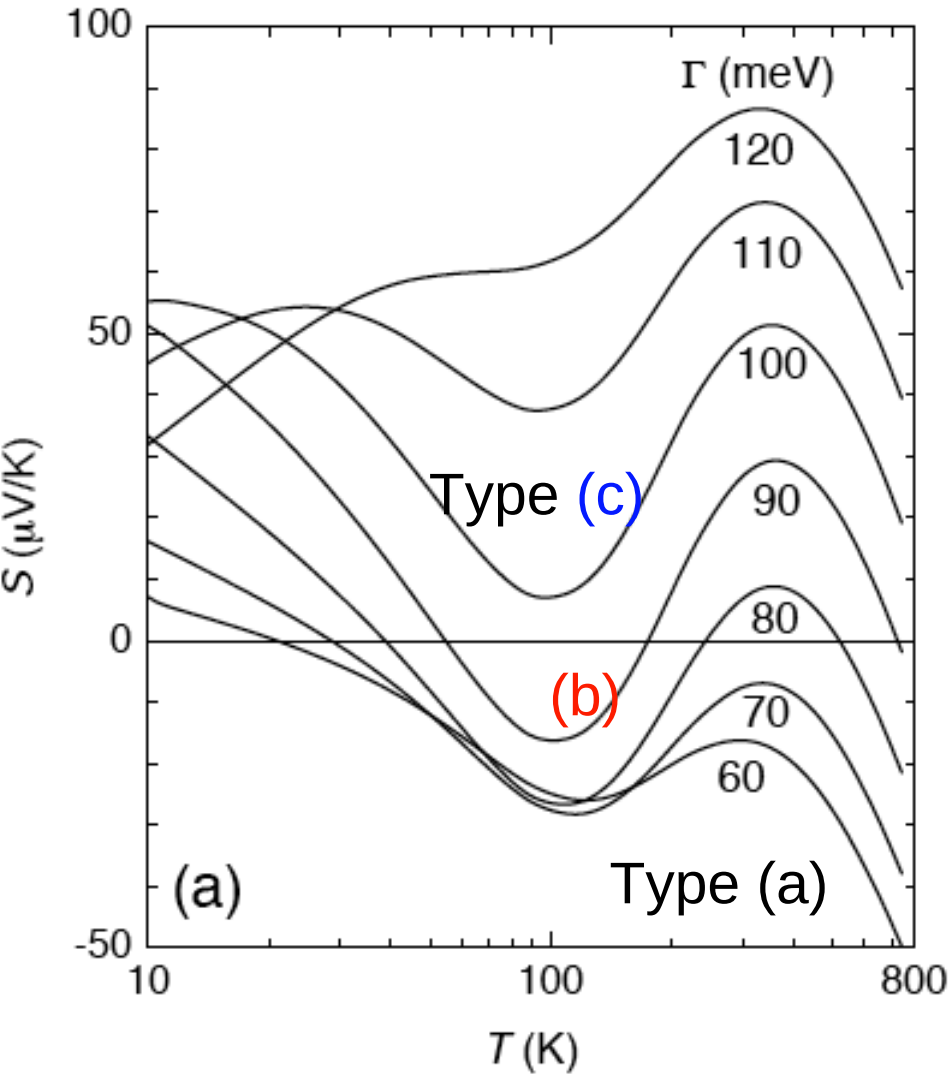
H. Wilhelm, D. Jaccard, V. Zlatic, R. Monnier, B. Delley and B. Coqblin, J. Phys. : Condens. Matter **17**, S823 (2005).

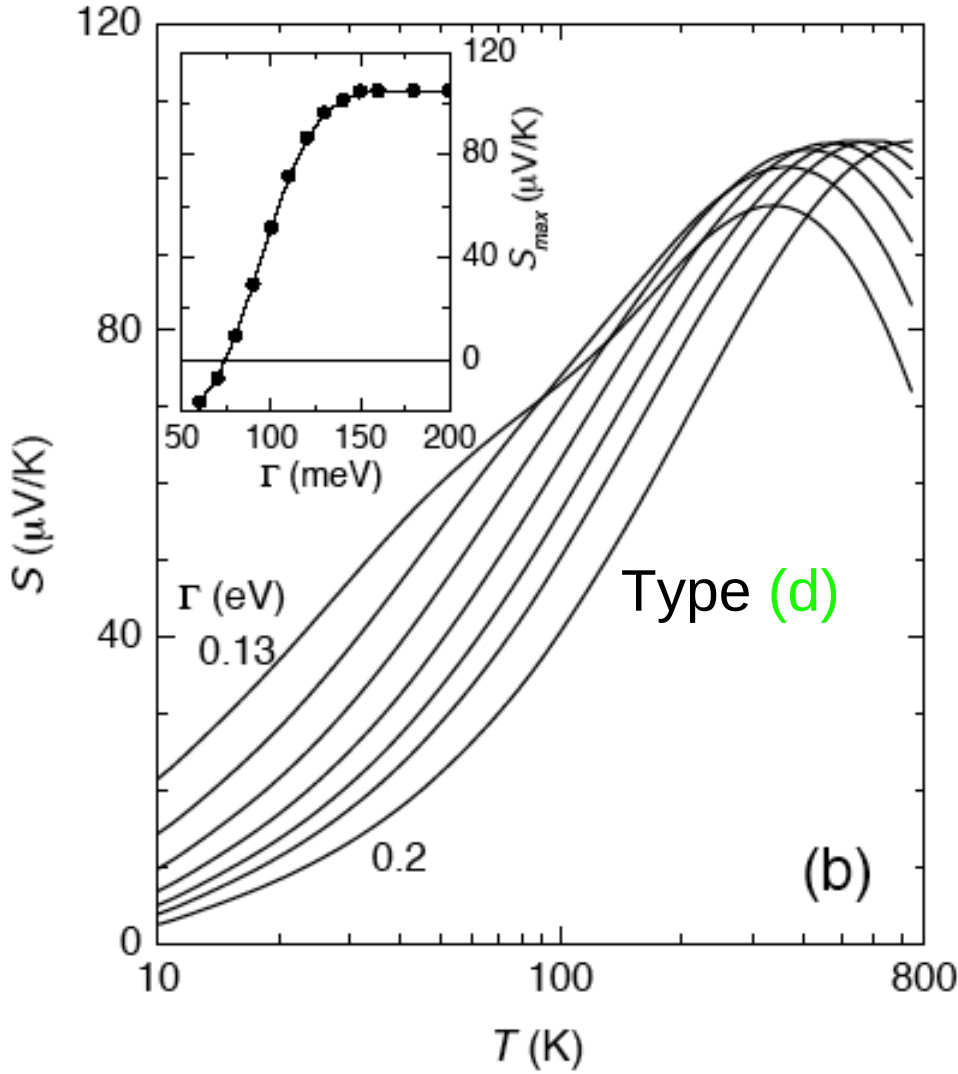
## Theoretical model to account for the high pressure transport properties of $CeRu_2Ge_2$ :

Anderson Model with a semi-elliptic conduction band of W = 4 eV, a ground state level at $E_f$ = -0.7 eV and a crystal-field splitting $\Delta$ = 0.07 eV.

The c-f hybridization parameter $V_{kf}$ is considered here to increase with pressure. The parameter $\Gamma = \pi(V_{kf})^2/W$ increases with pressure from a value of $\Gamma$ = 0.06 eV at normal pressure up to a value of order 0.2 eV at 15 GPa.

# Theory : Changing the width of the f-state (with pressure)

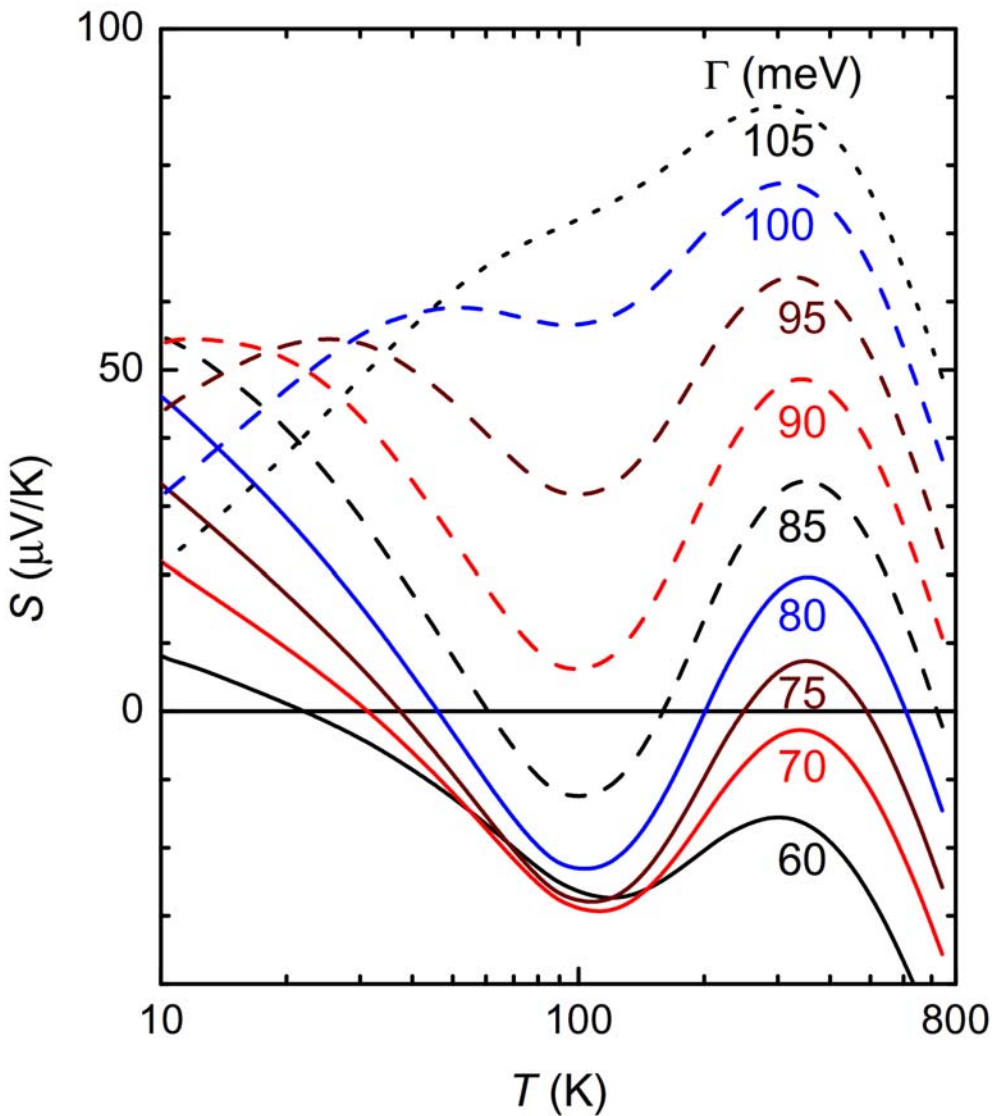


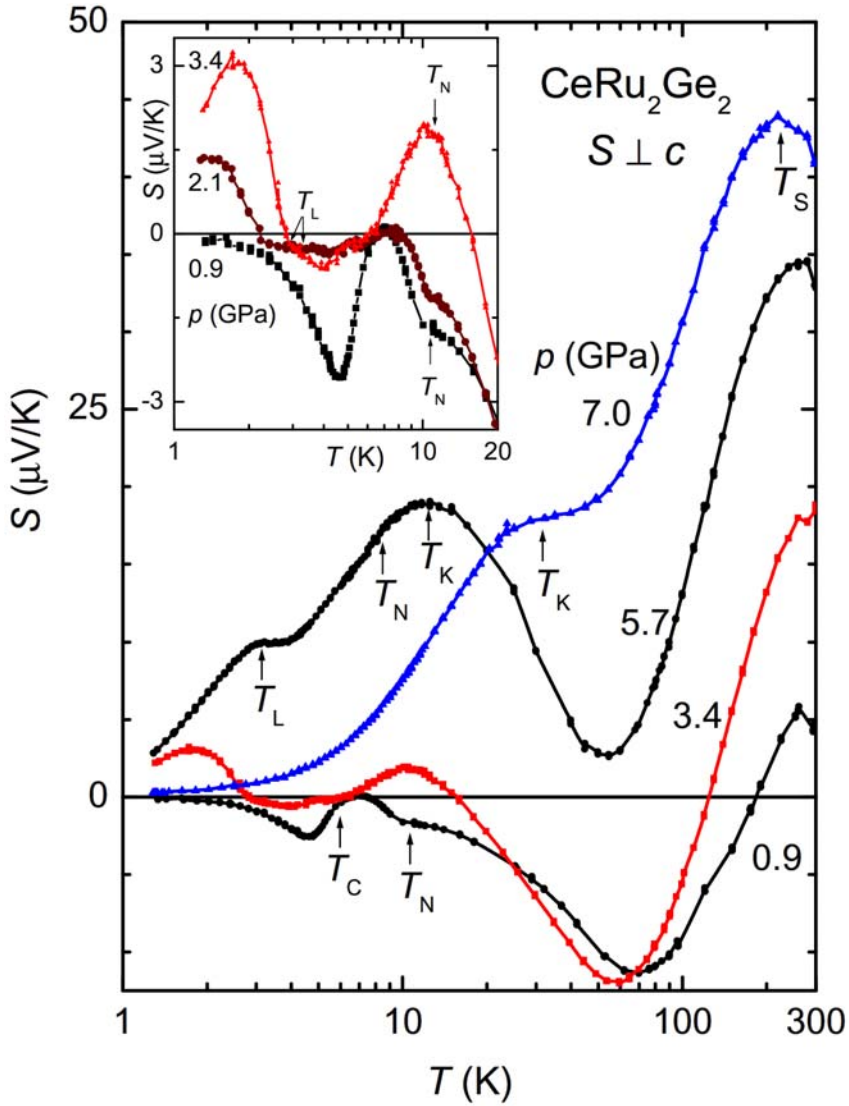

Low pressure

High pressure

# $CeRu_2Ge_2$ at **low pressure**.

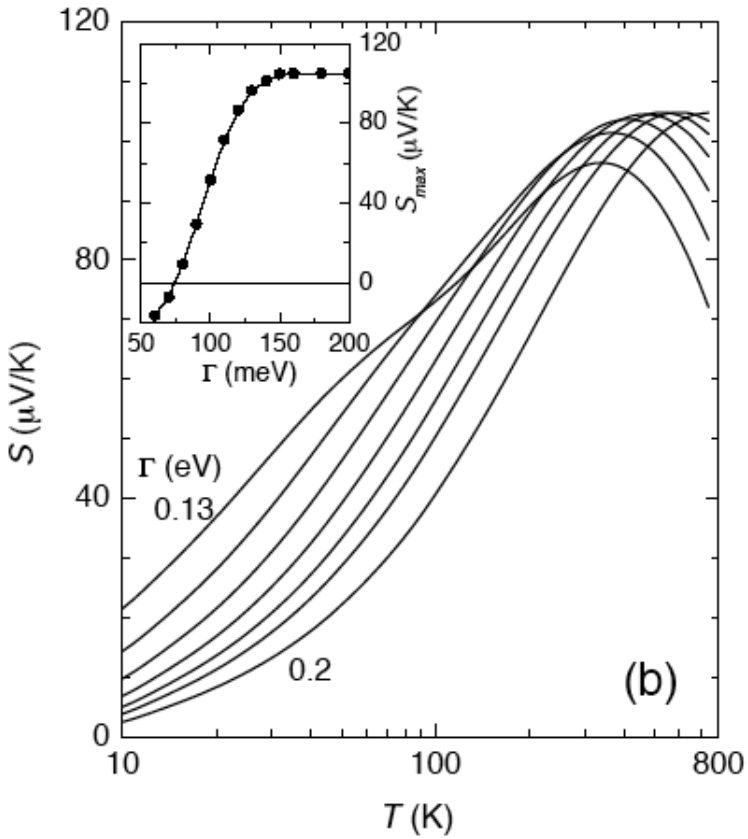


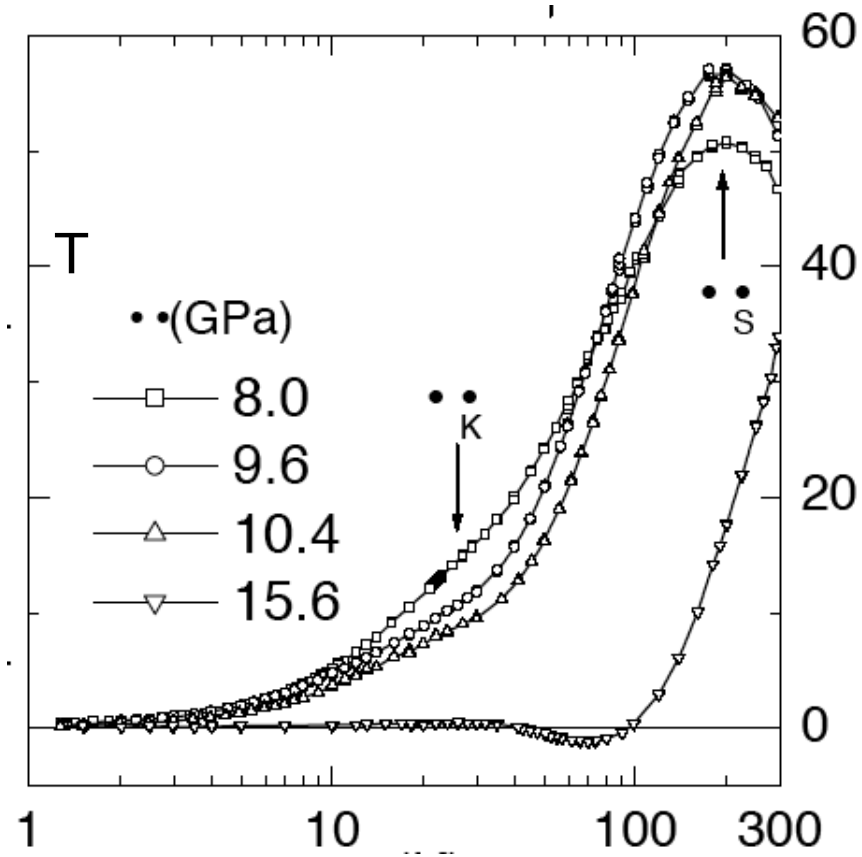

Theory




Experiment

# $CeRu_2Ge_2$ at **high pressure**.




Theory

Experiment

A.K Bhattacharjee and B. Coqblin, Phys. Rev B **38**, 338 (1988).

Z. Kletowski and B. Coqblin, Solid State Communications **135**, 711 (2005)

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**THE THERMAL CONDUCTIVITY of CERIUM KONDO COMPOUNDS**

The thermal « resistivity » W, equal to the inverse of the thermal conductivity K, can be written as :

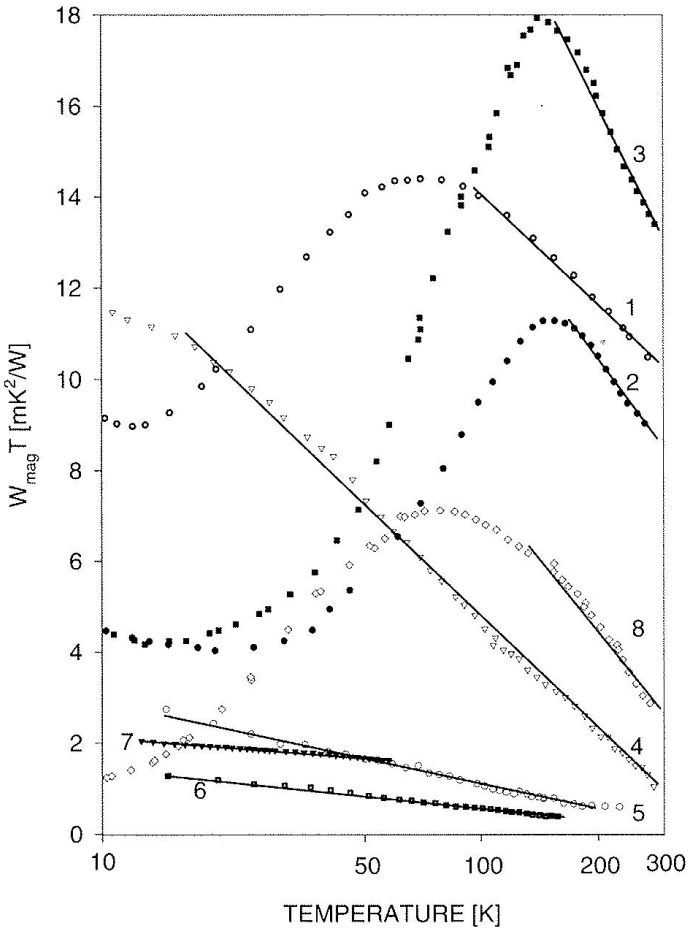
$$K^{-1} = W = W_{mag} + W_{ph}$$

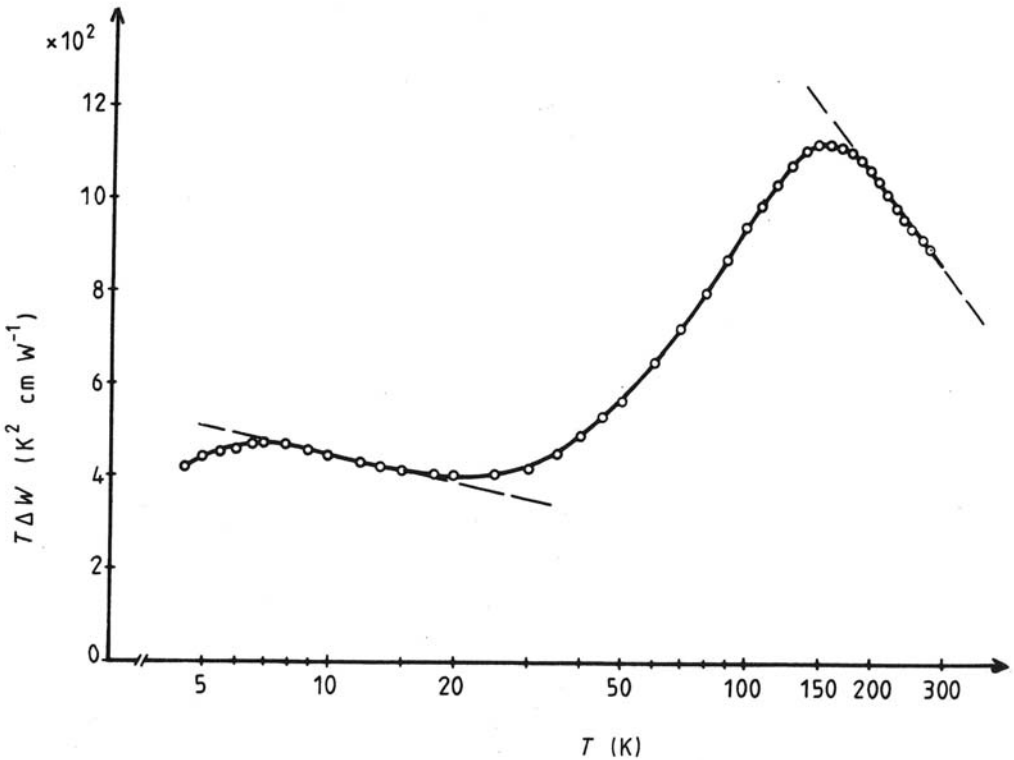
where the second term is taken here as the thermal resistivity of the equivalent nonmagnetic (such as La) compound.

For $T>T_k$, the Kondo contribution $T.W_{mag}$ behaves as Log T.

**Plot of $W_{mag}$.T versus LogT.**
**The numbers correspond to :**
**1 for $CeAl_2$, 2 for $CeCu_2$,**
**3 for $CeCu_5$, 4 for $CeCu_4Al$,**
**5 for $PrSn_3$, 6 for $TmGa_3$,**
**7 for $TmIn_3$ and 8 for $YbCu_4Ag$.**

**First analyzed curves of $CeCu_2$, $CeCu_5$ and $YbCu_4Ag$ by E. Bauer, E. Gratz, G. Hutflesz, A. K. Bhattacharjee and B. Coqblin, J.M.M.M. 108, 159 (1992) and Physica B 186-188, 494 (1993).**






**Plot of $W_{mag}$.T versus LogT for $CeCu_2$. (Exp. Ratio "highT/lowT" = 6.4 and Theoretical Ratio = 35/3)**

**CeRuSi + H**
**(B. Chevalier et al.)**

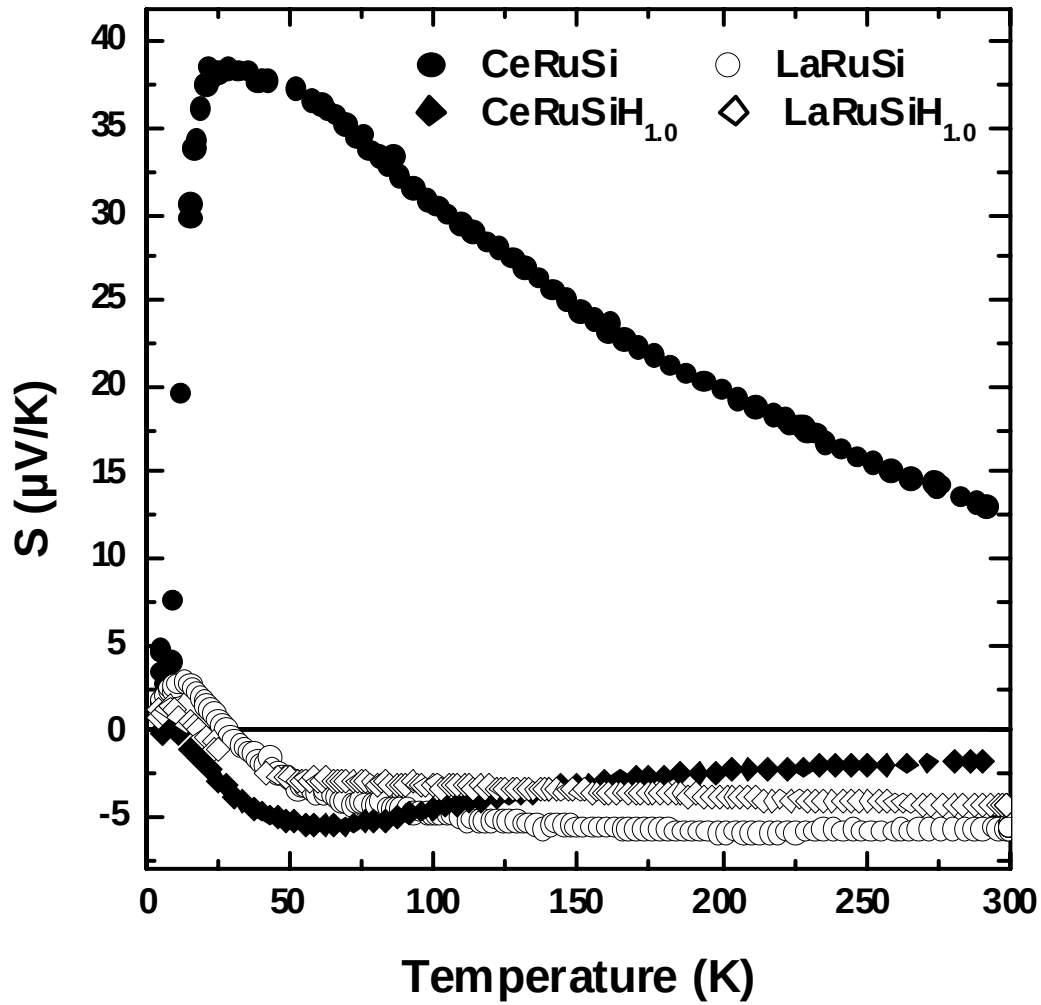



Fig.9. Temperature dependence of the thermoelectric power of CeRuSi, LaRuSi and their hydrides.

# CONCLUSIONS

- The Thermopower of Ce (Yb) compounds has generally a positive (negative) peak at roughly $\Delta/3$ and another one at $T_k/2$. The width of the Kondo peak is taken as increasing with pressure in $CeRu_2Ge_2$ compound.

- The analysis of the thermal conductivity is generally difficult, but $W_{mag}.T$ and $\rho_m$ have a similar behavior in LogT above $T_k$ in strongly Kondo systems.

- The « figure of merit » given by :

$$ZT = S^2.T/K\rho$$

can be large in heavy fermion compounds, because S and 1/K are large, but on the contrary $\rho$ is also large.