

**Ecole thermoélectricité, Carcans, 5-9 Mai 2008**

**Intermétalliques à base de  
Cérium.**

**Fermions lourds – Hydruration.**



**B. CHEVALIER**

**Institut de Chimie de la Matière Condensée de Bordeaux**

Physical properties of Ce-compounds result from  $J_{cf}$  interaction between 4f(Ce) and conduction electrons

**Kondo interaction**

$T_K = \exp(1/N(E_F)J_{cf})$   
causes quenching of the  
Ce-magnetic moment

**RKKY interaction**

$T_{RKKY} = J_{cf}^2 N(E_F)$   
favours occurrence of a  
long range magnetic order

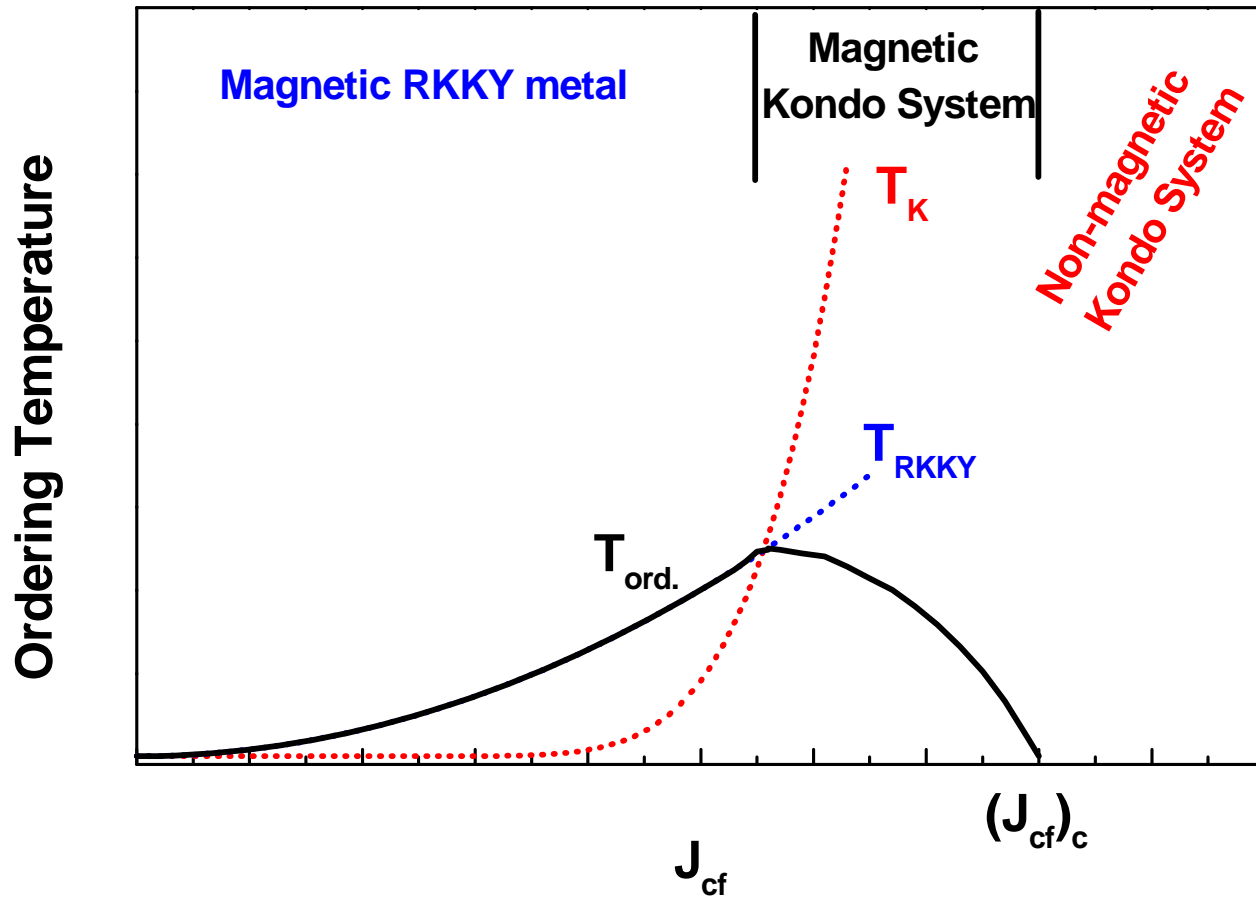
**Kondo – RKKY competition**

=

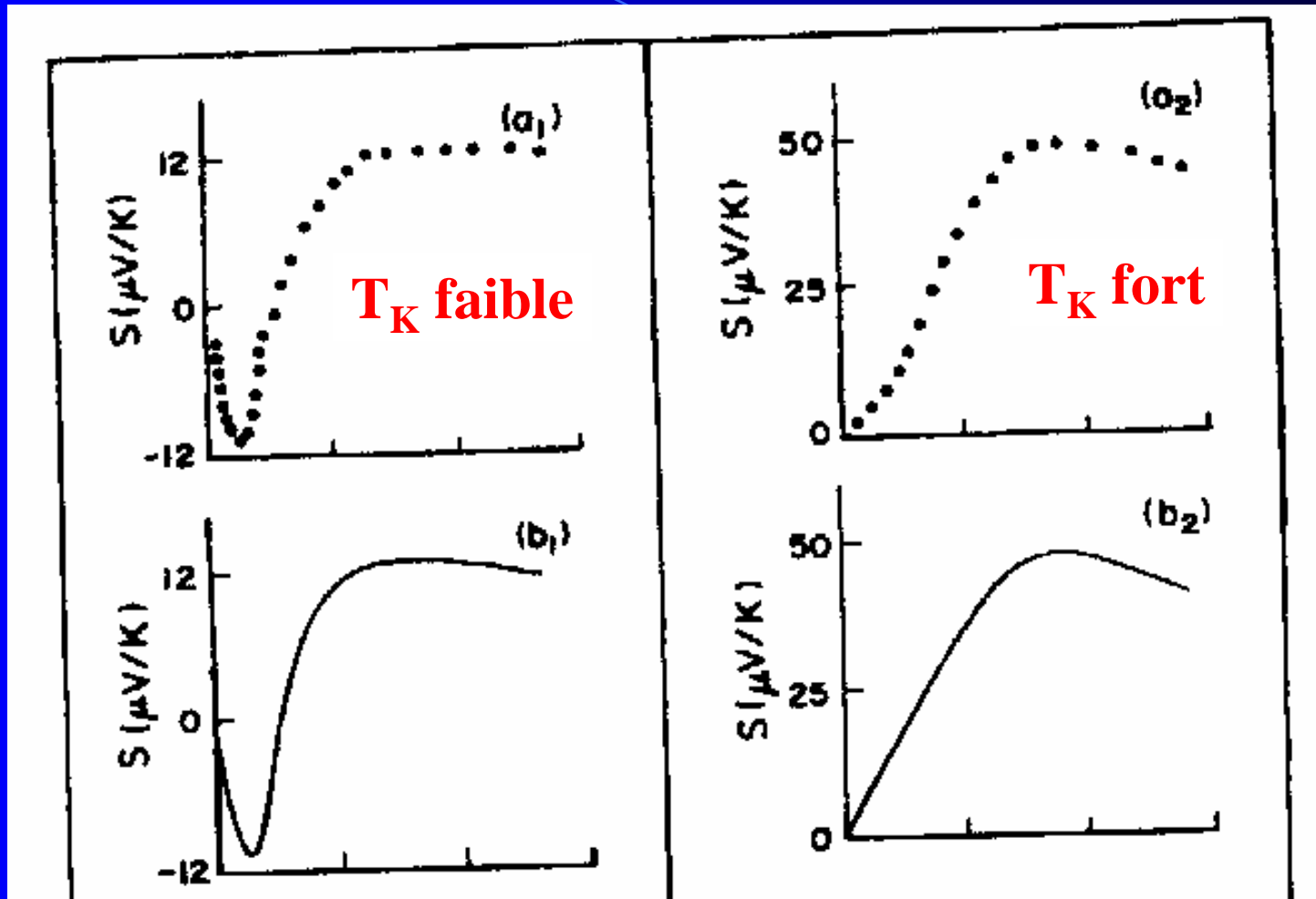
Intermediate valence, 'Heavy Fermions',  
magnetic or non-magnetic Kondo systems,  
superconductors, non Fermi liquid behaviour...

**Strongly correlated electrons systems.**

# Diagramme de Doniach

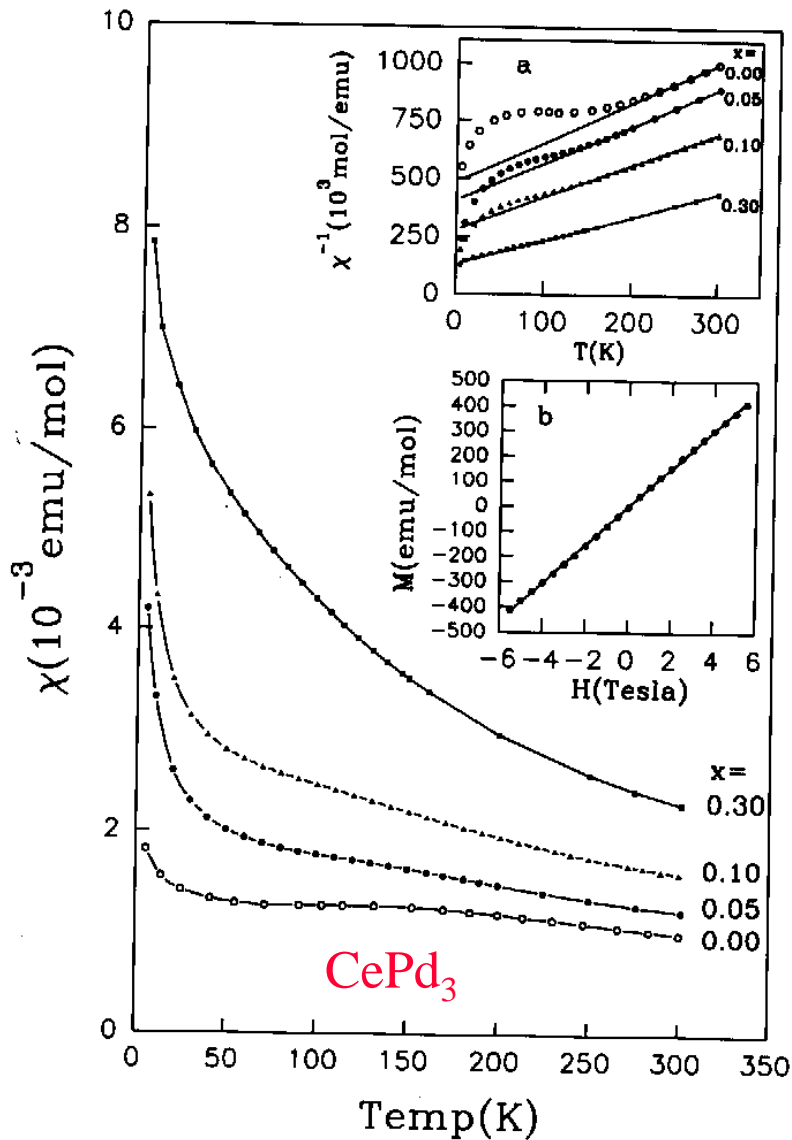


# Pouvoir thermoélectrique et effet Kondo



Hybridation entre électrons 4f(Ce) et électrons de conduction  
⇒ effet Kondo ( $T_K$ )

**$T_K$  fort : cas du composé de valence intermédiaire  $CePd_3$**



**Figure 1.** Magnetic susceptibility ( $\chi$ ) versus temperature for  $Ce_{1-x}U_xPd_3$  alloys measured in an applied field of  $H = 1.0$  T. The top inset shows  $\chi^{-1}$  versus  $T$  for different  $x$  values, from which  $\mu_{\text{eff}}$  and  $\theta_p$  were extracted. The bottom inset shows  $M$  versus  $H$  data for  $x = 0.3$  at 4.2 K.

# $(\text{Nd}_x\text{Ce}_{1-x})\text{Pd}_3$ : propriétés de transport

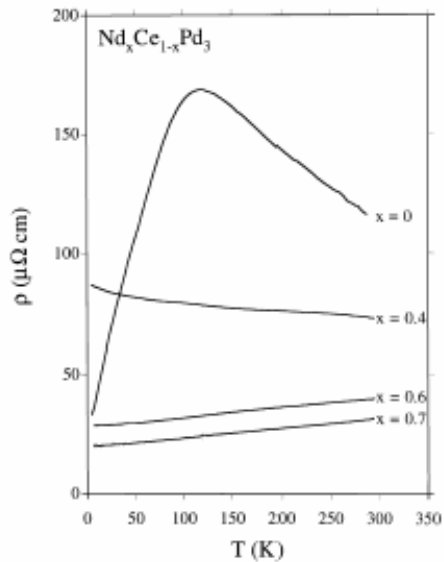


Fig. 2. Electrical resistivity of  $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$ . The  $x=0$  and  $x=0.4$  data are from Ref. 15.

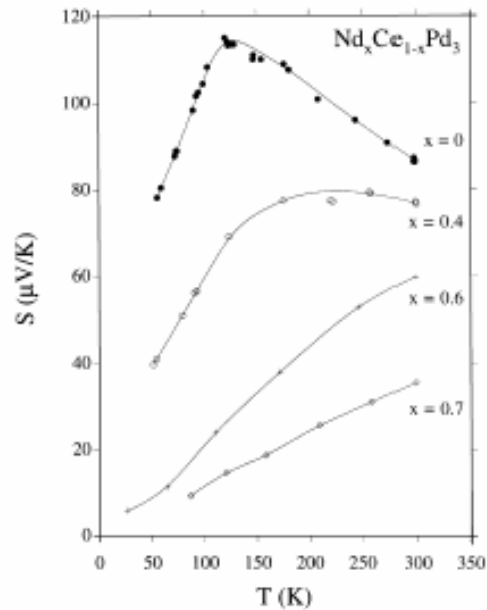


Fig. 3. Thermopower of  $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$ .

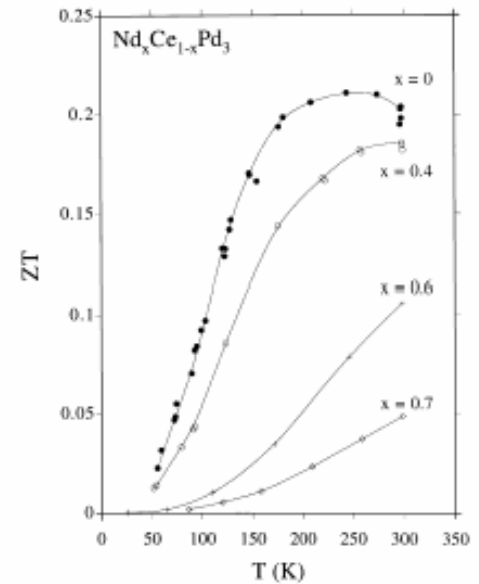


Fig. 6. The dimensionless Figure of Merit for  $\text{Nd}_x\text{Ce}_{1-x}\text{Pd}_3$  showing the maximum of more than 0.2, for  $\text{CePd}_3$ .

K. J. Proctor et al., JPCS (1999)

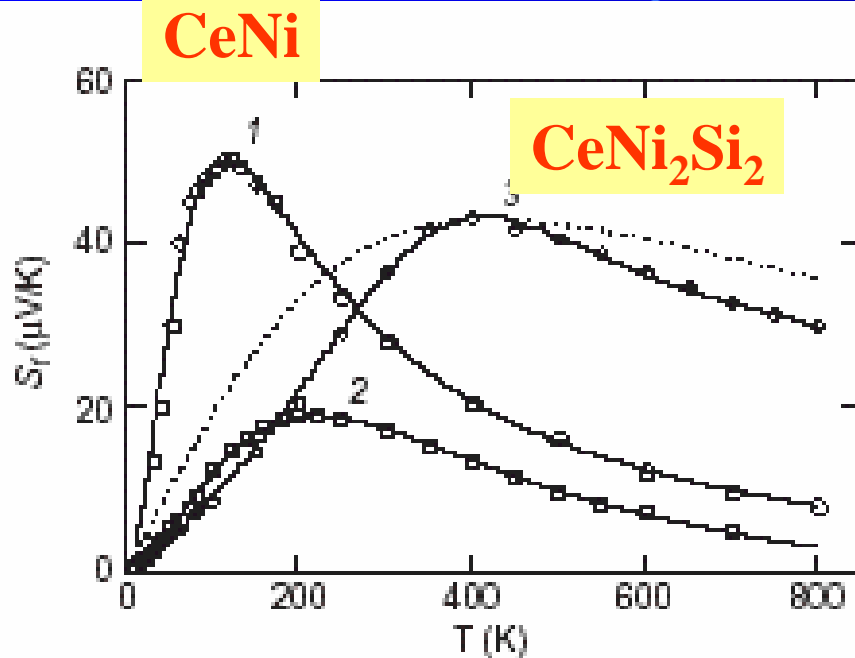


Fig. 1. Temperature dependencies of the contribution of Ce *f* states to the total thermopower of CeNi (1), CeNi<sub>2</sub> (2) and CeNi<sub>2</sub>Si<sub>2</sub> (3). The solid lines show the thermopower calculated from Eq. (2) in the suggestion temperature dependence of parameter  $T_K$ . The dotted curve depicts the behavior of the thermopower according to Eq. (2) under the assumption that  $T_K = \text{const}$ .

**CeNi, CeNi<sub>2</sub> et CeNi<sub>2</sub>Si<sub>2</sub>  
(valence intermédiaire)**

**La température de  
Kondo influence le  
maximum de  $S = f(T)$**

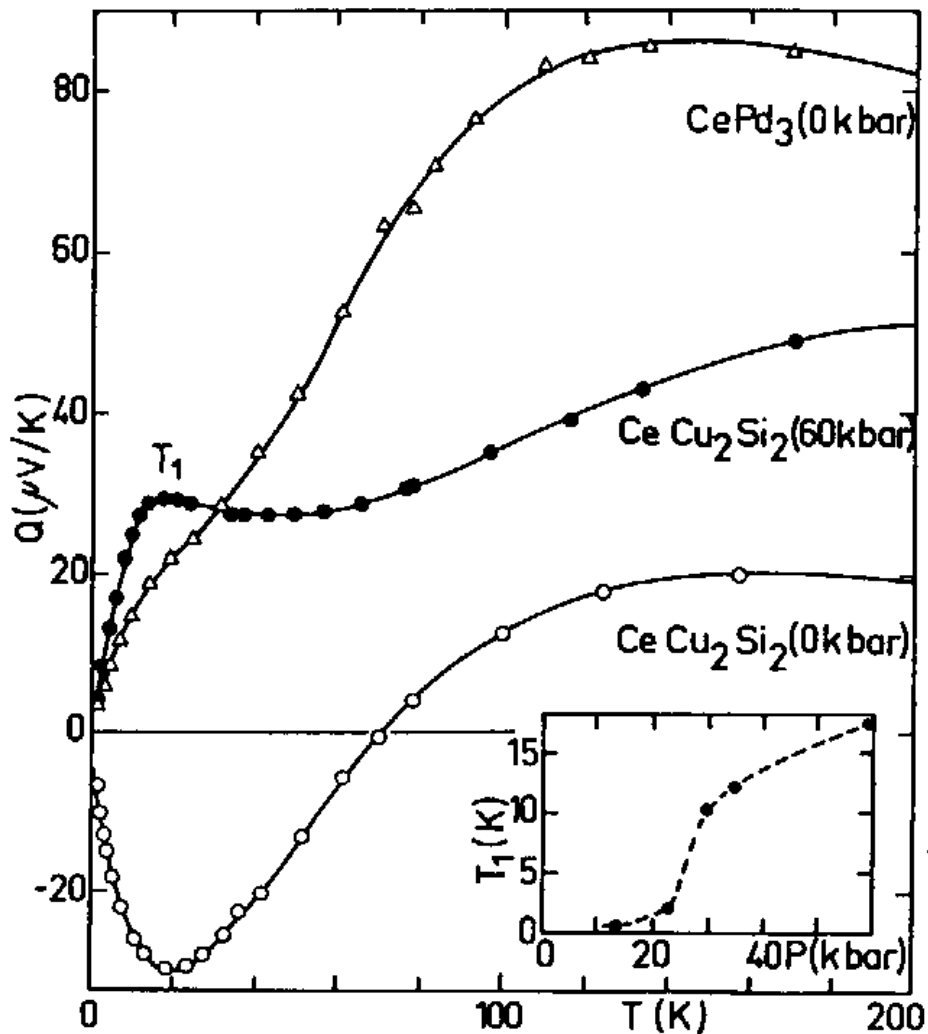


FIG. 1. TEP of  $\text{CePd}_3$  and of  $\text{CeCu}_2\text{Si}_2$  at 0 kbar and at 60 kbar. For  $\text{CeCu}_2\text{Si}_2$ , the insert shows the pressure dependence of the temperature  $T_1$  of the low  $T$  positive maximum.

**Influence de la pression  
sur  $\text{CeCu}_2\text{Si}_2$  :  
transition  $\text{Ce}^{3+}$  (supra) -  
valence intermédiaire.**

**Sous pression  
l'hybridation 4f(Ce)-  
électrons de conduction  
augmente.**



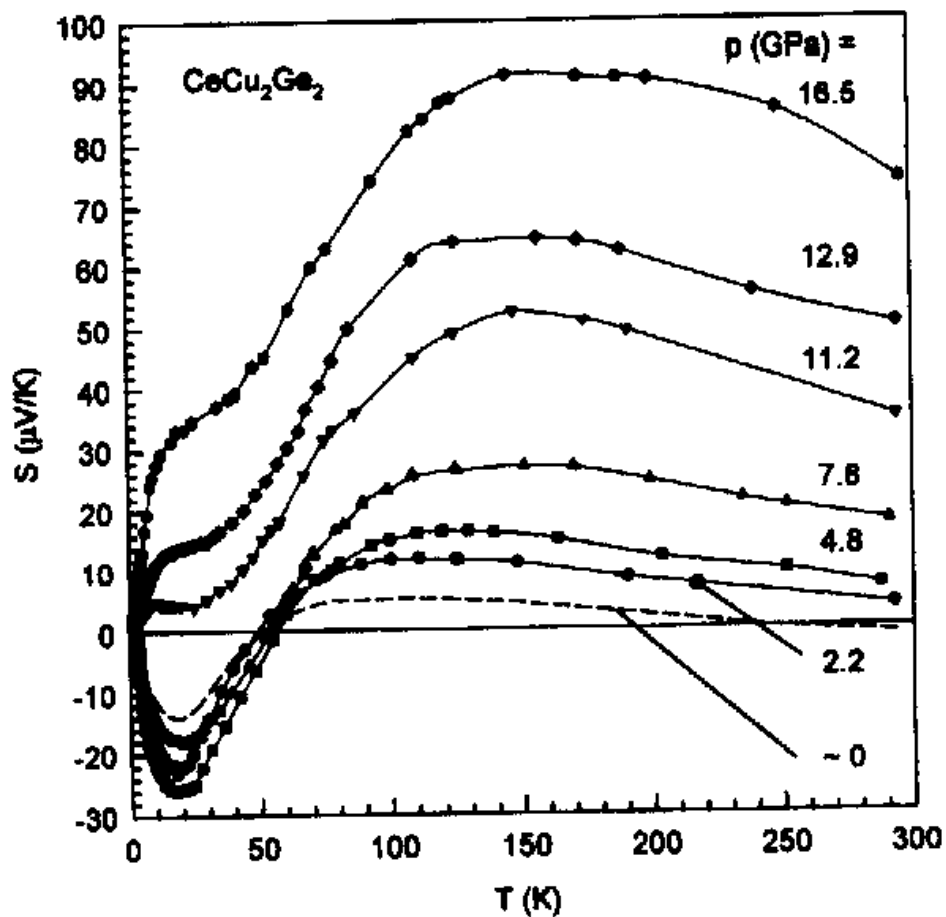


Fig. 2. Absolute thermopower of  $\text{CeCu}_2\text{Ge}_2$  at high pressure; the dashed line represents the  $p = 0$  thermopower taken from Ref. [1].

Influence de la pression  
sur  $\text{CeCu}_2\text{Ge}_2$  :  
**Transition**  
**antiferromagnétique ( $\text{Ce}^{3+}$ )**  
**- supraconducteur.**

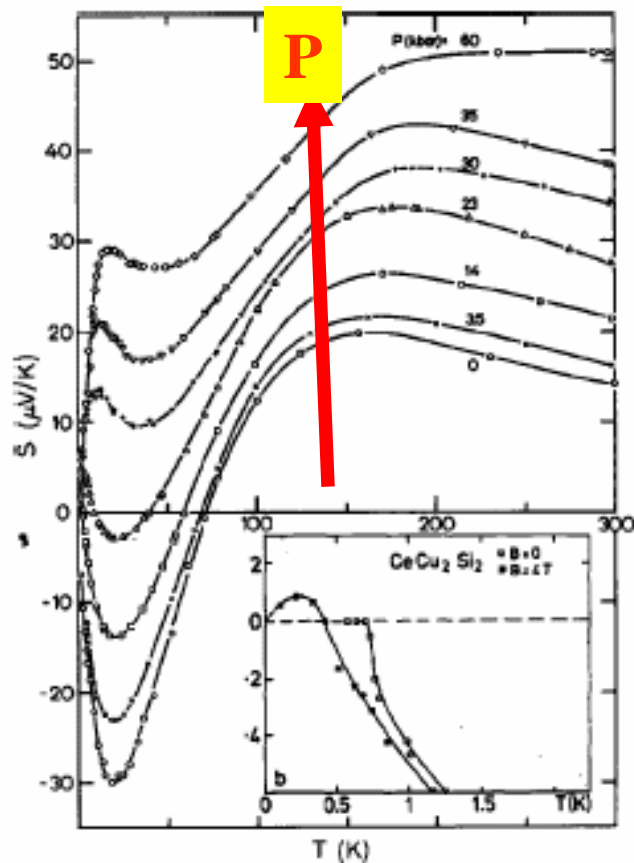


FIG. 1. The thermopower of  $\text{CeCu}_2\text{Si}_2$  plotted as a function of temperature for various pressures (Ref. 13). The inset shows the low-temperature data (Ref. 8) at ambient pressure and small magnetic field, which suppresses the superconducting transition and reveals the positive TEP peak. Type (a) behavior is seen at zero pressure, type (b) between 14 kbar and 23 kbar, and type (c) at 30 kbar and above.

**Intermétalliques à base de cérium  
et pression ( $\text{CeCu}_2\text{Si}_2$ )**

**P augmente : transition trivalent -  
valence intermédiaire (S croit)**

**S élevé pour les composés de  
valence intermédiaire**

**V. Zlatic et al., Phys. Rev. B (2003)**

## **$J_{cf}$ modification by hydrogenation**

**Hydrogen insertion  $\Rightarrow$   
changes the density of states at  $E_F$ .  
Occurrence of Ce-H bonding.  
Electronic state of H ?**

**Hydrogen absorption  $\Rightarrow$  unit cell volume increases,  
 $J_{cf}$  decreases.**

**Transition non-magnetic  $\rightarrow$  magnetic ?**

**Transition Kondo magnetic  $\rightarrow$  RKKY magnetic?**

**Change the thermoelectric power.**

## OUTLINE

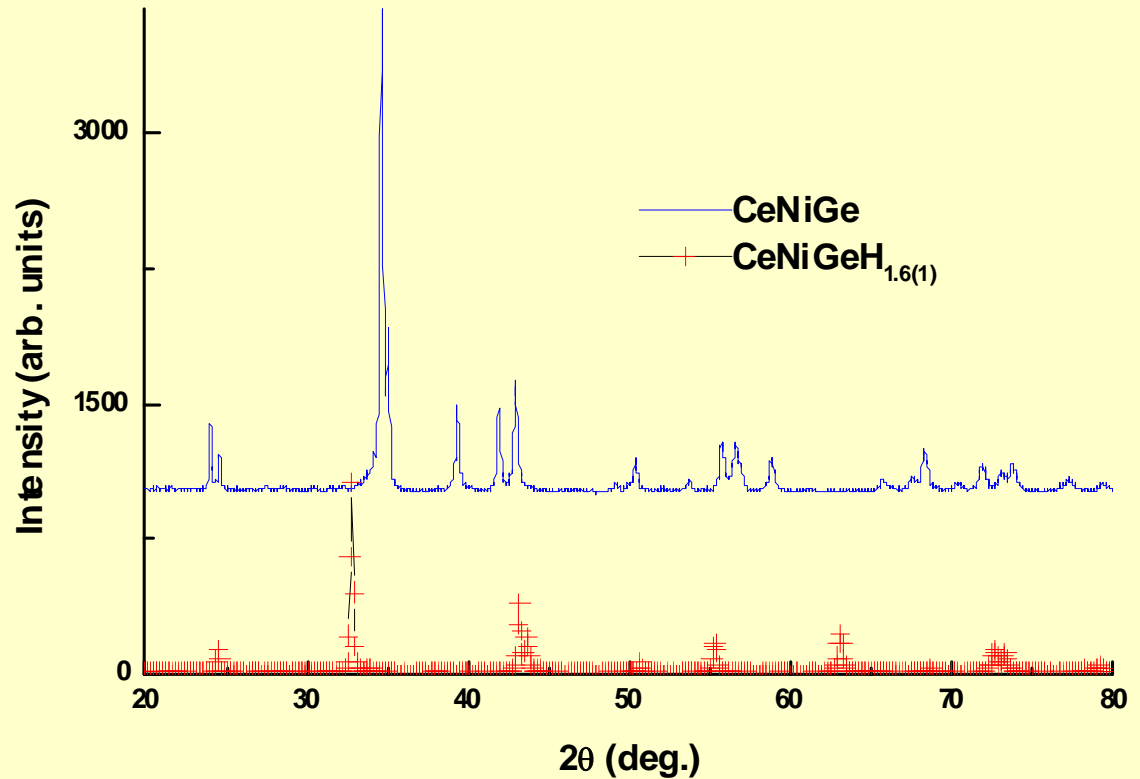
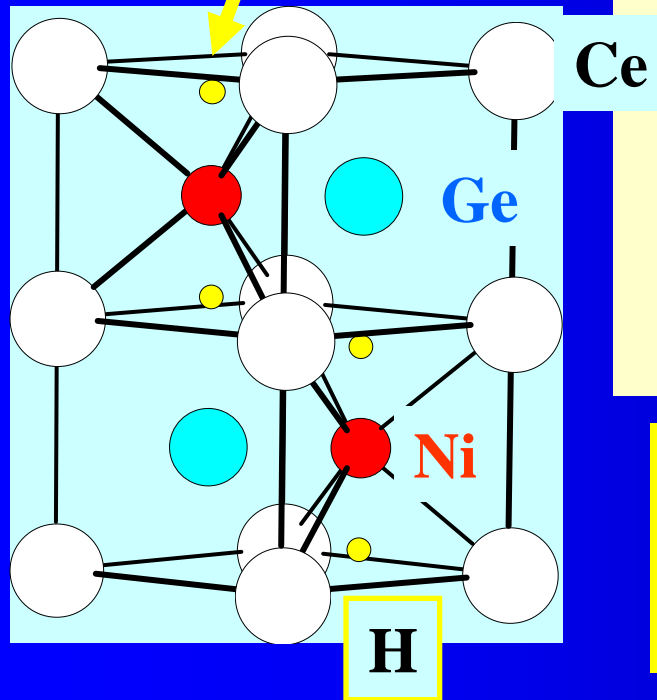
- Hydrogenation of intermediate valence compounds :  
**CeNiGe, CeRhSn and CeIrSn.**
- Unusual transitions induced by hydrogenation of compounds crystallizing in the tetragonal CeFeSi-type structure : **from antiferromagnetism (CeCoSi, CeCoGe) to spin fluctuation behaviour (CeCoSiH, CeCoGeH) or from non-magnetic heavy-fermion (CeRuSi) to antiferromagnetism (CeRuSiH).**

**Hydrogenation of CeNiGe :**  
**decrease of the spin fluctuation temperature**

*B. Chevalier et al., J. Solid State Chem., 177 (2004) 752.*

# CeNiGeH<sub>1.6</sub> : structural properties

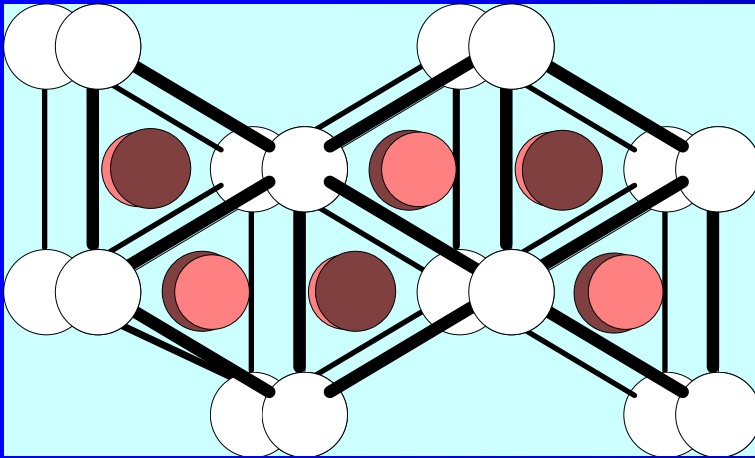
H (or D) in tetrahedral sites [Ce<sub>3</sub>Ni]



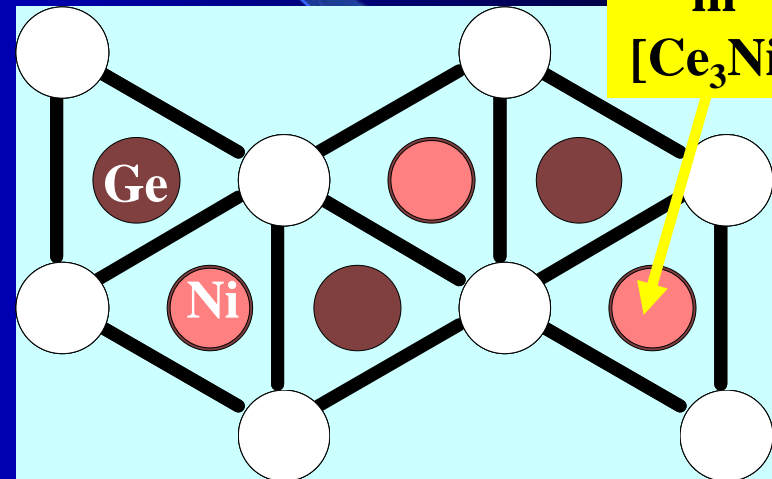
H-insertion induces a structural transition from orthorhombic TiNiSi-type (CeNiGe) to hexagonal ZrBeSi-type (CeNiGeH<sub>1.6</sub>)

# Structural transition : $\text{CeNiGe} \rightarrow \text{CeNiGeH}_{1.6}$

**CeNiGe (orthorhombic)**



**CeNiGeH<sub>1.6</sub> (hexagonal)**



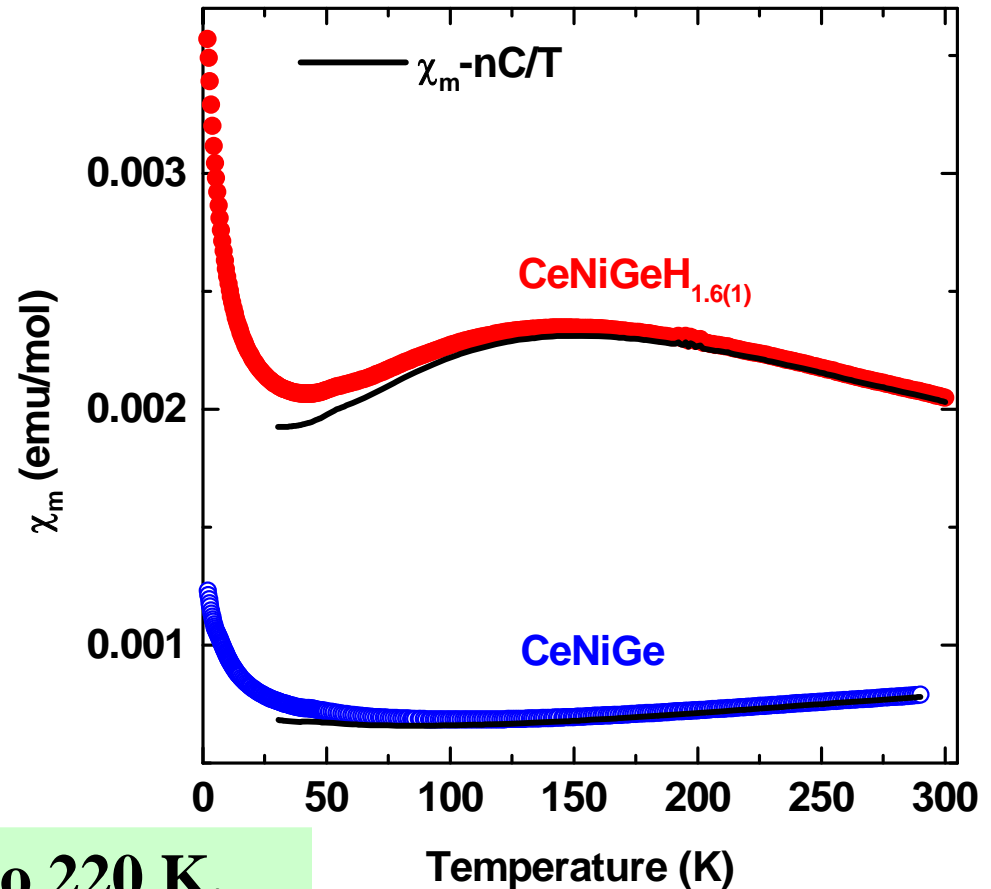
**[Ce<sub>6</sub>] trigonal prisms surrounding alternatively Ni- and Ge-atoms.  
In CeNiGe these prisms are distorted.  
H-atoms in the tetrahedral [Ce<sub>3</sub>Ni]-site.  
Increase of the unit cell volume 11.6 % (CeNiGeH<sub>1.8</sub>).**

# CeNiGe $\rightarrow$ CeNiGeH<sub>1.6</sub>: reduction of the Kondo temperature

CeNiGe is a nearly Pauli paramagnet.

$\chi_m$  of CeNiGeH<sub>1.6</sub> shows a broad maximum around 130 K.

$T_K$  decreases from 600 K to 220 K.  
Reduction of the mixing between 4f(Ce) states and conduction electrons.

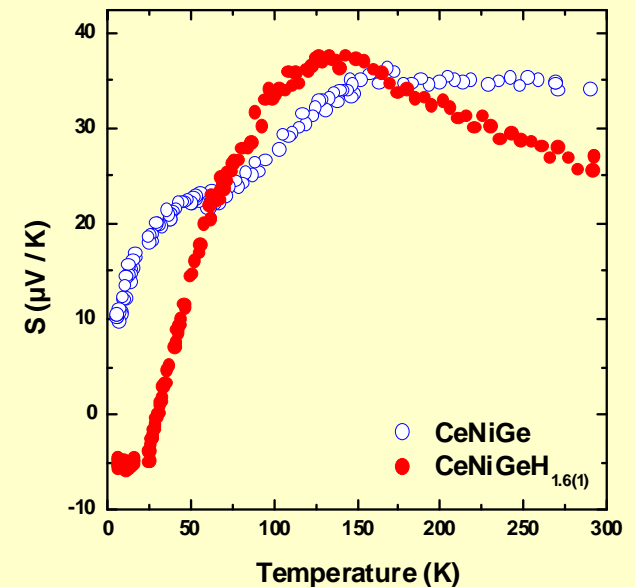
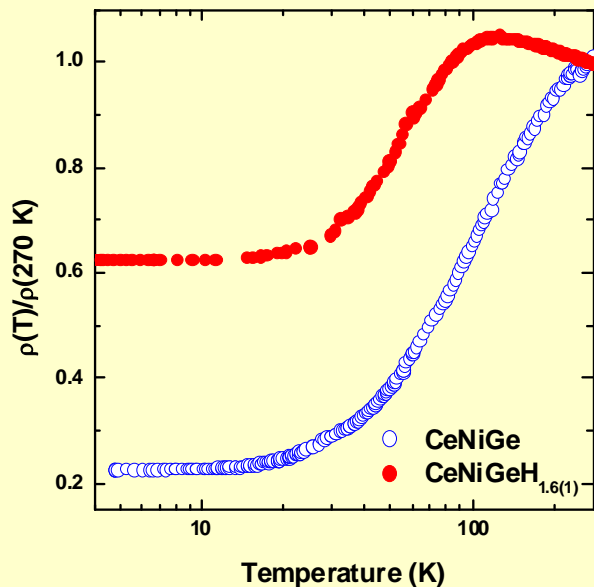




# CeNiGe and CeNiGeH<sub>1.6</sub> : electrical and thermoelectric properties

$\rho = f(T)$  characterizes intermediate valence systems having high (CeNiGe) and lower (CeNiGeH<sub>1.6</sub>) Kondo temperature

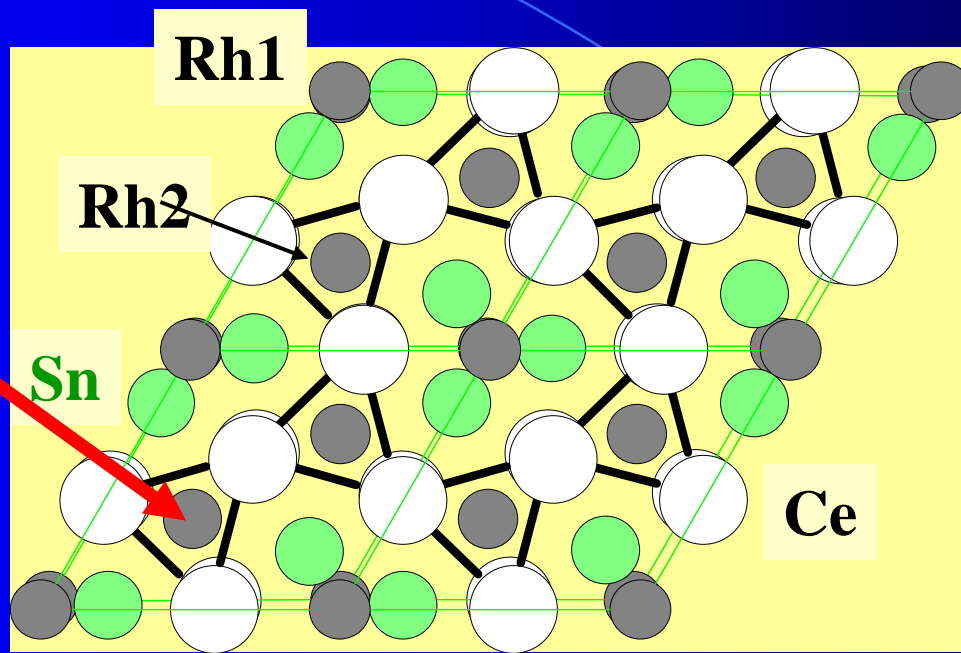
$S = f(T)$  characterizes for CeNiGe intermediate valence system (positive, two maximums) whereas for CeNiGeH<sub>1.6</sub> a nearly trivalent state (change in sign, maximum and minimum)



**Hydrogenation of CeRhSn and CeIrSn :**  
**from intermediate valence to the nearly**  
**trivalent state (CeRhSnH<sub>0.8</sub> and CeIrSnH<sub>0.7</sub>)**

*B. Chevalier et al., Solid State Sciences, 8 (2006) 1000.*

**CeRhSn, CeIrSn and hydrides  $\text{CeRhSnH}_{0.8}$  and  $\text{CeIrSnH}_{0.7}$  :  
same hexagonal crystal structure (by neutron diffraction)**



**CeRhSn**

$a = 7.448 \text{ \AA}$   
 $c = 4.080 \text{ \AA}$

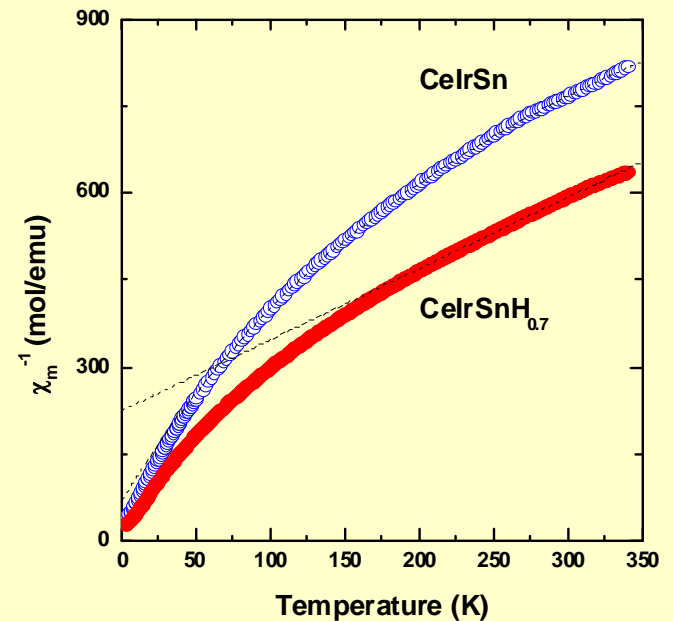
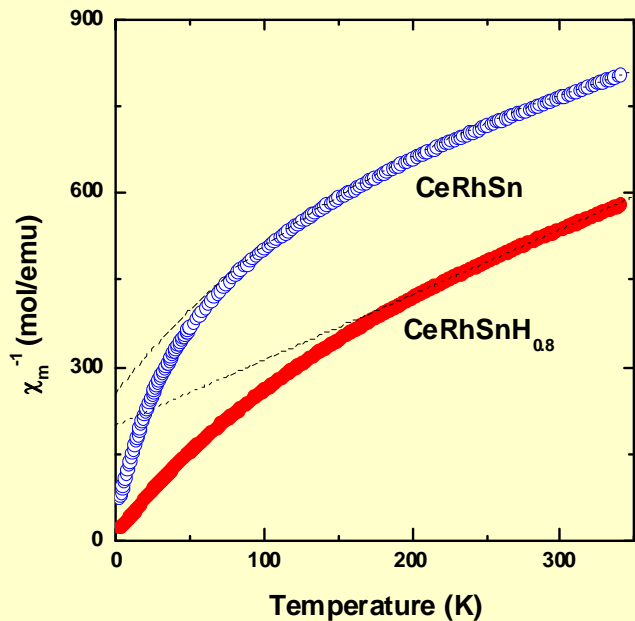
**Isotropic expansion  
of the unit cell parameters.**

**Unit cell volume increases (4.4 %)**

**$\text{CeRhSnH}_{0.8}$**

$a = 7.557 \text{ \AA}$   
 $c = 4.136 \text{ \AA}$

Magnetic properties : **CeRhSn, CeIrSn** → **CeRhSnH<sub>0.8</sub>, CeIrSnH<sub>0.7</sub>**

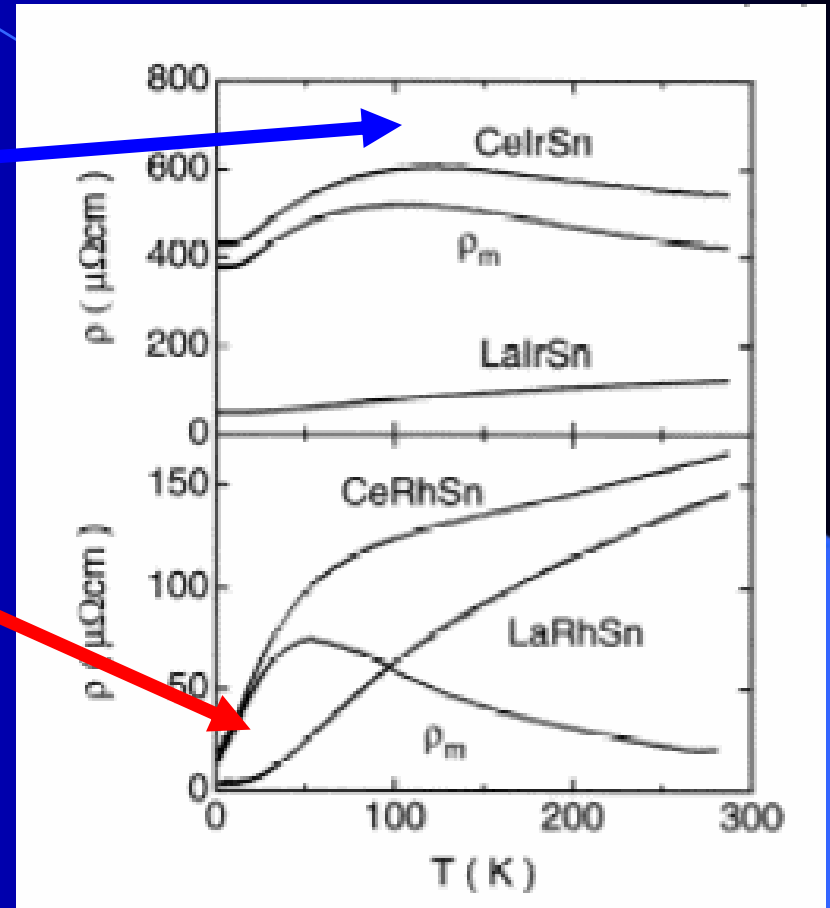
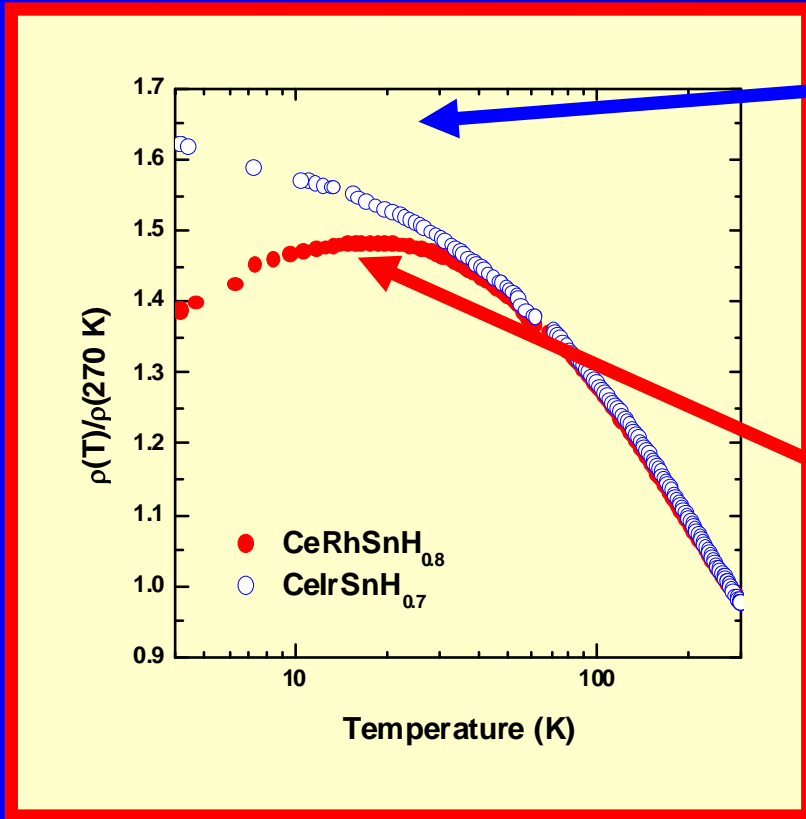


**CeRhSn** :  $\chi_m = \chi_0 + C_m / (T - \theta_p) \Rightarrow \mu_{\text{eff}} = 1.25 \mu_B / \text{Ce}$

**CeRhSnH<sub>0.8</sub>** :  $\chi_m = C_m / (T - \theta_p) \Rightarrow \mu_{\text{eff}} = 2.66 \mu_B / \text{Ce}$  (close to Ce<sup>3+</sup>).

**H-insertion induces a valence change of cerium.**

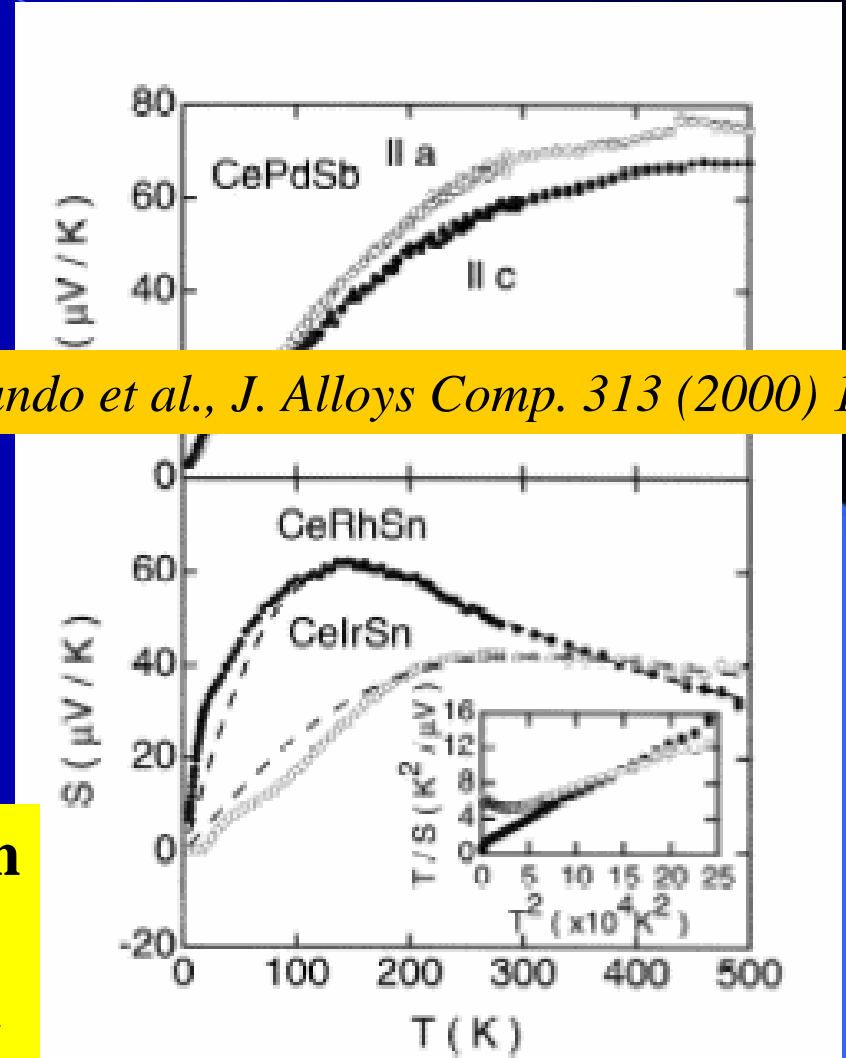
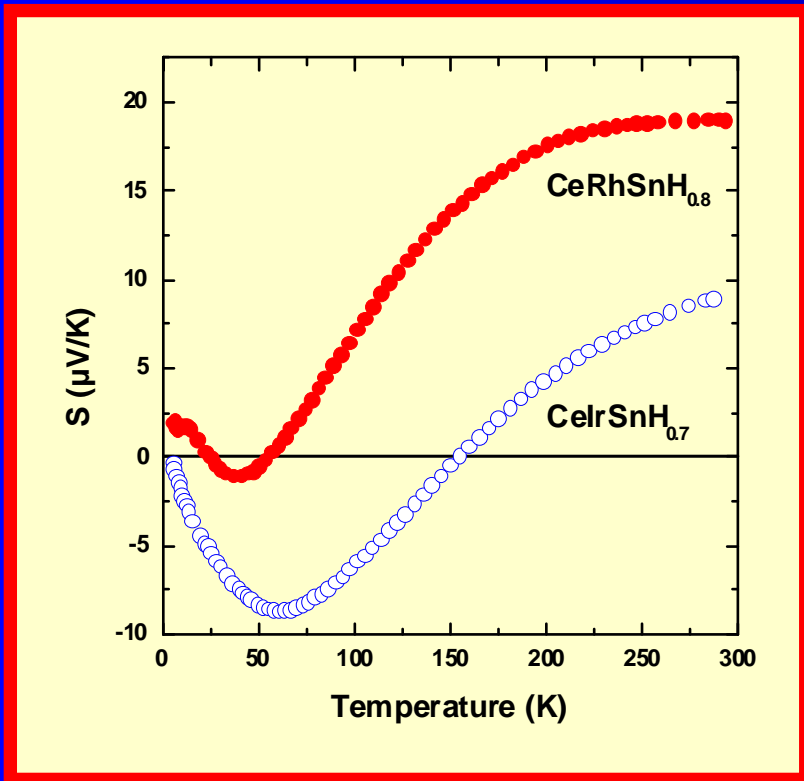
# Electrical properties : $\text{CeRhSn}$ , $\text{CeIrSn} \rightarrow \text{CeRhSnH}_{0.8}$ , $\text{CeIrSnH}_{0.7}$



*Bando et al., J. Alloys Comp. 313 (2000) 1*

The temperature of the maximum decreases after hydrogenation  
 $\Rightarrow$  **Kondo effect decreases.**

Thermoelectric properties : **CeRhSn, CeIrSn** →  
**CeRhSnH<sub>0.8</sub>, CeIrSnH<sub>0.7</sub>**



*Bando et al., J. Alloys Comp. 313 (2000) 1*

Two positive maximums for **CeRhSn** and **CeIrSn** (intermediate valence).  
Change of sign for **CeRhSnH<sub>0.8</sub>** and **CeIrSnH<sub>0.7</sub>** (trivalent).

# Hydrogenation comparable to the application of negative pressure

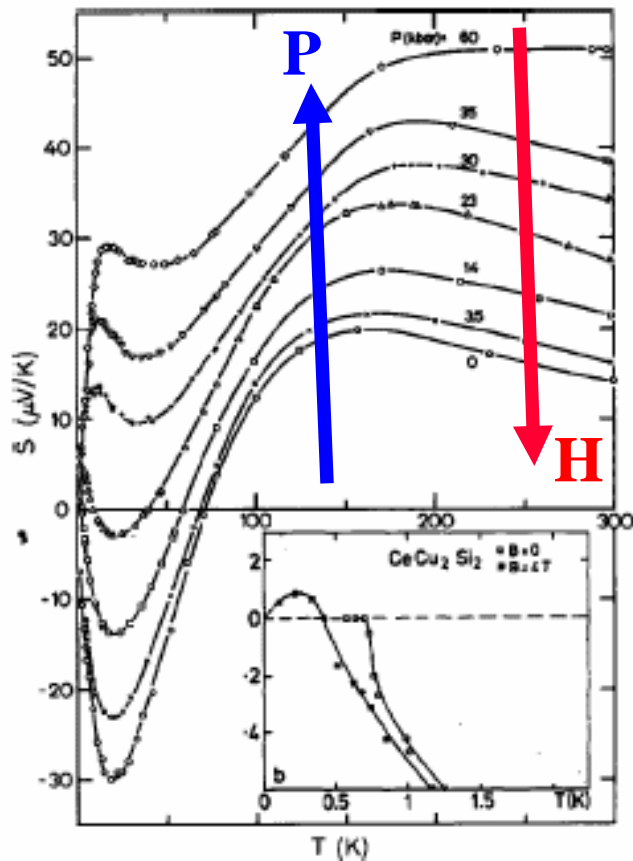


FIG. 1. The thermopower of  $\text{CeCu}_2\text{Si}_2$  plotted as a function of temperature for various pressures (Ref. 13). The inset shows the low-temperature data (Ref. 8) at ambient pressure and small magnetic field, which shows a transition from intermediate valence to trivalent state.

**P increases** : transition from nearly trivalent ( $\text{CeCu}_2\text{Si}_2$ ) to intermediate valence

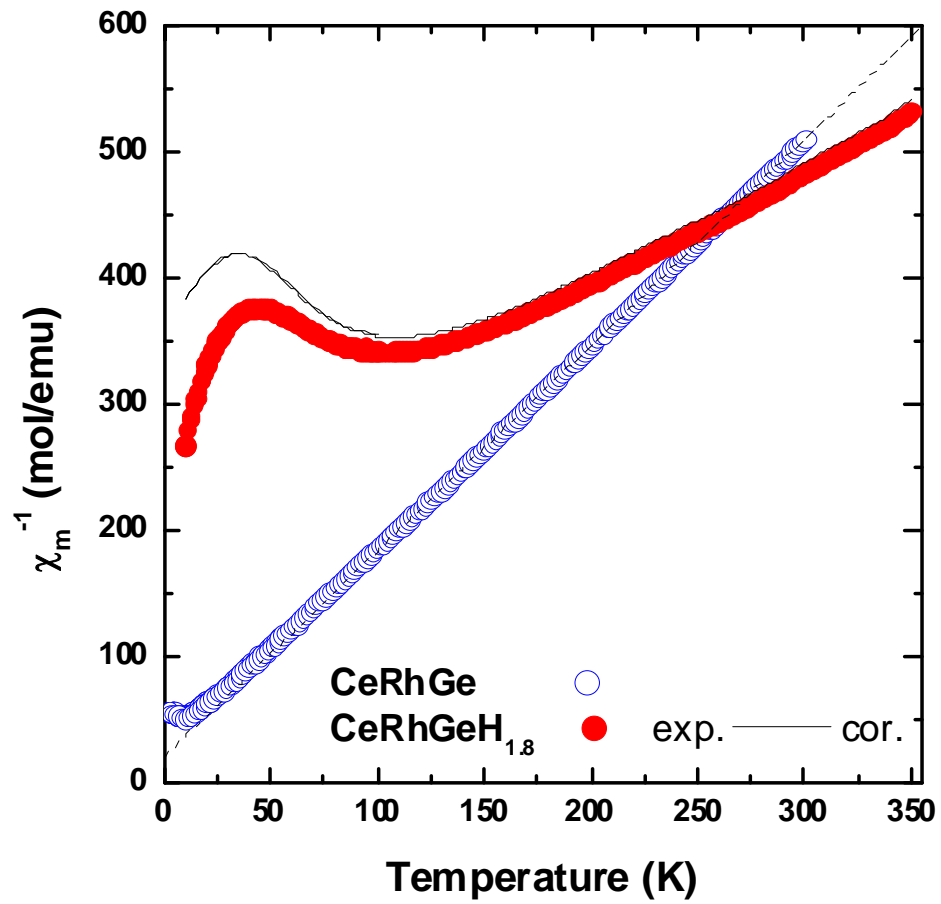
**H-insertion** : transition from intermediate valence ( $\text{CeRhSn}$ ) to trivalent state ( $\text{CeRhSnH}_{0.8}$ )

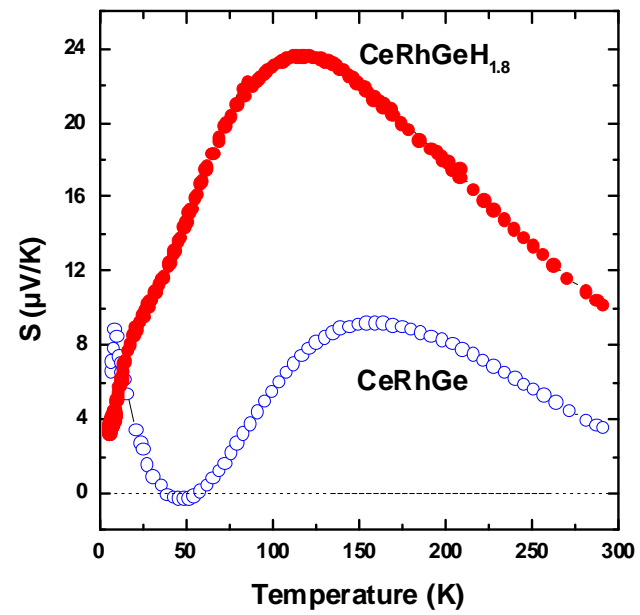
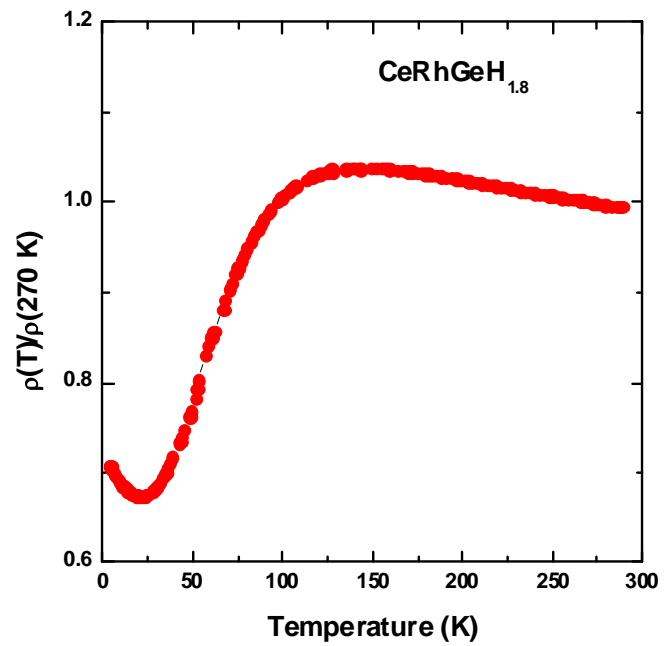
*V. Zlatic et al., Phys. Rev. B (2003)*

and above.

**Hydrogenation de CeRhGe :**  
**transition d'un antiferromagnétique à**  
**un composé de valence intermédiaire.**





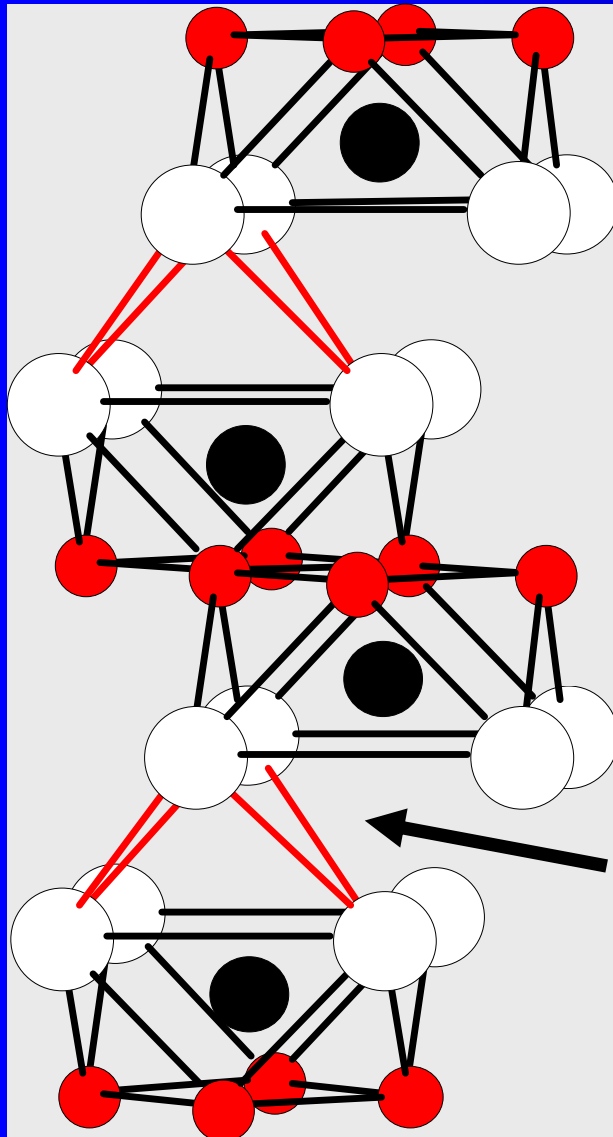


**Hydrogenation of compounds crystallizing in the tetragonal CeFeSi-type structure :**

**from antiferromagnetism (CeCoSi, CeCoGe) to spin fluctuation behaviour (CeCoSiH, CeCoGeH) or**

**from non-magnetic (CeRuSi) to antiferromagnetism (CeRuSiH).**

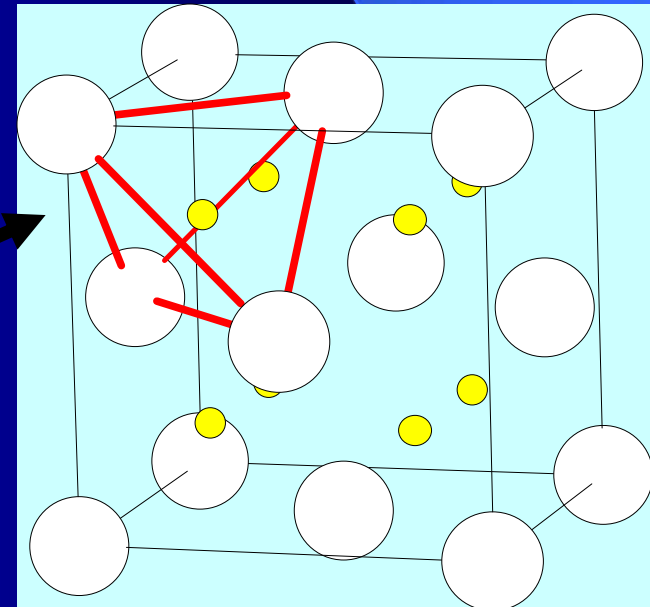
# The tetragonal CeFeSi-type structure



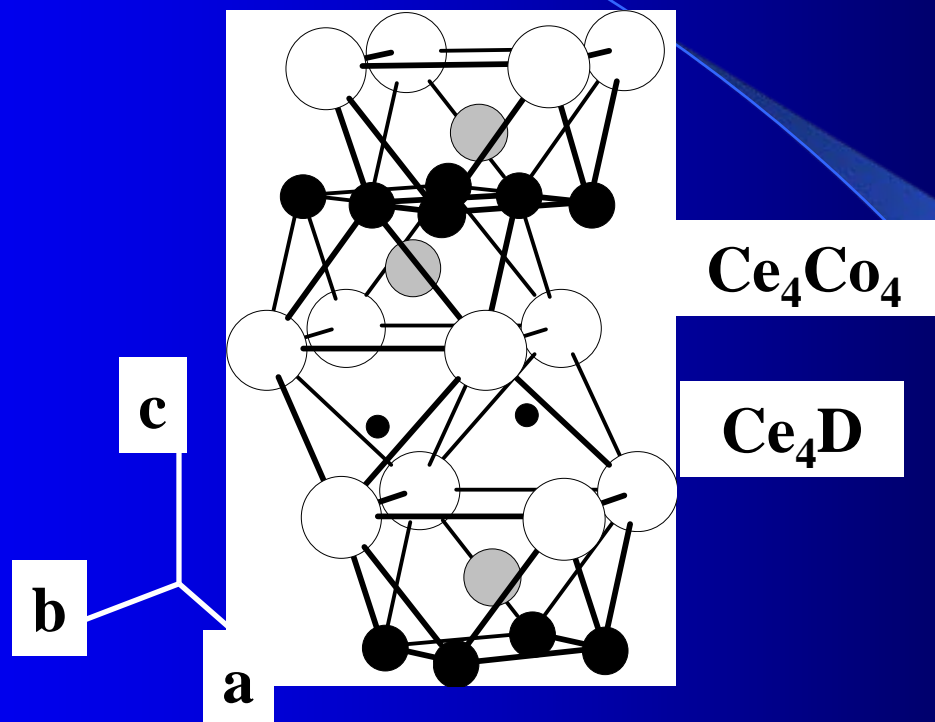
Along c-axis :  
two layers of [Ce<sub>4</sub>Fe<sub>4</sub>] antiprisms  
separated by one layer of [Ce<sub>4</sub>]  
pseudo-tetrahedral units (interesting  
for H-insertion as in CeH<sub>2</sub>).

[Ce<sub>4</sub>Fe<sub>4</sub>]

[Ce<sub>4</sub>]

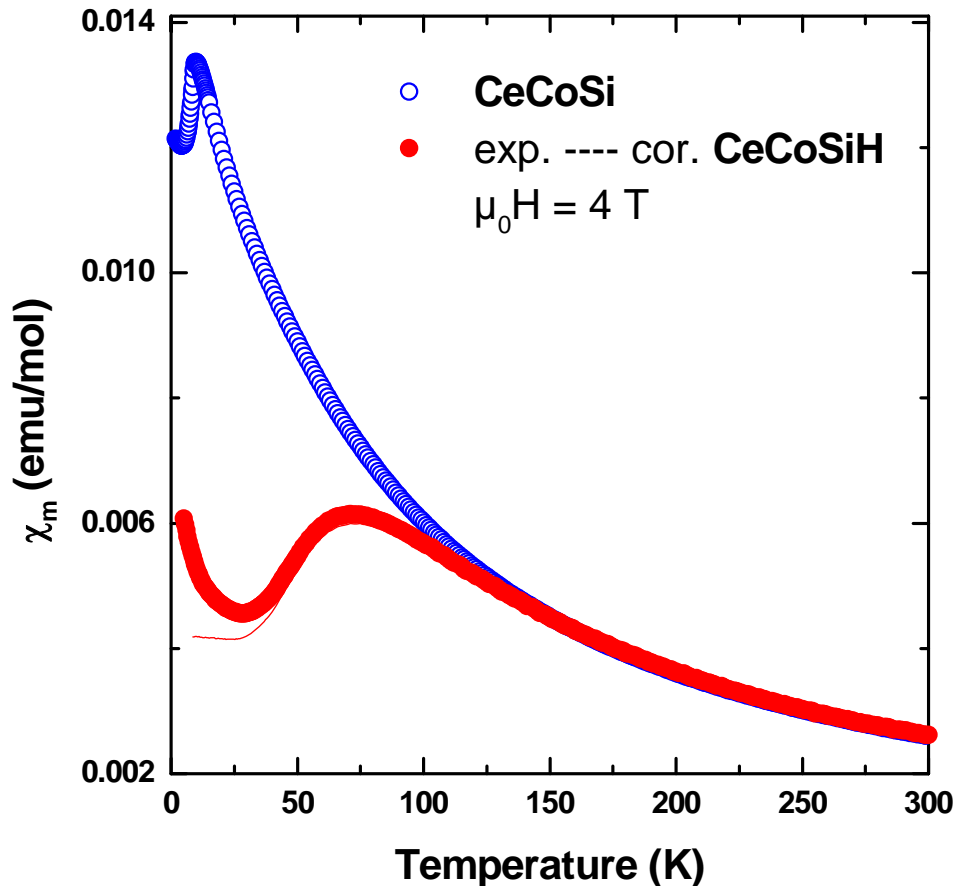


# Structural properties of CeCoSiH and CeCoGeH



**In CeCoSi, hydrogenation causes anisotropic expansion: a decreases ( $4.041 \text{ \AA} \rightarrow 3.955 \text{ \AA}$ ) whereas c increases ( $6.990 \text{ \AA} \rightarrow 7.861 \text{ \AA}$ ) but unit cell volume increases (7.8 %).**

# Hydrogenation of CeCoSi: transition from antiferromagnet to spin fluctuation behaviour



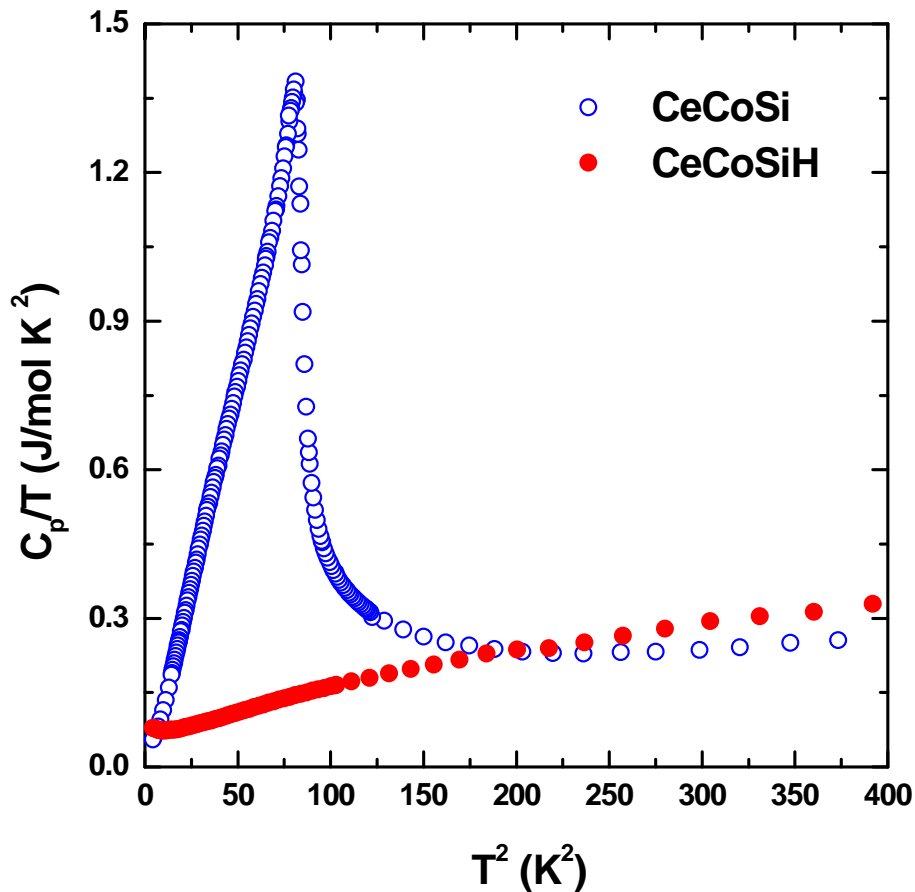
CeCoSi, sharp peak at  $T_N = 8.8$  K

CeCoSiH broad peak around 70 K



Spin fluctuation temperature  
 $T_{sf} = 130(5)$  K

# Specific heat measurements on **CeCoSi** and **CeCoSiH**



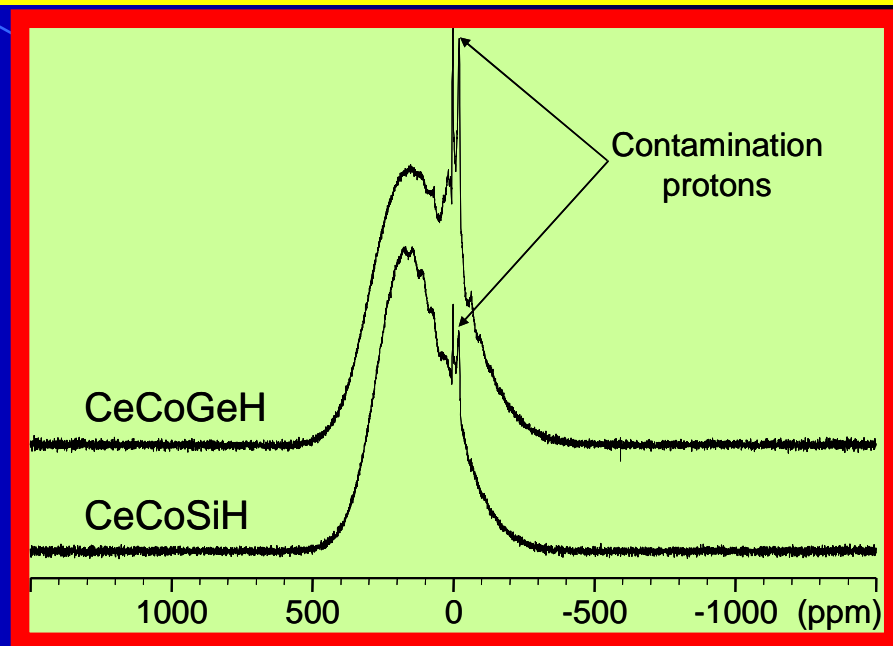
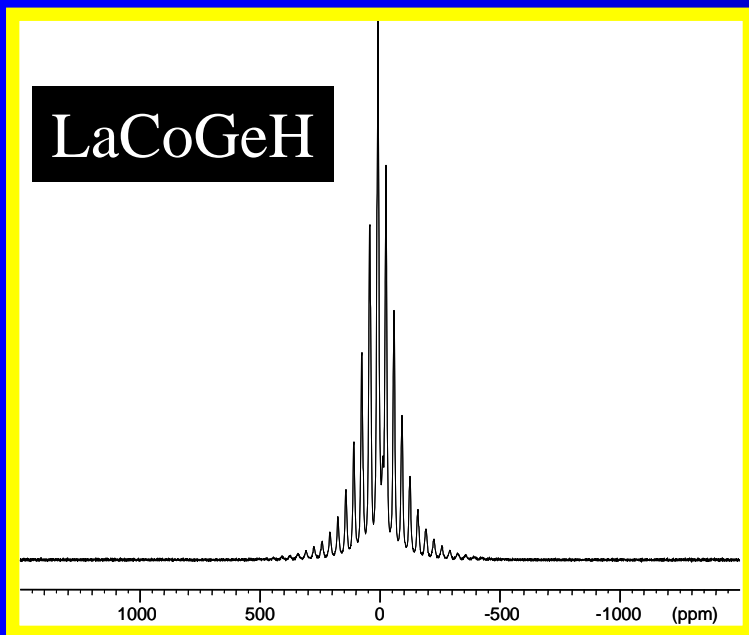
**No magnetic transition  
appears for CeCoSiH**

**$\gamma$  value decreases  
from 170 to 70  
J/mol K<sup>2</sup>**



**Increase of the Kondo  
effect after  
hydrogenation**

# $^1\text{H}$ NMR on $\text{LaCoGeH}$ , $\text{CeCoSiH}$ and $\text{CeCoGeH}$



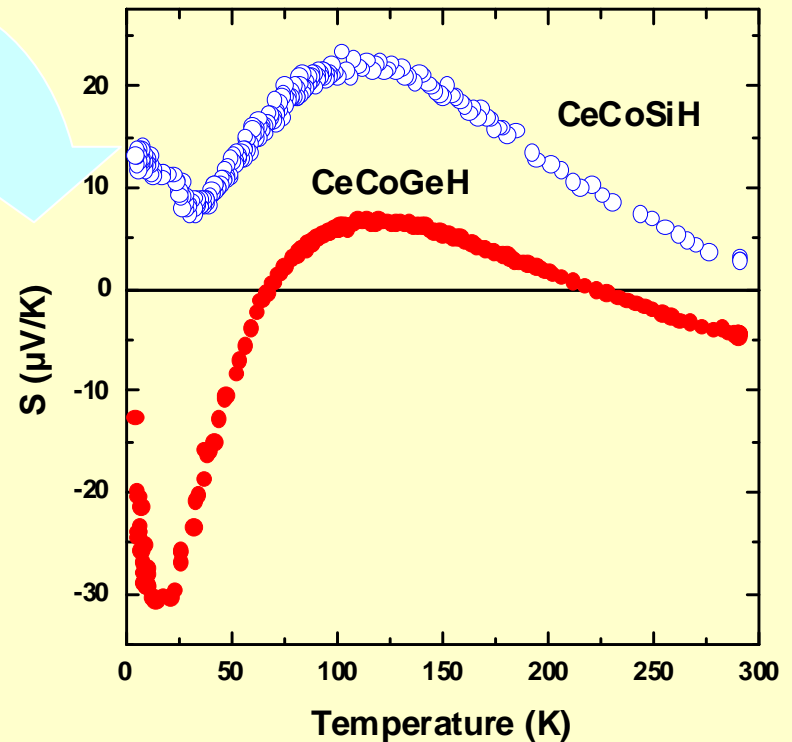
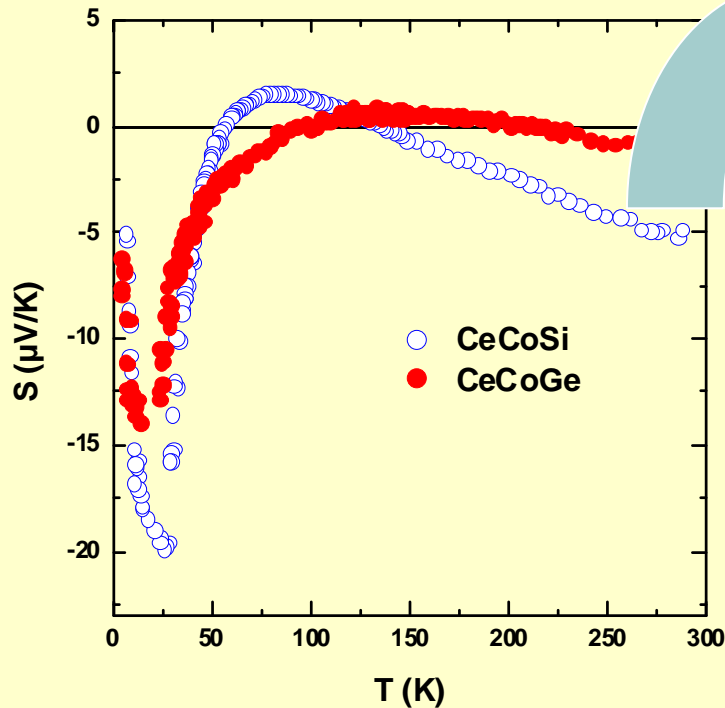
**LaCoGeH** : separation into spinning sidebands; no significant Knight Shift (8.7 ppm).

**CeCoSiH and CeCoGeH** : no spinning sidebands (strong dipolar interaction due to Ce), signal strongly shifted (150 ppm) (transfert of some density of electron from Ce to proton)

**-Occurrence of widening of the signal in the sequence CeCoSiH → CeCoGeH (increase of the number of f-electrons)**



# Thermoelectric properties of **CeCoSiH** and **CeCoGeH**



**$S=f(T)$  for CeCoSi changes of sign (trivalent state) whereas always positive for CeCoSiH (intermediate valence)**

# Hydrogenation of **CeRuSi** (heavy fermion, $\gamma = 220$ mJ/mol K<sup>2</sup>)

Anisotropic expansion of the unit cell parameters :

**CeRuSi** ( $a = 4.197$  Å et  $c = 6.894$  Å)

**CeRuSiH** ( $a = 4.175$  Å et  $c = 7.496$  Å)

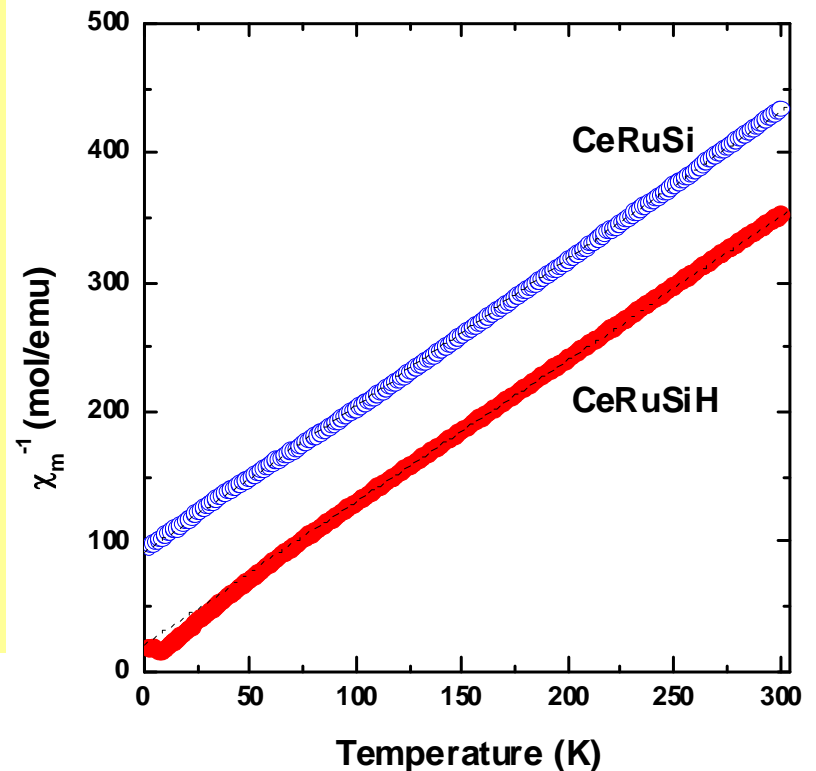
Strong increase of  $\theta_p$

**CeRuSi** ( $\theta_p = -81$  K)

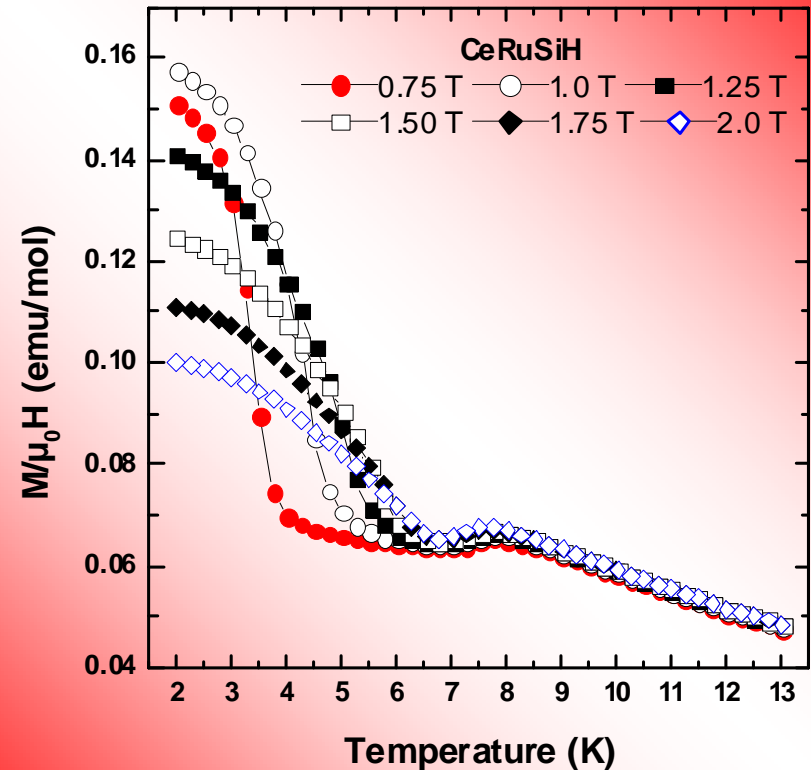
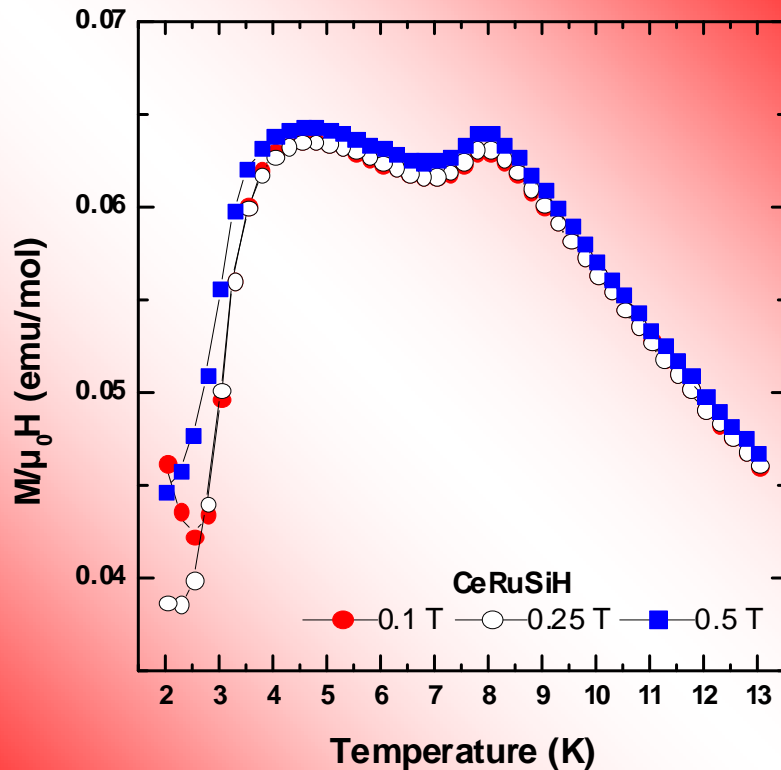
**CeRuSiH** ( $\theta_p = -18$  K)



**Decrease of the Kondo effect**

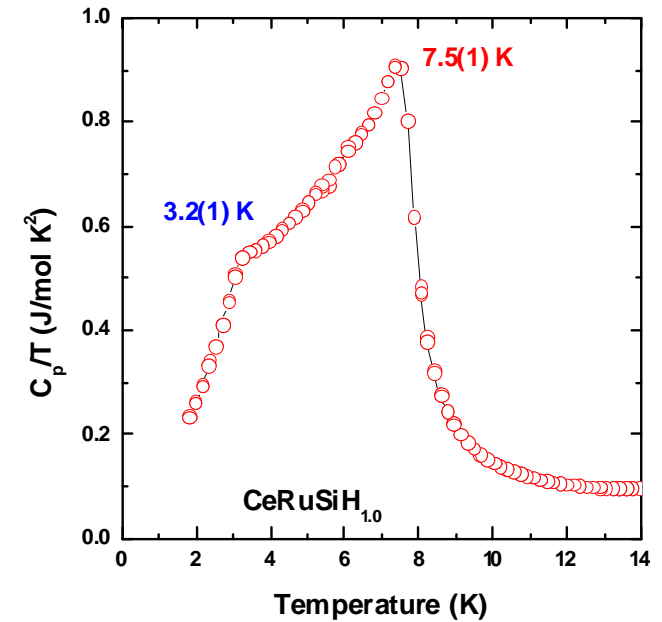
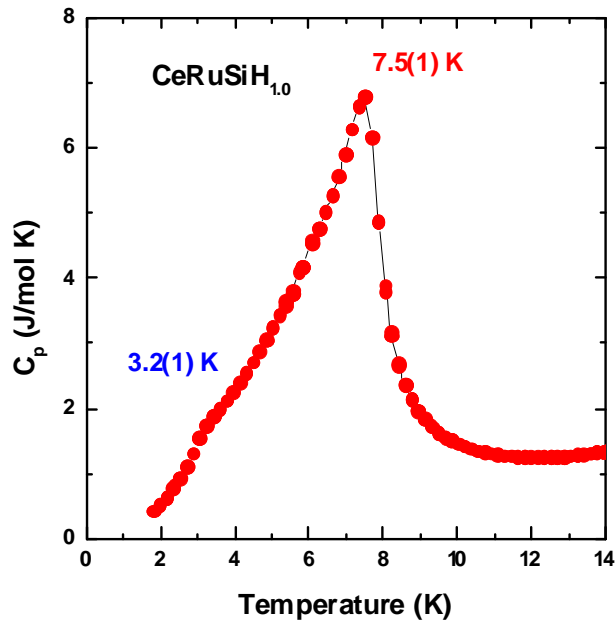


**CeRuSi  $\rightarrow$  CeRuSiH: transition from non magnetic to antiferromagnetic ordering (complex magnetic phase diagram)**



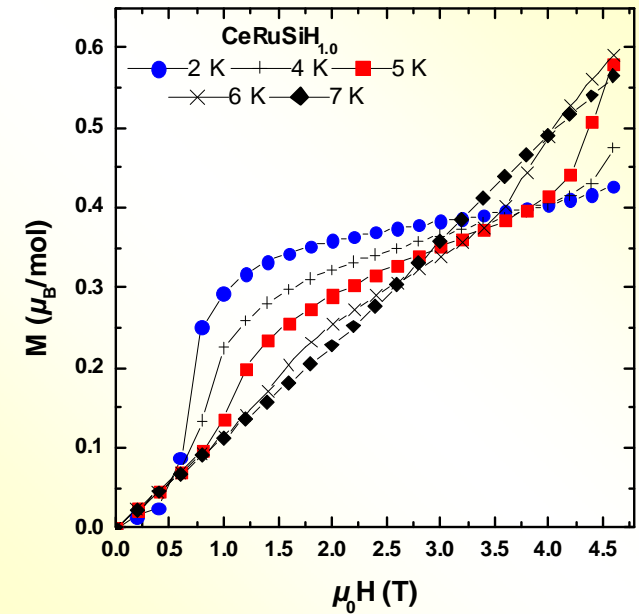
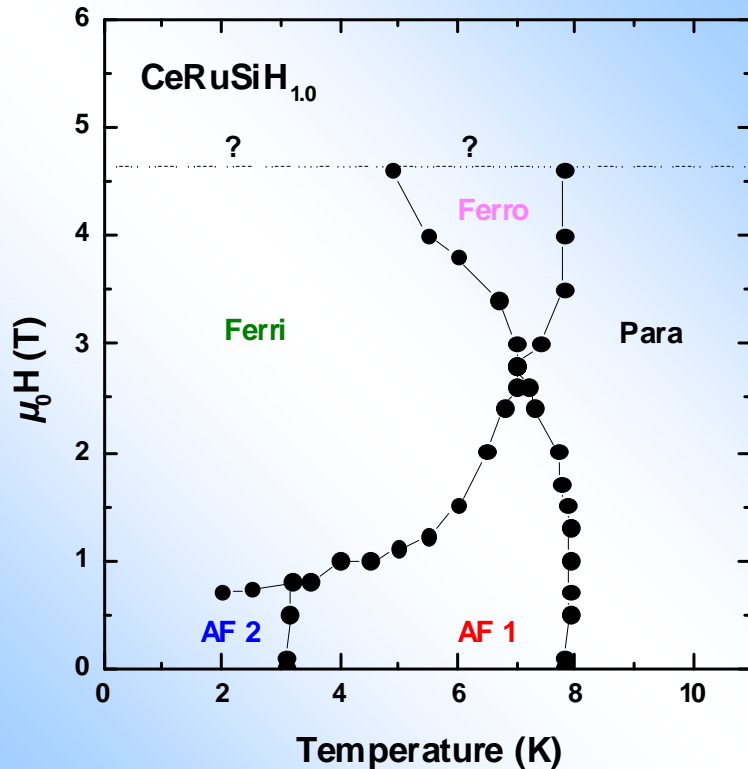
**CeRuSiH shows two antiferromagnetic transitions at 7.5 K and 3.2 K. One (7.5 K) is independent to the magnetic field but the other (3.2 K) is strongly influenced.**

# Specific heat measurements on $\text{CeRuSiH}_{1.0}$



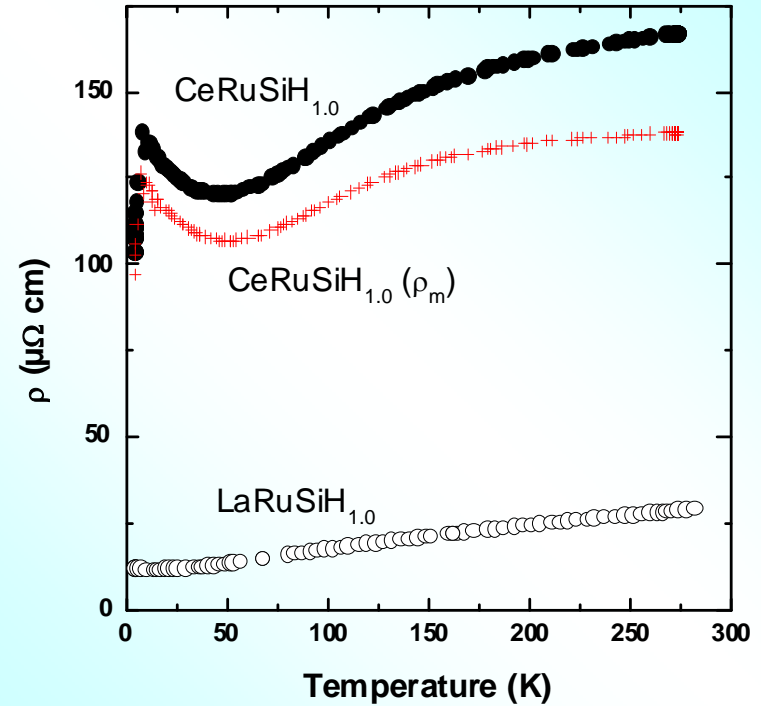
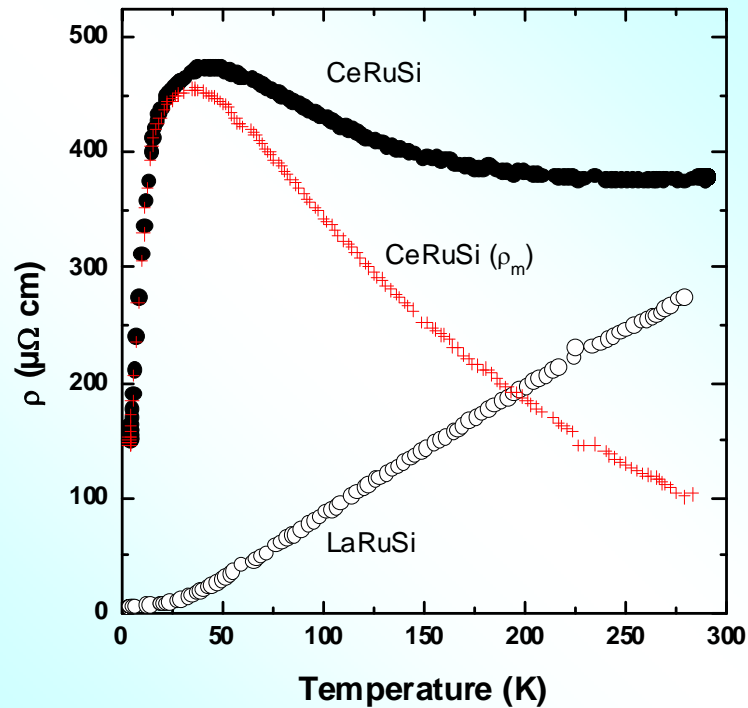
**The two antiferromagnetic transitions are evidenced by this investigation.**

# CeRuSiH<sub>1.0</sub> : complex magnetic phase diagram



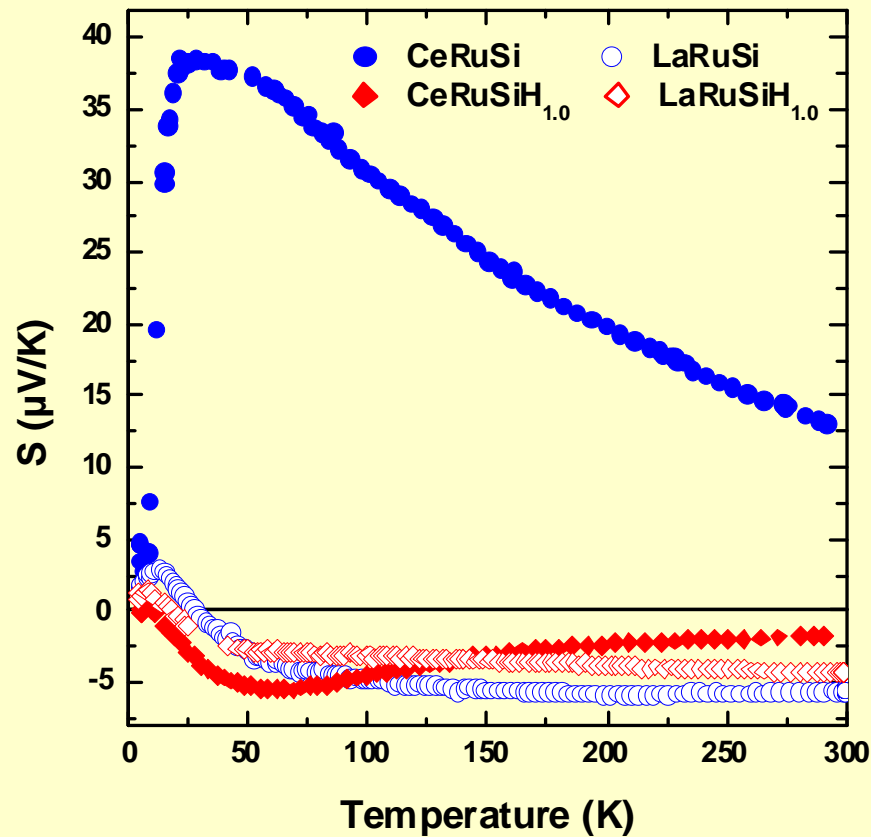
**At 6 K, two transitions are induced by the field : AF1 - Ferri - Ferro.**  
**At 2 K, only one is detected : AF2 - Ferri.**

# Electrical resistivity measurements on **CeRuSi** and **CeRuSiH<sub>1.0</sub>**



- $\rho_m = f(T)$  for CeRuSi shows a broad maximum near 36 K and follows above by a  $\rho_m = -A \log T$  dependence (crystal field effect).
- Hydrogenation induces an increase of the metallic character ( $\rho_m$  decreases); minima at 50 K followed by a maxima near 7.8 K (magnetic ordering).

# Thermoelectric properties of **CeRuSi** and **CeRuSiH**



**CeCoSi**

**AF**

**$T_N = 8.8$  K**

**CeCoGe**

**AF**

**$T_N = 5.0$  K**

**CeRuSi**

**heavy fermion  
no magnetic  
ordering**

**Hydrogenation**

**CeCoSiH<sub>1.0</sub>**

**Int. valence**

**$T_K = 130$  K**

**CeCoGeH<sub>1.0</sub>**

**Int. valence**

**$T_K = 13.3$  K**

**CeRuSiH<sub>1.0</sub>**

**AF**

**$T_N = 7.5$  and  $3.2$  K**

**Ce-H distance increases :  $2.391$  Å,  $2.410$  Å and  $2.443$  Å.  
Ce-H bonding decreases.**



# CONCLUSION

H-atoms inserted in  $[\text{Ce}_4]$  pseudo-tetrahedral sites of  $\text{CeCoSi}$ ,  $\text{CeCoGe}$  and  $\text{CeRuSi}$ .



Competition between **the increase of the unit cell volume** and **the occurrence of strong Ce – H bond** (hybridization of  $4f(\text{Ce})$  states).



**Various transitions:**

**antiferromagnetic ( $\text{CeCoSi}$ ,  $\text{CeCoGe}$ ) → spin fluctuations ( $\text{CeCoSiH}$ ,  $\text{CeCoGeH}$ ), chemical effect of H prevails over the unit cell expansion effect.**

**non magnetic ( $\text{CeRuSi}$ ) → antiferromagnetic ( $\text{CeRuSiH}$ ), opposite effect.**

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graph TD; A[Acknowledgements] --> B[ICMCB]; A --> C[Orsay]; A --> D[LLB, Saclay]; A --> E[Nancy]; A --> F[Santander]; B --> B1[S. Tencé, E. Gaudin]; B --> B2[S. F. Matar]; B --> B3[M. Ménétrier]; B --> B4[R. Decourt]; C --> C1[B. Coqblin]; D --> D1[G. André]; E --> E1[B. Malaman]; F --> F1[J. Sanchez Marcos]; F --> F2[J. Rodriguez Fernandez];
```

## **ICMCB**

**S. Tencé, E. Gaudin**  
**S. F. Matar**  
**M. Ménétrier**  
**R. Decourt**

## **Orsay**

**B. Coqblin**

## **LLB, Saclay**

**G. André**

## **Santander**

**J. Sanchez Marcos**  
**J. Rodriguez Fernandez**

## **Nancy**

**B. Malaman**

**Thanks you for your attention**

