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

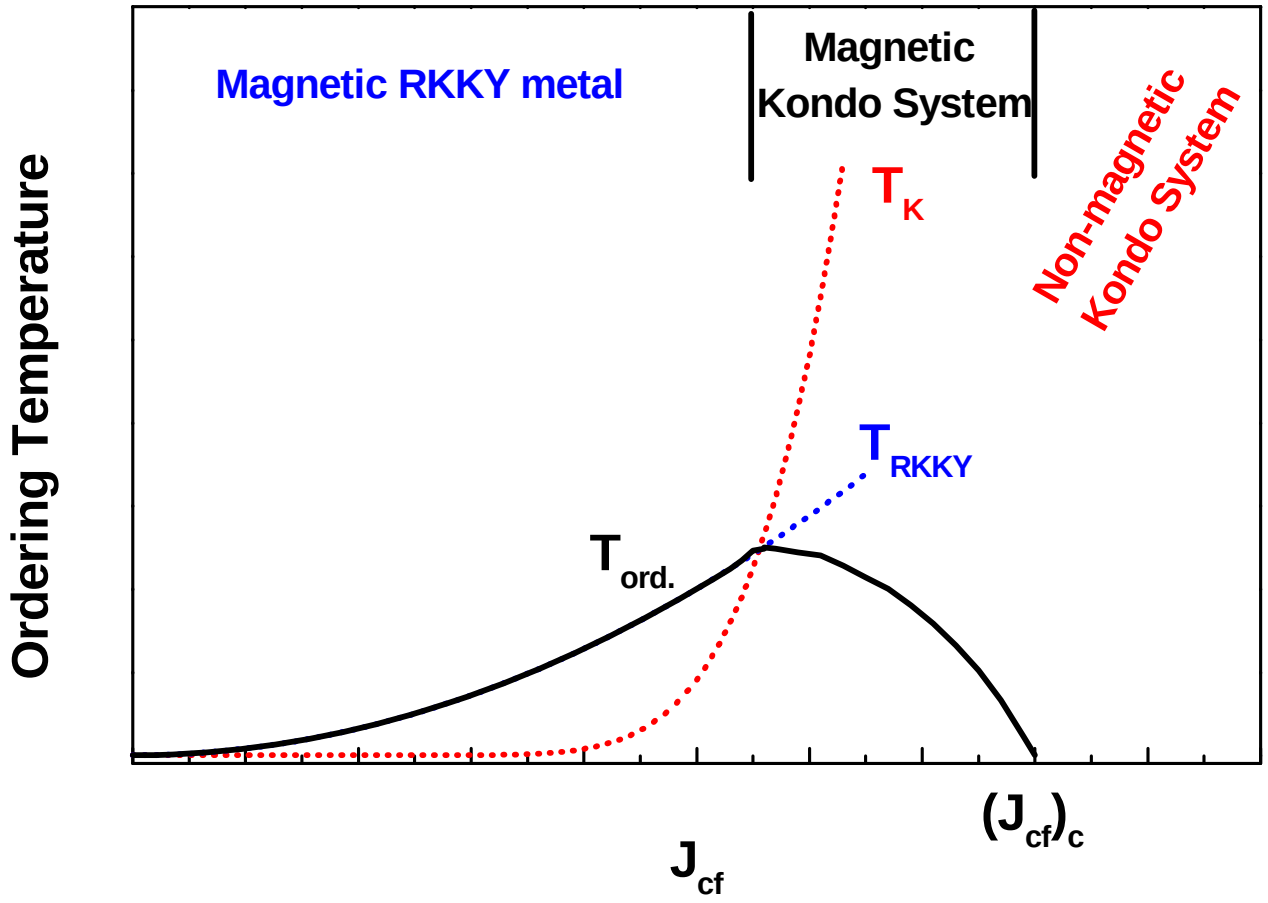
RKKY interaction
$T_{RKKY} = J_{cf}^2 N(E_F)$
favours occurrence of a long range magnetic order

Kondo – RKKY competition

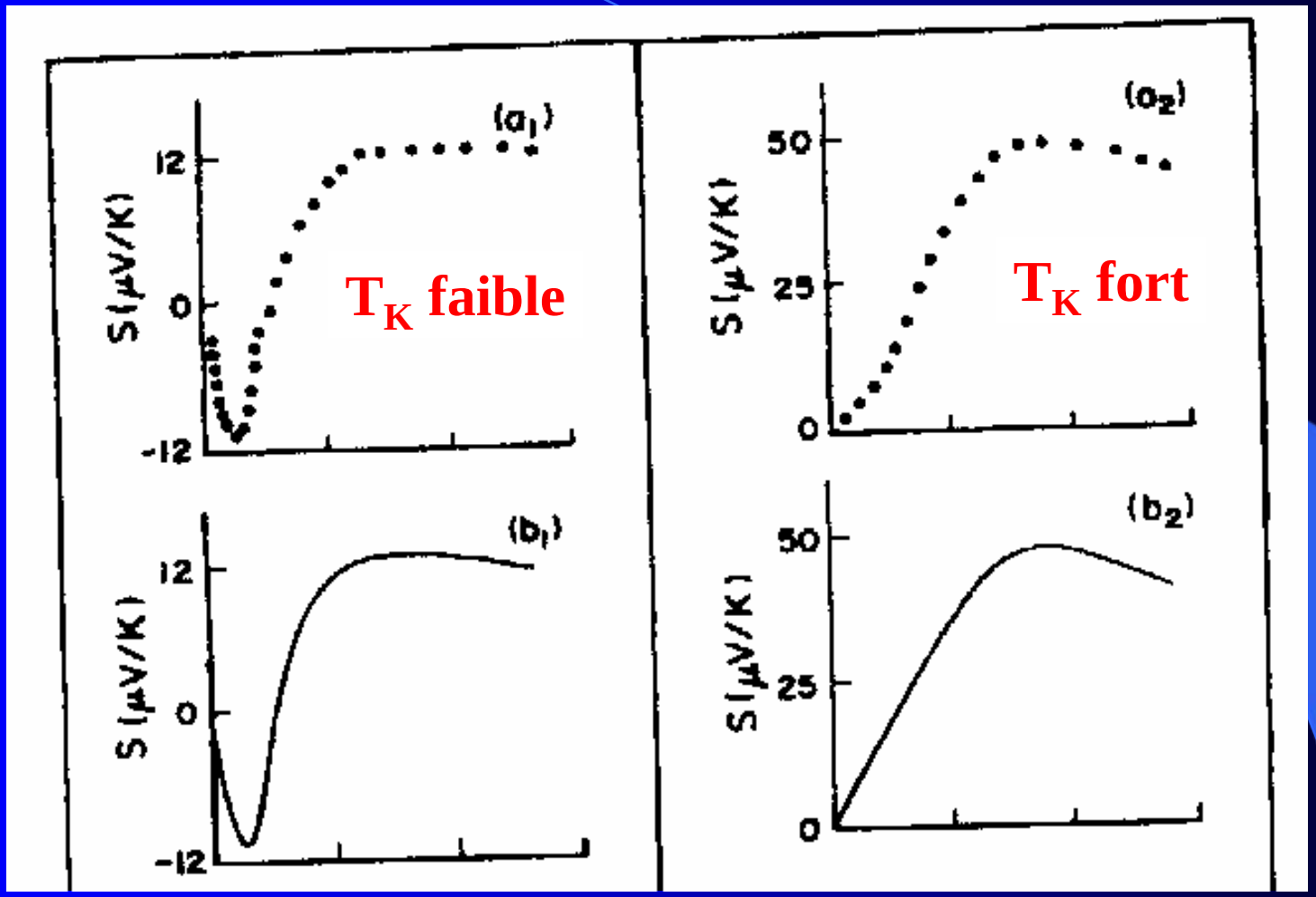
=

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

$\Rightarrow$ effet Kondo (T_K)

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

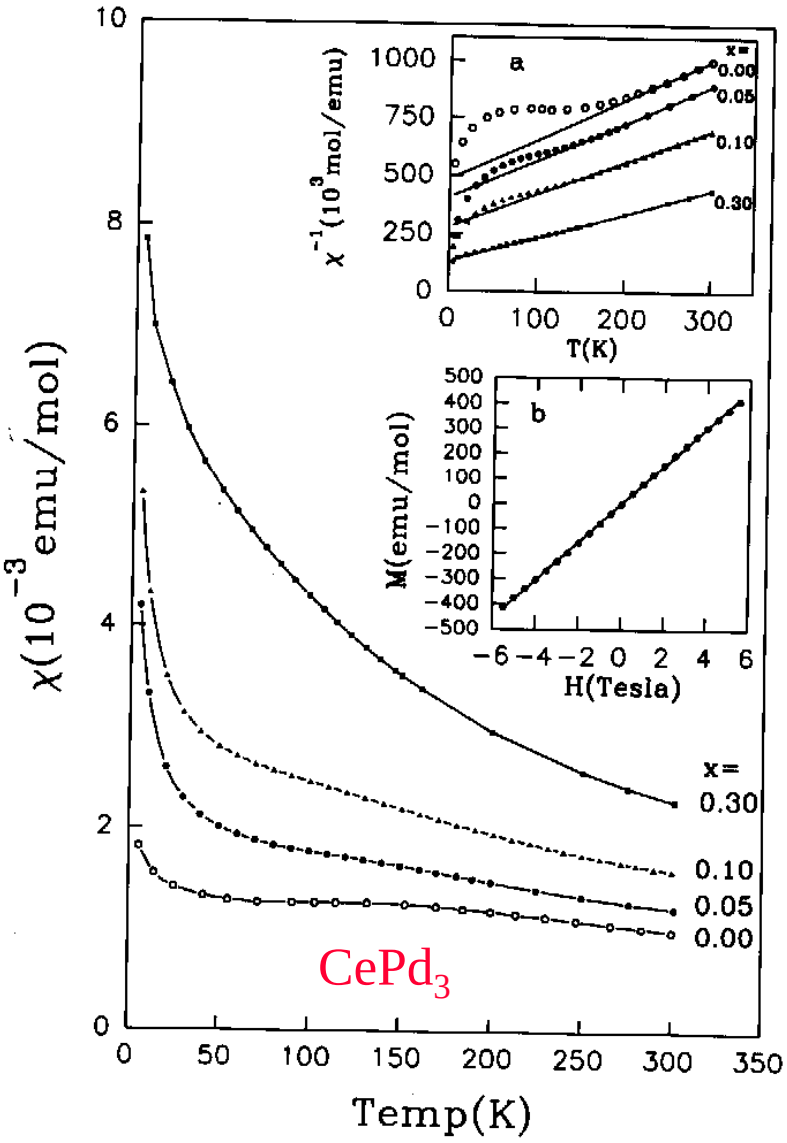


Figure 1. Magnetic susceptibility (χ) versus temperature for $Ce_{1-x}U_xPd_3$ alloys measured in an applied field of $H = 1.0$ T. The top inset shows χ^{-1} versus T for different x values, from which μ_{eff} and θ_P were extracted. The bottom inset shows M versus H data for $x = 0.3$ at 4.2 K.

$(Nd_xCe_{1-x})Pd_3$: propriétés de transport

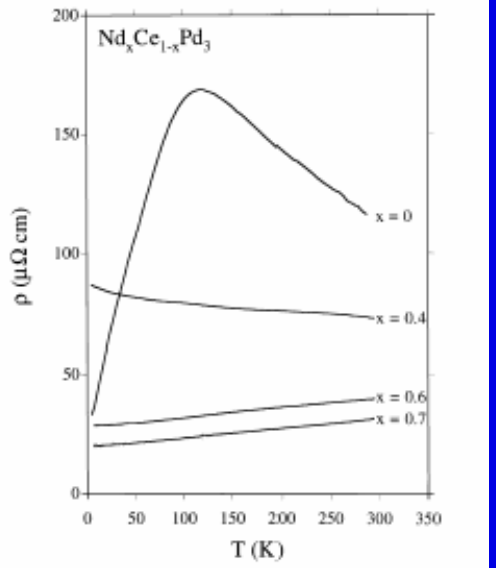


Fig. 2. Electrical resistivity of $Nd_xCe_{1-x}Pd_3$. The x=0 and x=0.4 data are from Ref. 15.

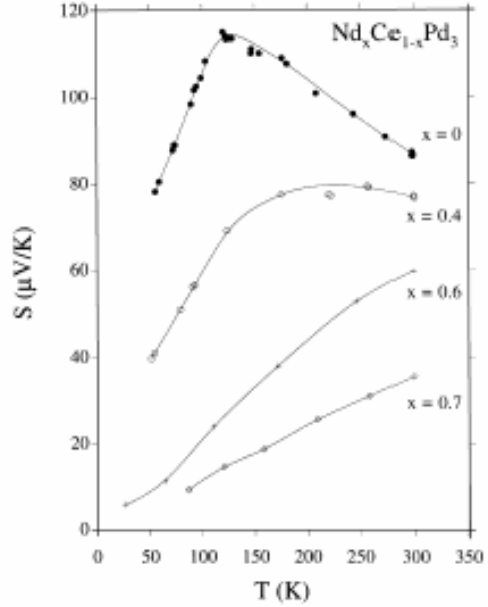


Fig. 3. Thermopower of $Nd_xCe_{1-x}Pd_3$.

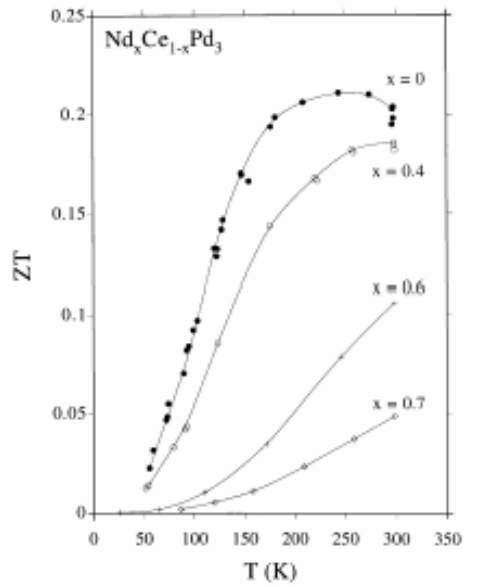


Fig. 6. The dimensionless Figure of Merit for $Nd_xCe_{1-x}Pd_3$ showing the maximum of more than 0.2. for $CePd_3$.

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

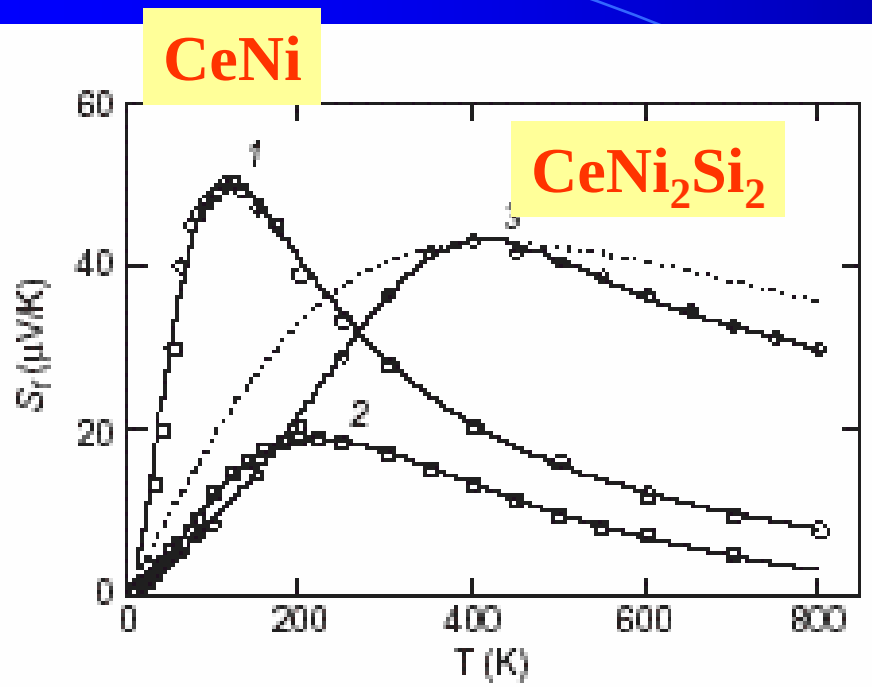


Fig. 1. Temperature dependencies of the contribution of Ce f states to the total thermopower of CeNi (1), $CeNi_2$ (2) and $CeNi_2Si_2$ (3). The solid lines show the thermopower calculated from Eq. (2) in the suggestion temperature dependence of parameter T_K. The dotted curve depicts the behavior of the thermopower according to Eq. (2) under the assumption that T_K = const.

CeNi, $CeNi_2$ et $CeNi_2Si_2$ (valence intermédiaire)

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

M. D. Koterlyn et al., Physica B (2005)

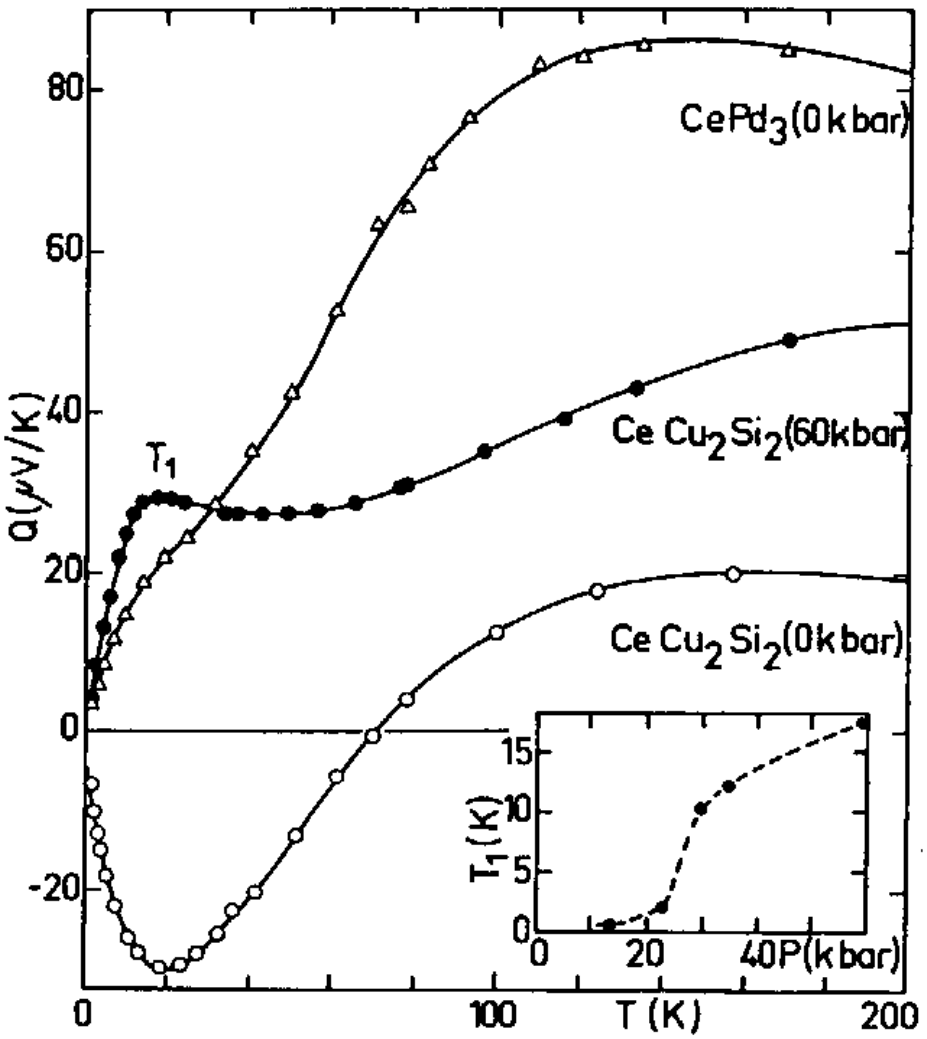


FIG. 1. TEP of $CePd_3$ and of $CeCu_2Si_2$ at 0 kbar and at 60 kbar. For $CeCu_2Si_2$ the insert shows the pressure dependence of the temperature T_1 of the low T positive maximum.

Influence de la pression sur $CeCu_2Si_2$: transition Ce^{3+} (supra) - valence intermédiaire.

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

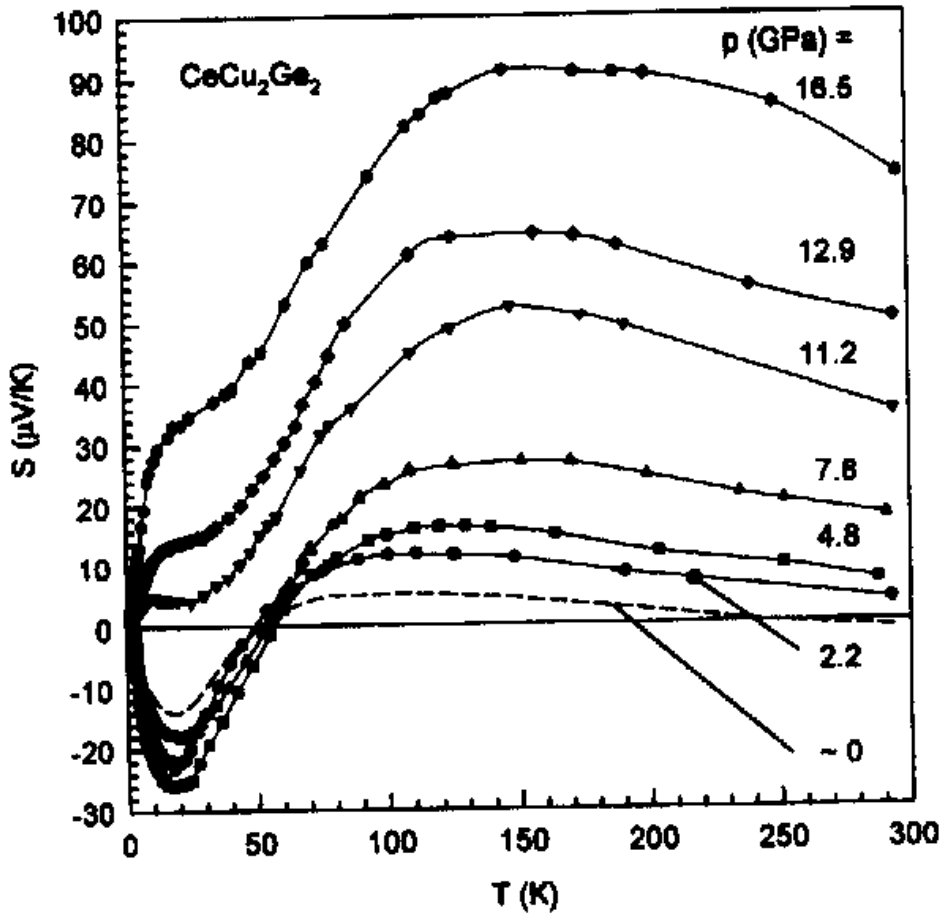


Fig. 2. Absolute thermopower of $CeCu_2Ge_2$ at high pressure; the dashed line represents the $p = 0$ thermopower taken from Ref. [1].

Influence de la pression sur $CeCu_2Ge_2$:
Transition antiferromagnétique (Ce^{3+}) - supraconducteur.

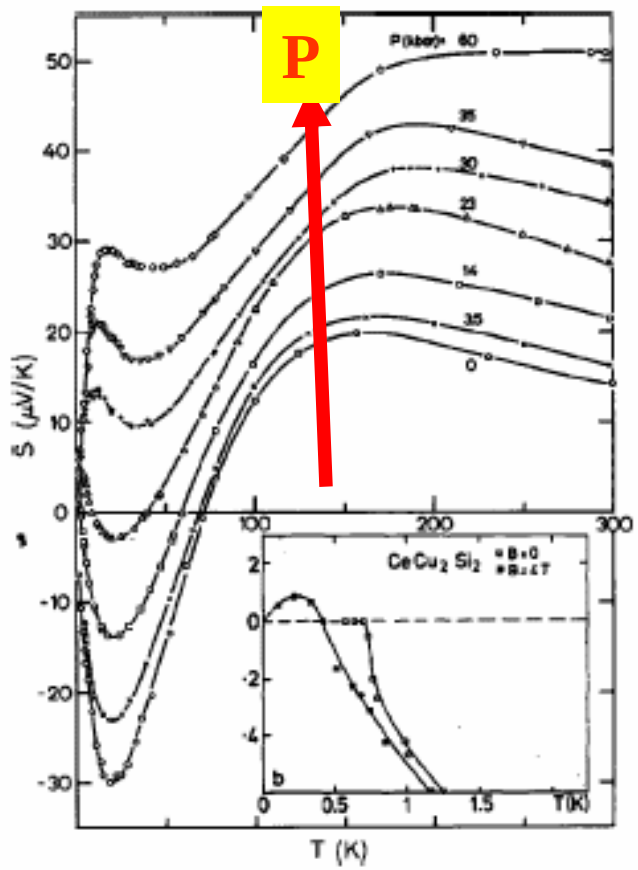


FIG. 1. The thermopower of $CeCu_2Si_2$ plotted as a function of temperature for various pressures (Ref. 13). The inset shows the low-temperature data (Ref. 8) at ambient pressure and small magnetic field, which suppresses the superconducting transition and reveals the positive TEP peak. Type (a) behavior 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 ($CeCu_2Si_2$)

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 ⇒
changes the density of states at E_F.
Occurrence of Ce-H bonding.
Electronic state of H ?

Hydrogen absorption ⇒ unit cell volume increases,
J_{cf} decreases.
Transition non-magnetic → magnetic ?
Transition Kondo magnetic → RKKY magnetic?
Change the thermoelectric power.

OUTLINE

- Hydrogenation of intermediate valence compounds : CeNiGe, CeRhSn and CeIrSn.

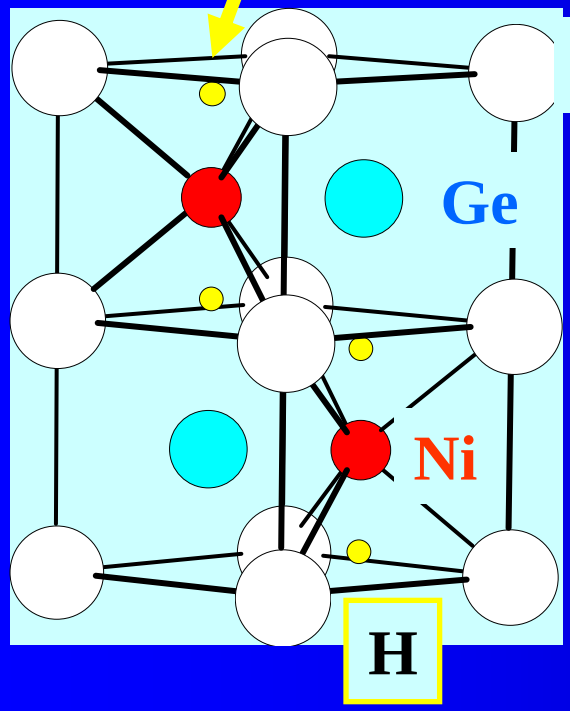
- Unusual transitions induced by hydrogenation of compounds crystallizing in the tetragonal CeFeSi-type structure : from antiferromagnetism (CeCoSi, CeCoGe) to spin fluctuation behaviour (CeCoSiH, CeCoGeH) or from non-magnetic heavy-fermion (CeRuSi) to antiferromagnetism (CeRuSiH).

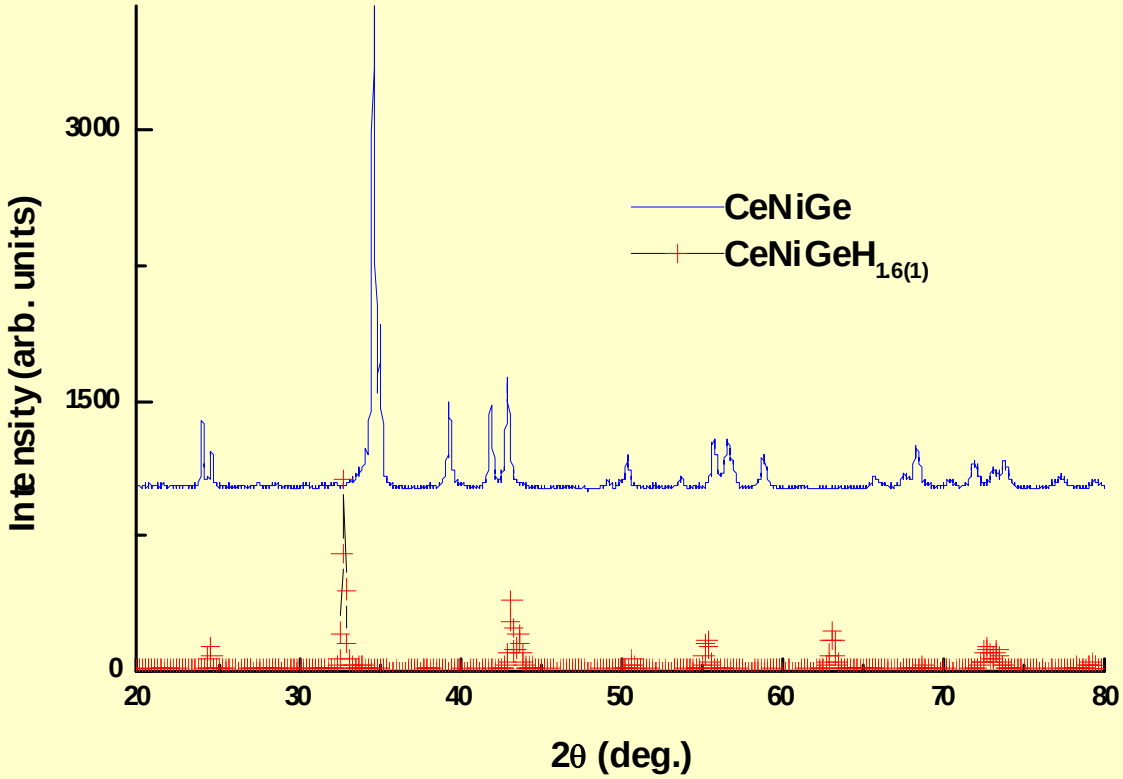
Hydrogenation of CeNiGe :
decrease of the spin fluctuation temperature

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

$CeNiGeH_{1.6}$: structural properties

H (or D) in tetrahedral sites [Ce_3Ni]

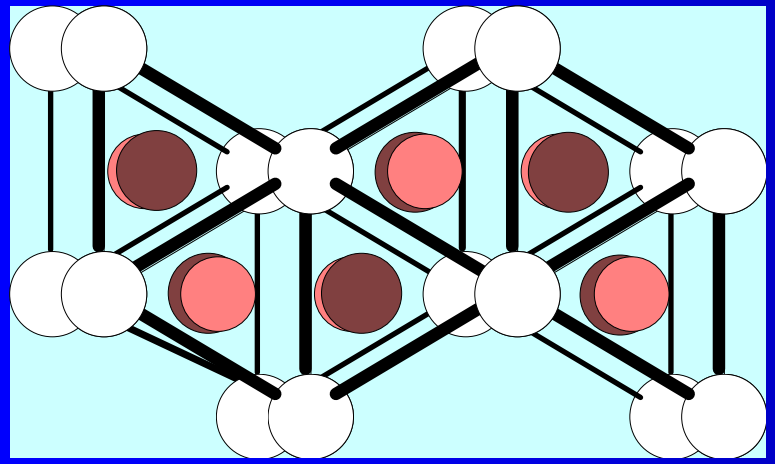




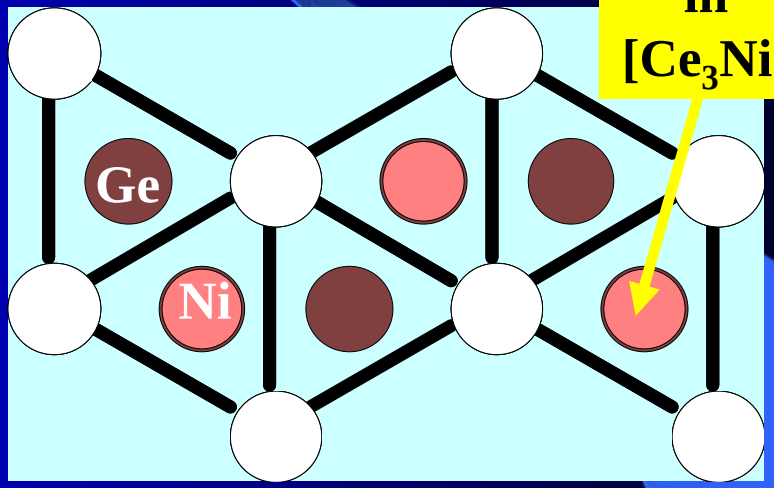
H-insertion induces a structural transition from orthorhombic TiNiSi-type (CeNiGe) to hexagonal ZrBeSi-type ($CeNiGeH_{1.6}$)

Structural transition : CeNiGe → $CeNiGeH_{1.6}$

CeNiGe (orthorhombic)



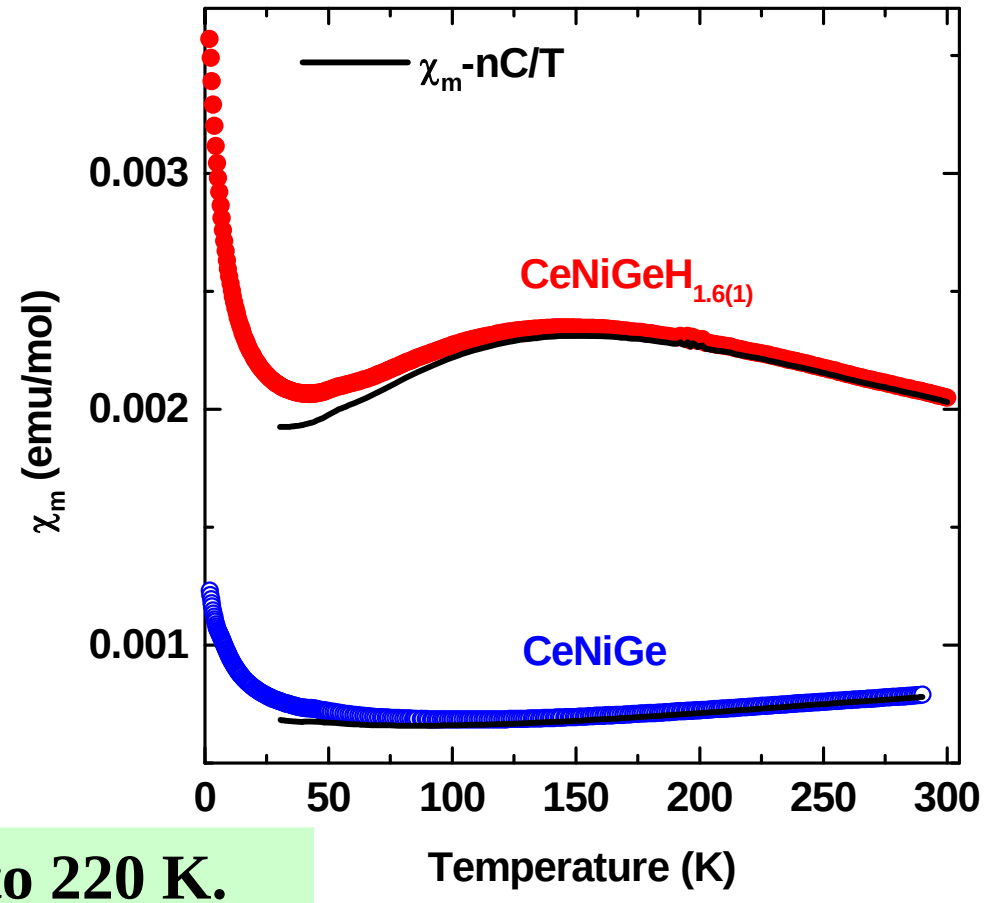
$CeNiGeH_{1.6}$ (hexagonal)



[Ce_6] trigonal prisms surrounding alternatively Ni- and Ge-atoms.
In CeNiGe these prisms are distorted.
H-atoms in the tetrahedral [Ce_3Ni]-site.
Increase of the unit cell volume 11.6 % ($CeNiGeH_{1.8}$).

CeNiGe → $CeNiGeH_{1.6}$: reduction of the Kondo temperature

CeNiGe is a nearly Pauli paramagnet.
χ_m of $CeNiGeH_{1.6}$ shows a broad maximum around 130 K.

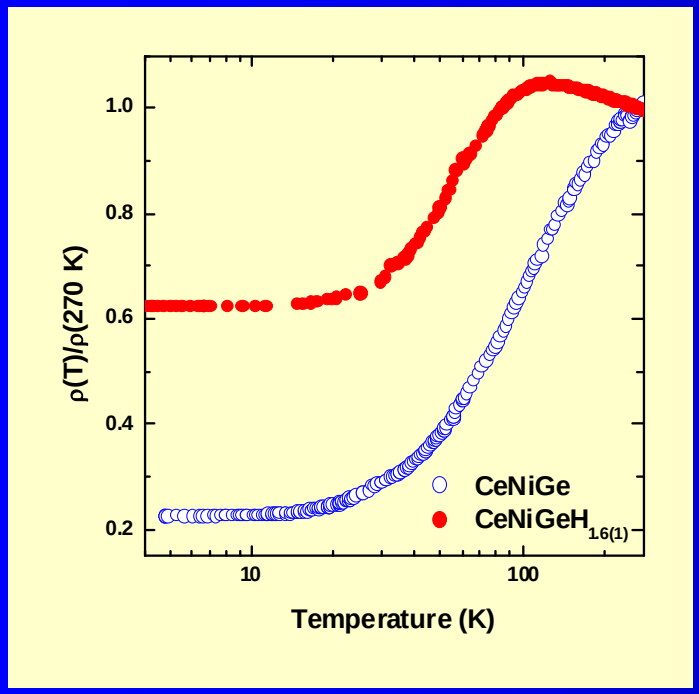


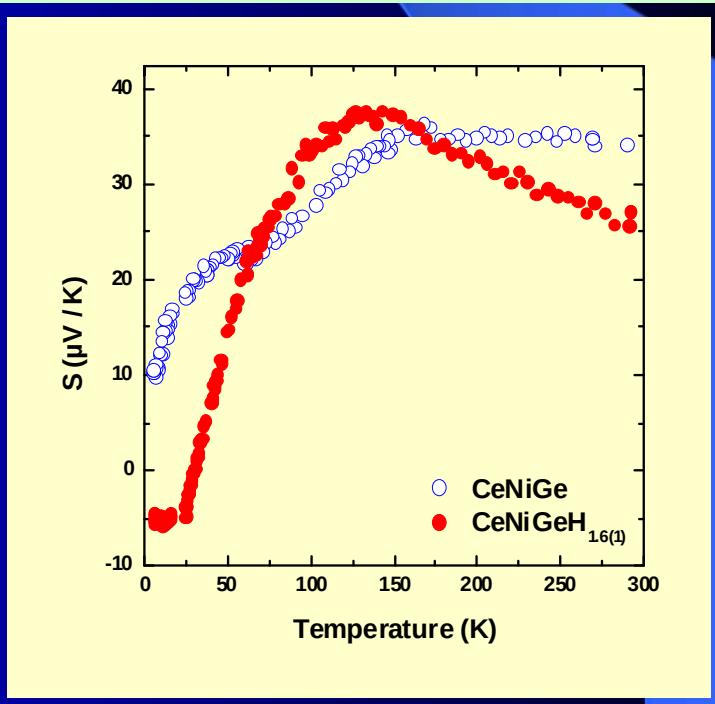
T_K decreases from 600 K to 220 K.
Reduction of the mixing between 4f(Ce) states and conduction electrons.

CeNiGe and $CeNiGeH_{1.6}$: electrical and thermoelectric properties

ρ= f(T) characterizes intermediate valence systems having high (CeNiGe) and lower ($CeNiGeH_{1.6}$) Kondo temperature

S= f(T) characterizes for CeNiGe intermediate valence system (positive, two maximums) whereas for $CeNiGeH_{1.6}$ a nearly trivalent state (change in sign, maximum and minimum)

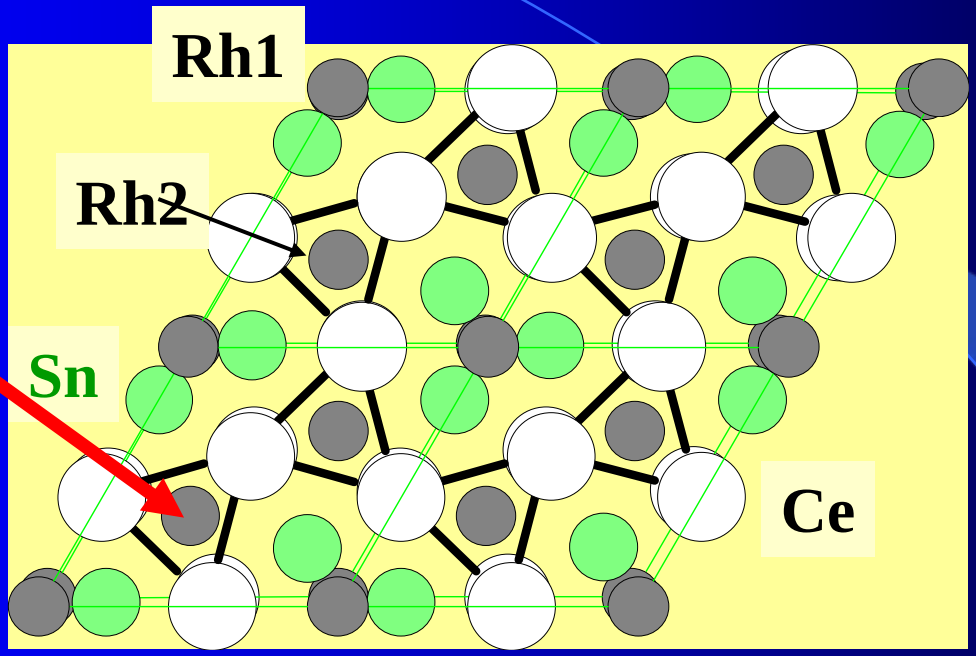




Hydrogenation of CeRhSn and CeIrSn : from intermediate valence to the nearly trivalent state ($CeRhSnH_{0.8}$ and $CeIrSnH_{0.7}$)

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

CeRhSn, CeIrSn and hydrides $CeRhSnH_{0.8}$ and $CeIrSnH_{0.7}$: same hexagonal crystal structure (by neutron diffraction)



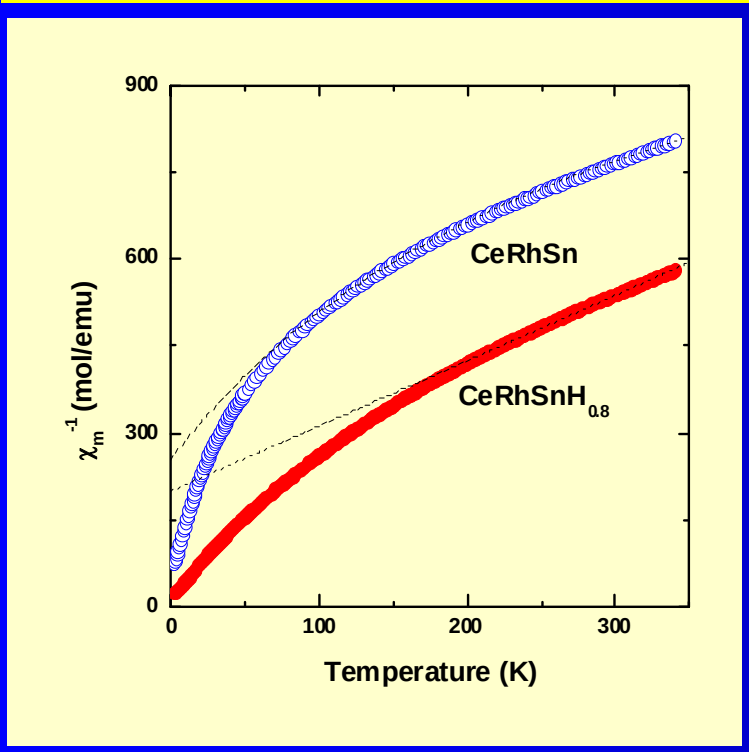
H or D in $[Ce_3Rh]$

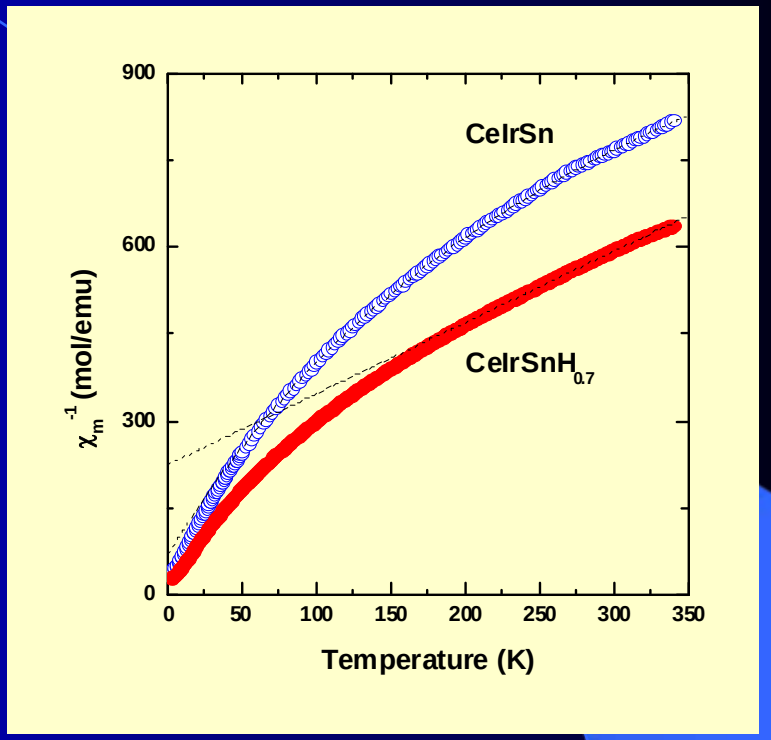
CeRhSn
a = 7.448 Å
c = 4.080 Å

Isotropic expansion of the unit cell parameters.
Unit cell volume increases (4.4 %)

$CeRhSnH_{0.8}$
a = 7.557 Å
c = 4.136 Å

Magnetic properties : CeRhSn, CeIrSn → $CeRhSnH_{0.8}$, $CeIrSnH_{0.7}$



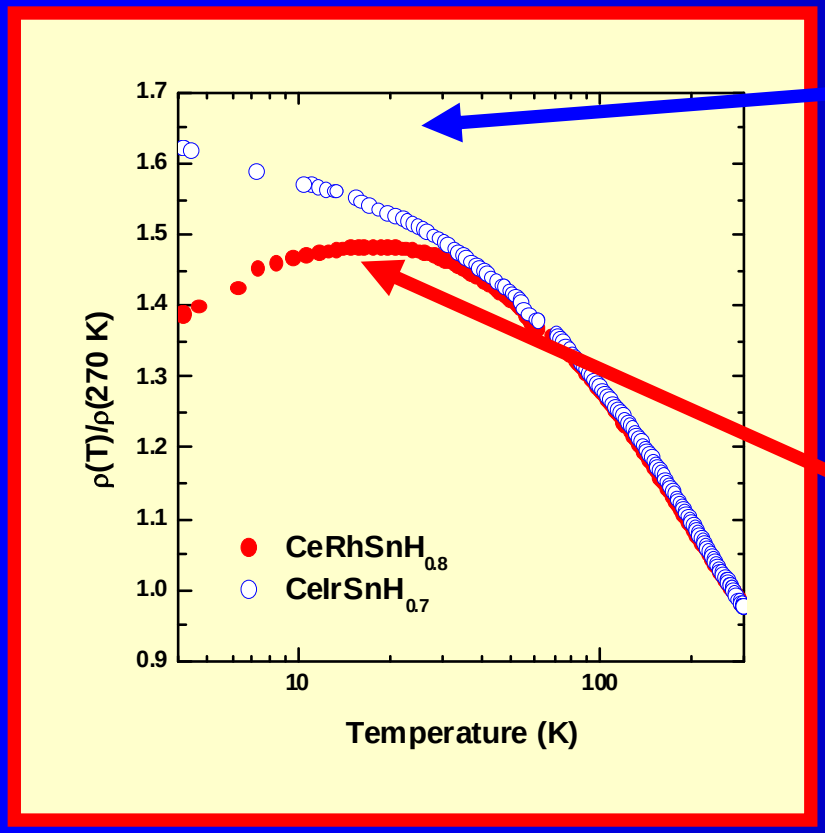


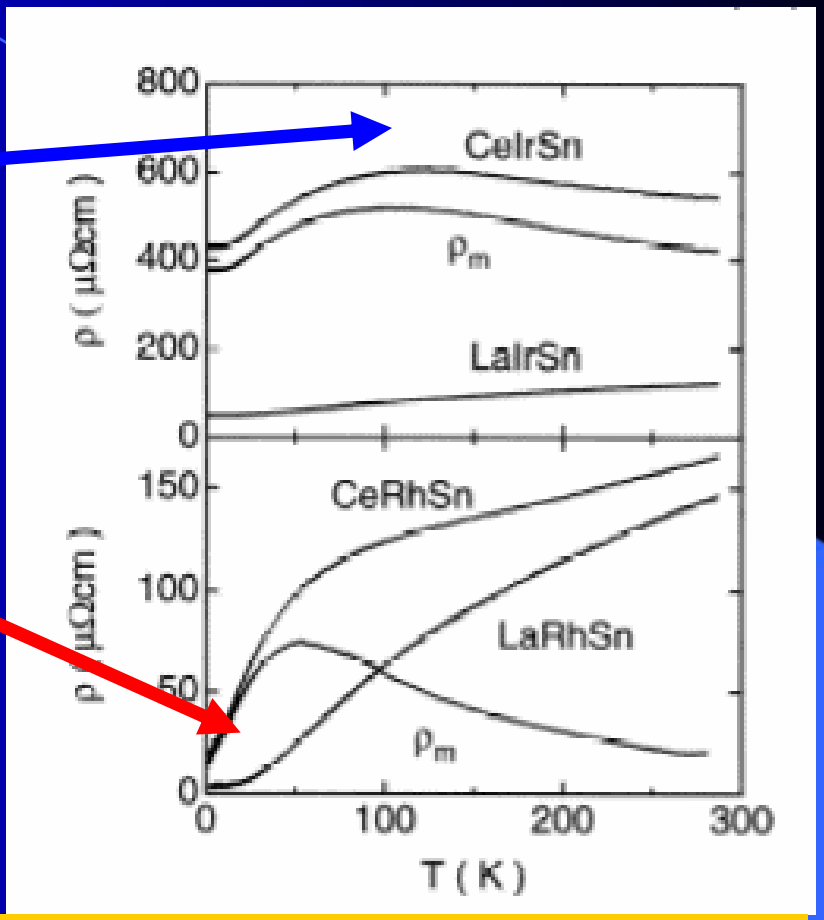
$CeRhSn : \chi_m = \chi_0 + C_m/(T-\theta_p) \Rightarrow \mu_{eff} = 1.25\ \mu_B/Ce$

$CeRhSnH_{0.8} : \chi_m = C_m/(T-\theta_p) \Rightarrow \mu_{eff} = 2.66\ \mu_B/Ce$ (close to Ce^{3+}).

H-insertion induces a valence change of cerium.

Electrical properties : CeRhSn, CeIrSn → $CeRhSnH_{0.8}$, $CeIrSnH_{0.7}$



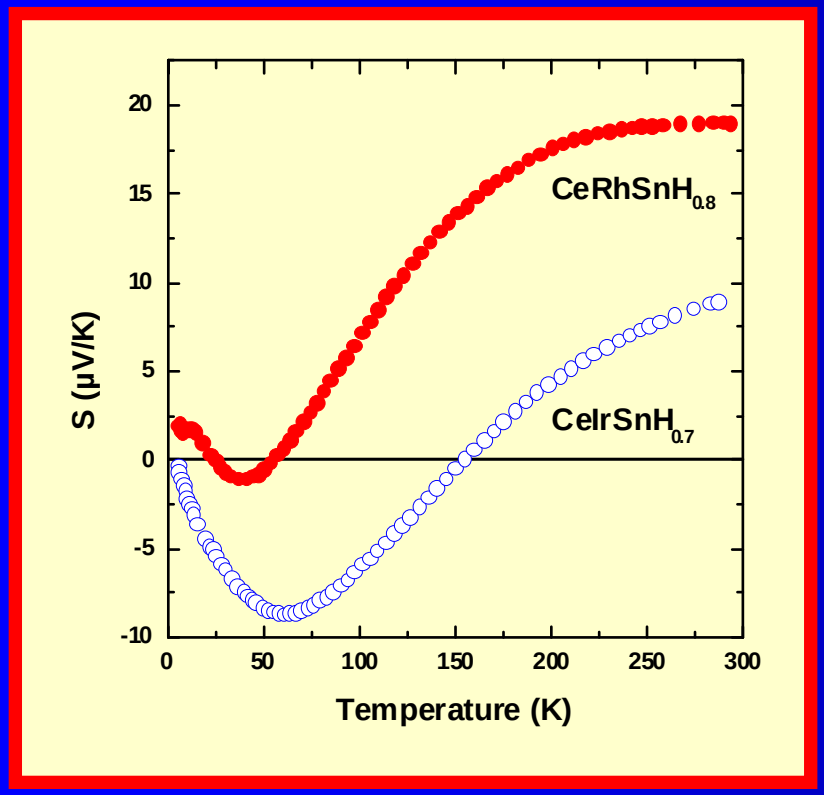


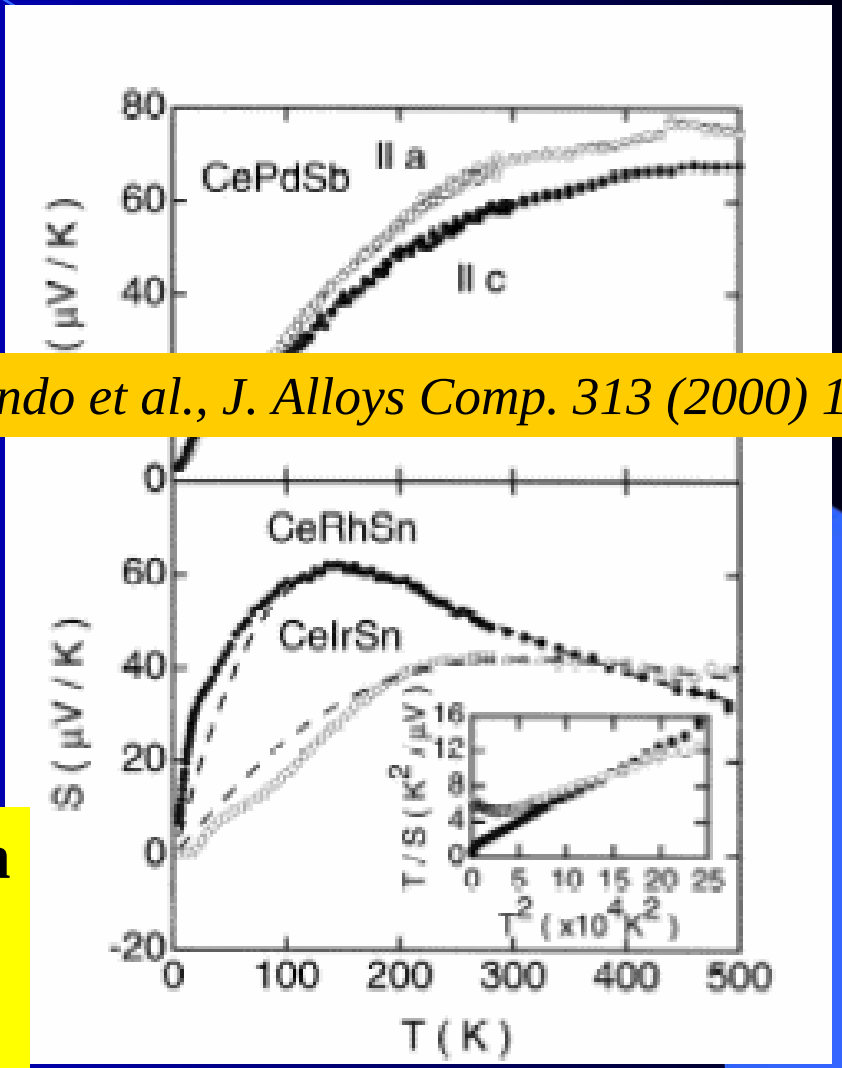
Bando et al., J. Alloys Comp. 313 (2000) 1

The temperature of the maximum decreases after hydrogenation

⇒ Kondo effect decreases.

Thermoelectric properties : CeRhSn, CeIrSn → $CeRhSnH_{0.8}$, $CeIrSnH_{0.7}$





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

Two positive maximums for CeRhSn and CeIrSn (intermediate valence).

Change of sign for $CeRhSnH_{0.8}$ and $CeIrSnH_{0.7}$ (trivalent).

Hydrogenation comparable to the application of negative pressure

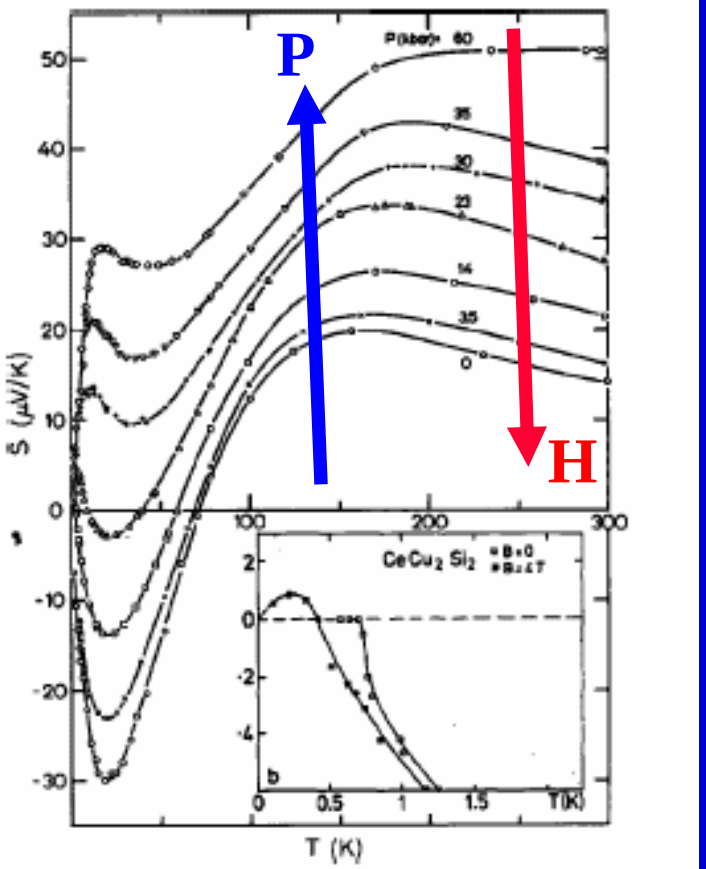


FIG. 1. The thermopower of $CeCu_2Si_2$ plotted as a function of temperature for various pressures (Ref. 13). The inset shows the low-temperature data (Ref. 8) at ambient pressure and small mag-

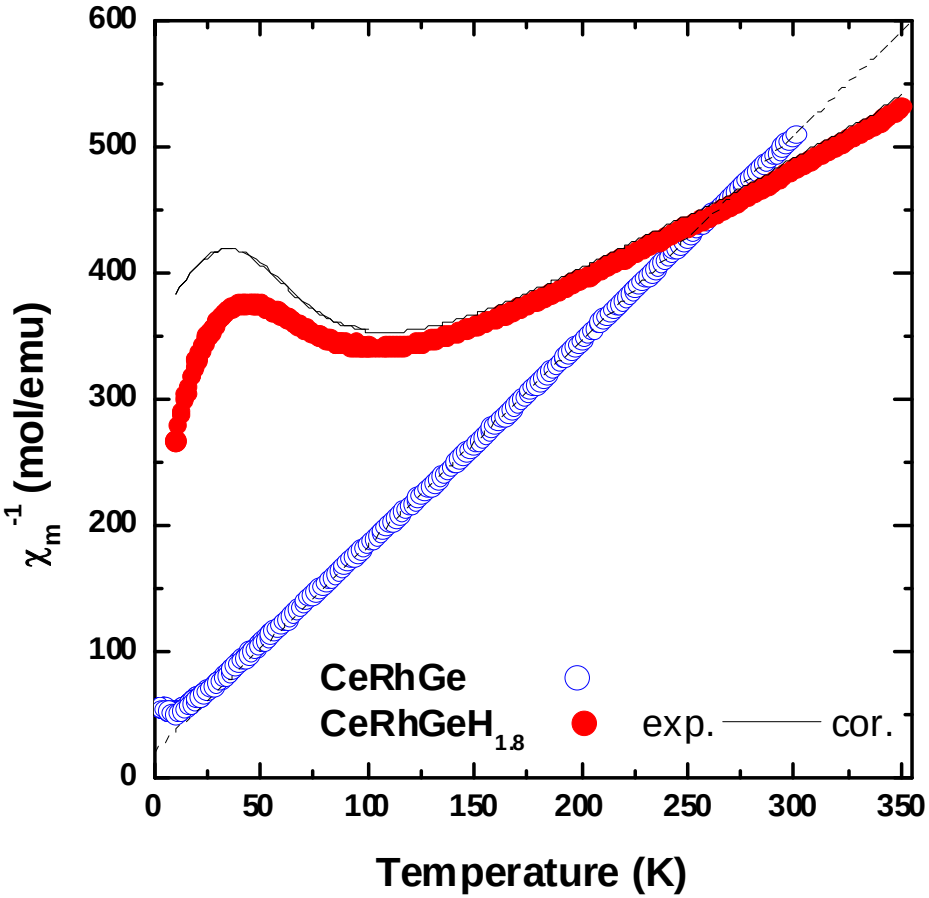
and above.

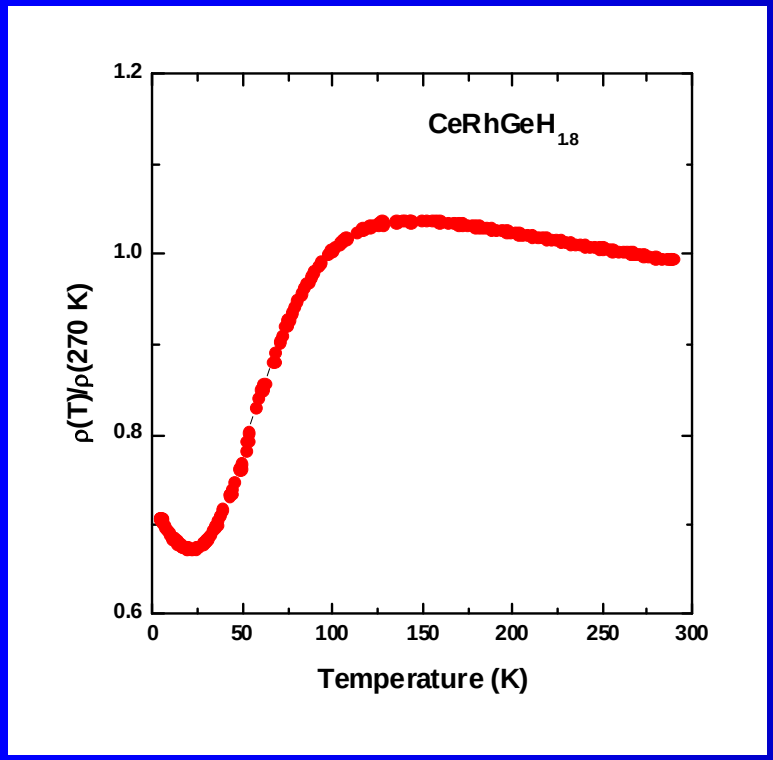
V. Zlatic et al., Phys. Rev. B (2003)

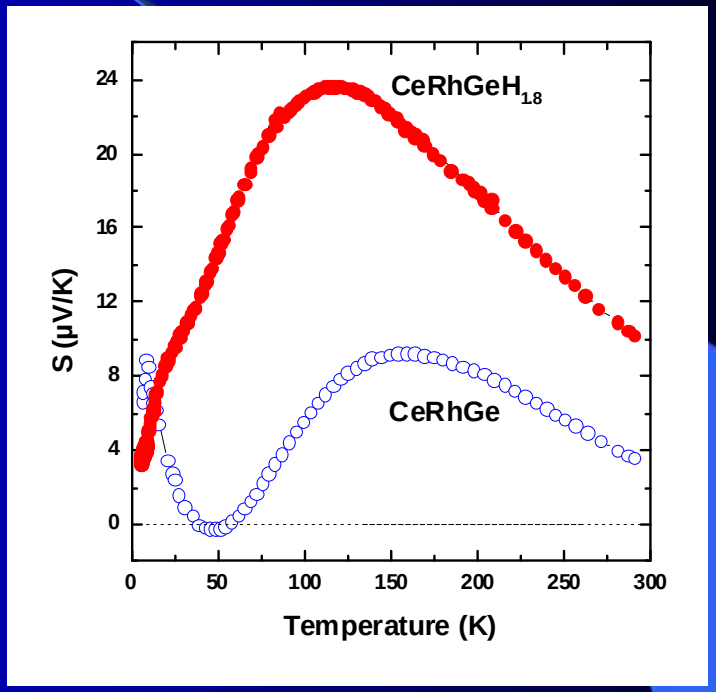
P increases : transition from nearly trivalent ($CeCu_2Si_2$) to intermediate valence

H-insertion : transition from intermediate valence (CeRhSn) to trivalent state ($CeRhSnH_{0.8}$)

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


600
500
400
300
200
100
0
0
50
100
150
200
250
300
350
χ_m^{-1} (mol/emu)
Temperature (K)
CeRhGe
CeRhGeH$_{1.8}$
exp.
cor.


CeRhGeH1.8
ρ(T)/ρ(270 K)
Temperature (K)
1.2
1.0
0.8
0.6
0
50
100
150
200
250
300

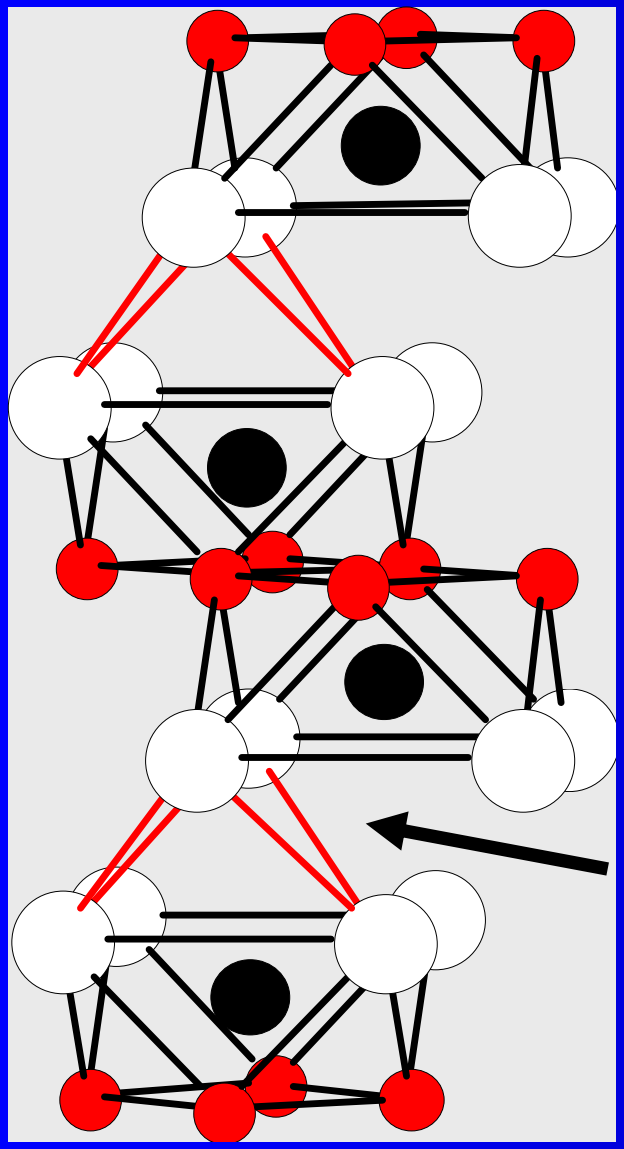

CeRhGeH1.8
CeRhGe
S (μV/K)
Temperature (K)
24
20
16
12
8
4
0
0
50
100
150
200
250
300

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).

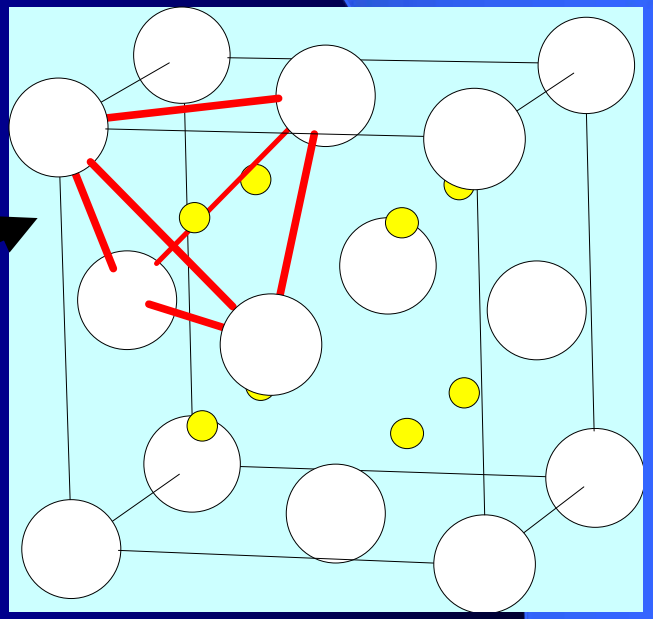
The tetragonal CeFeSi-type structure



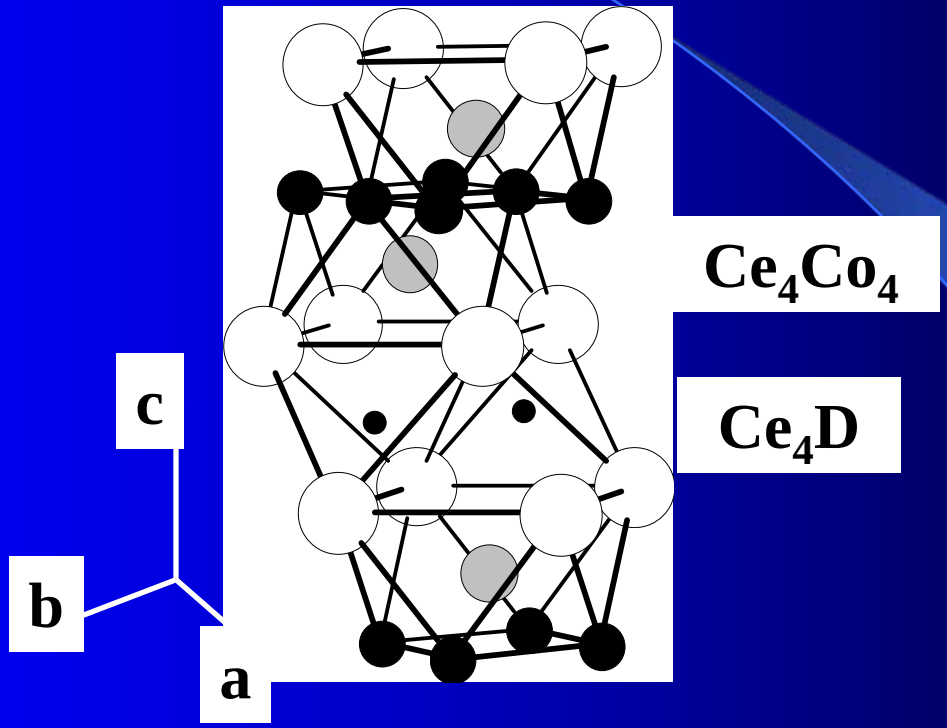
Along c-axis :
two layers of $[Ce_4Fe_4]$ antiprisms
separated by one layer of $[Ce_4]$ pseudo-tetrahedral units (interesting for H-insertion as in CeH_2.

$[Ce_4Fe_4]$

$[Ce_4]$



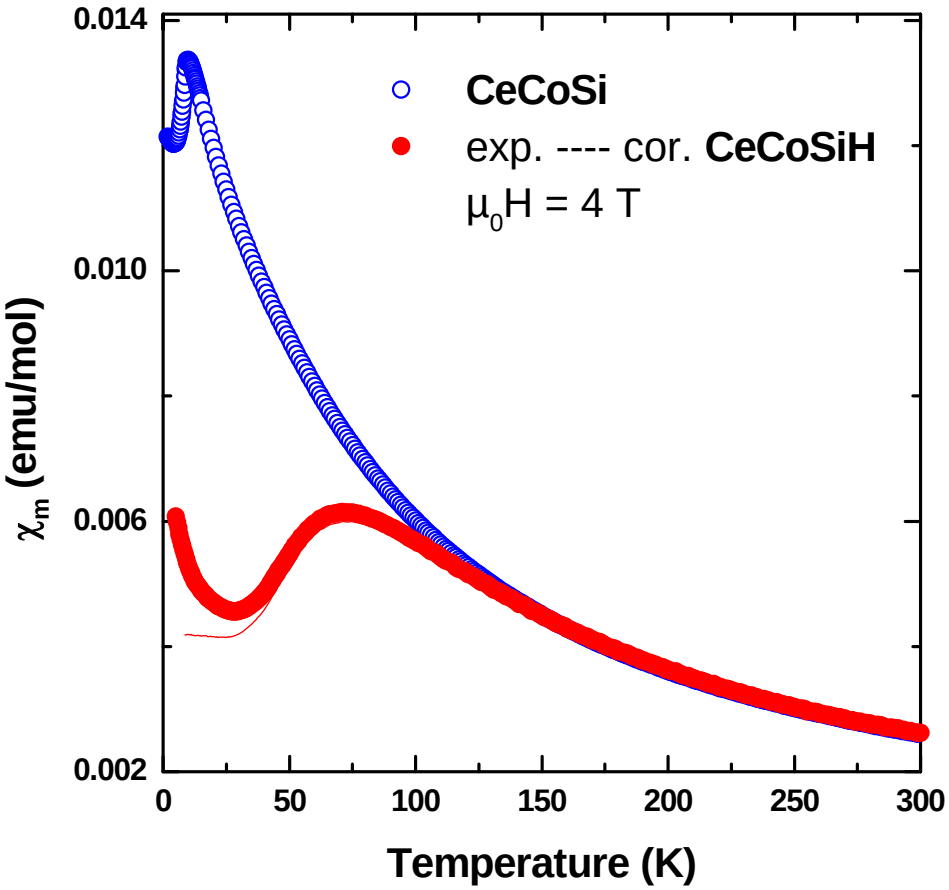
Structural properties of CeCoSiH and CeCoGeH



In CeCoSi, hydrogenation causes anisotropic expansion: a decreases (4.041 Å → 3.955 Å) whereas c increases (6.990 Å → 7.861Å) but unit cell volume increases (7.8 %).

B. Chevalier et al., Solid State Comm., 134 (2005) 529.

Hydrogenation of CeCoSi: transition from antiferromagnet to spin fluctuation behaviour



CeCoSi, sharp peak at T_N = 8.8 K

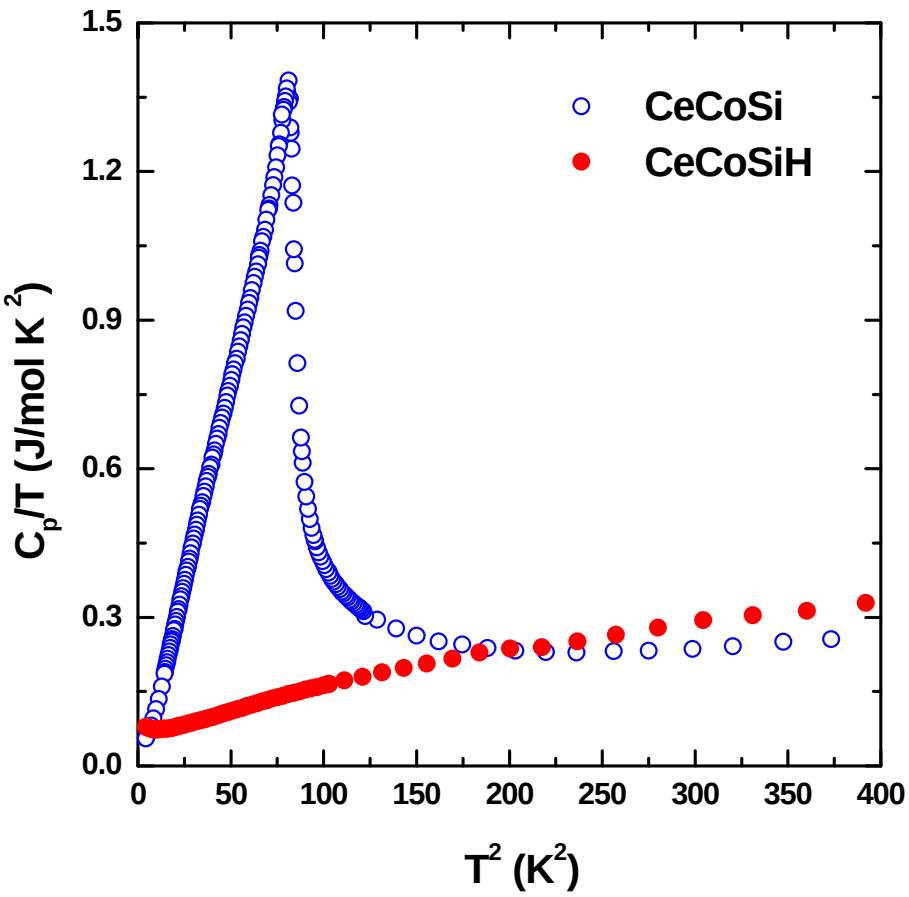
CeCoSiH broad peak around 70 K

⇓

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

B. Chevalier et al., Phys. Rev. B, 70 (2004) 174408.

Specific heat measurements on CeCoSi and CeCoSiH



No magnetic transition appears for CeCoSiH

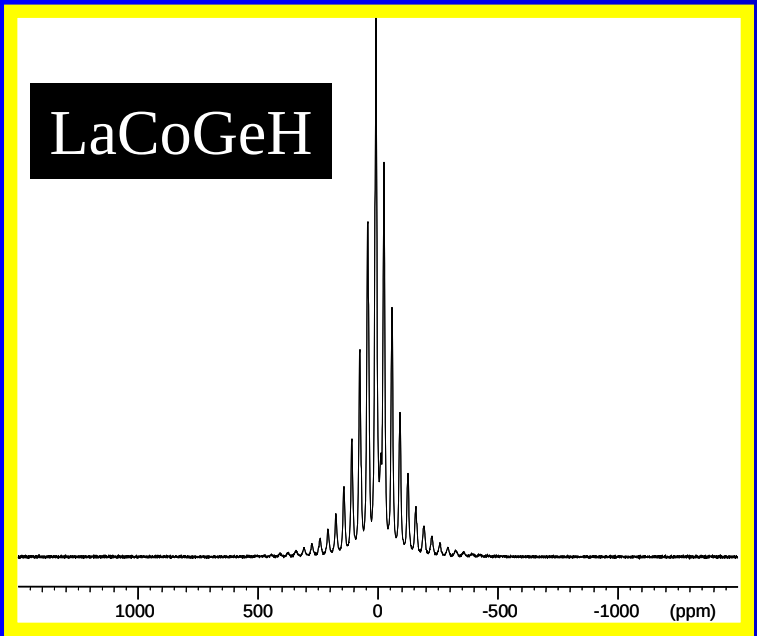
γ value decreases from 170 to 70 J/mol K^2

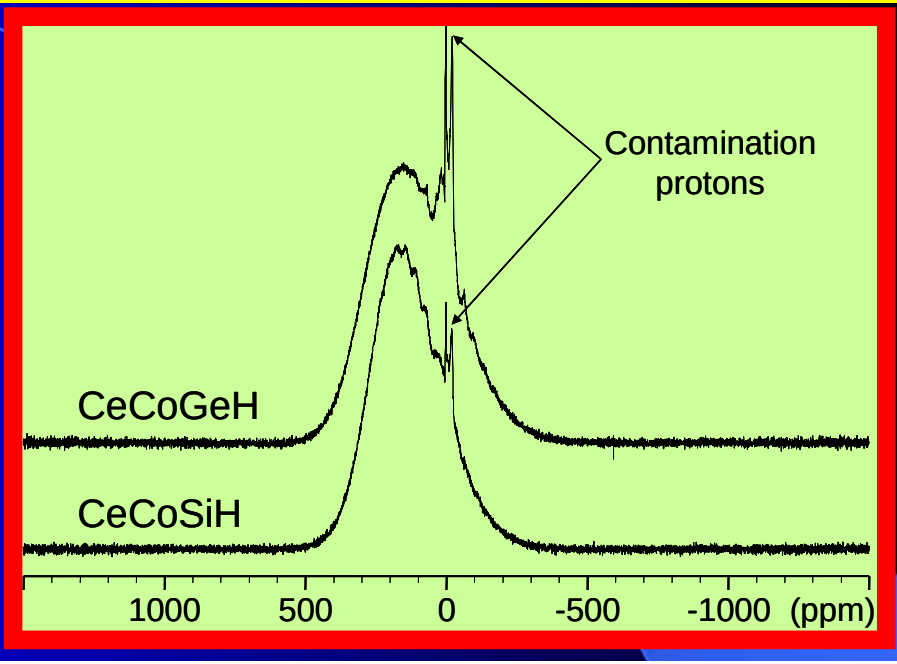
⇓

Increase of the Kondo effect after hydrogenation

B. Chevalier et al., Physica B, 378-380 (2006) 795

^{1}H NMR on LaCoGeH, CeCoSiH and CeCoGeH



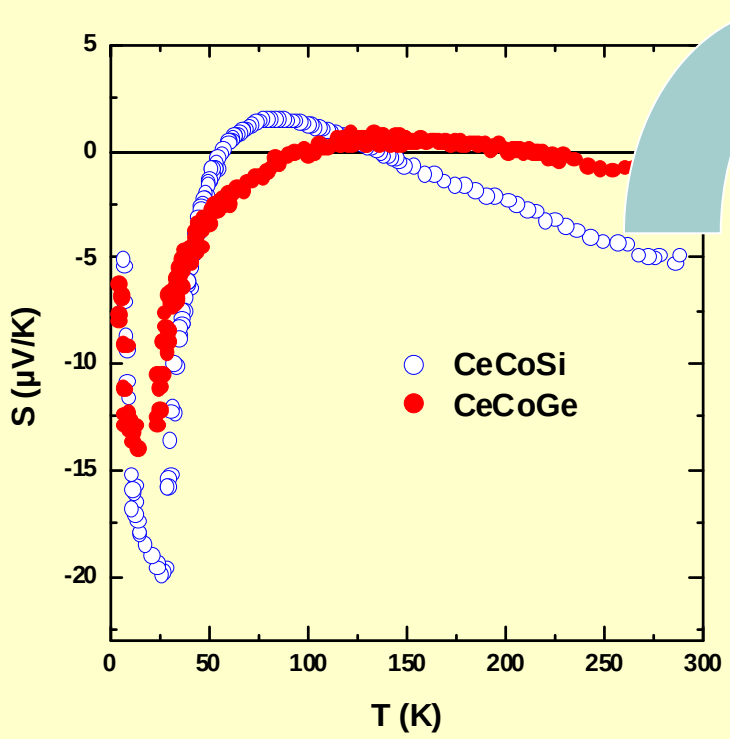


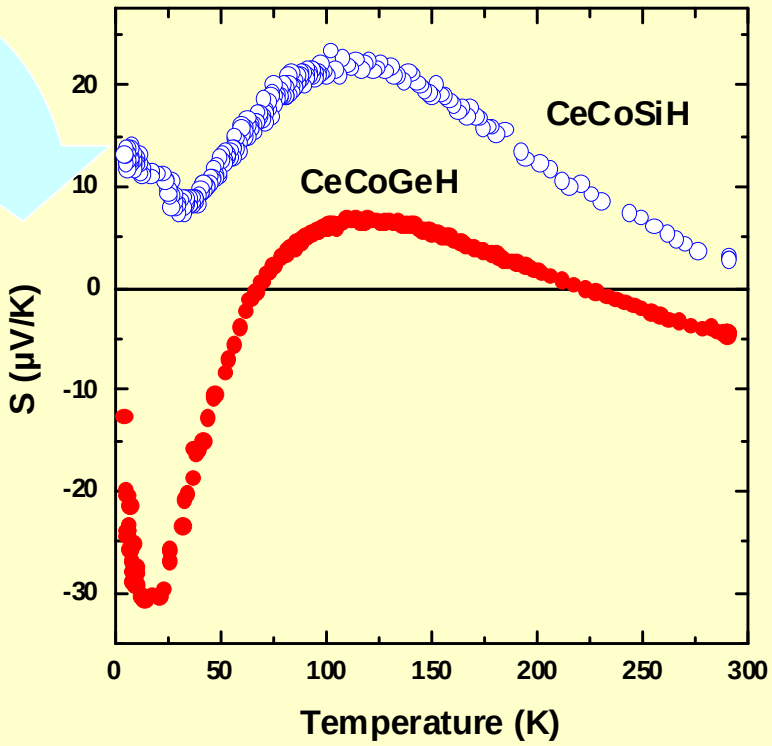
LaCoGeH : separation into spinning sidebands; no significant Knight Shift (8.7 ppm).

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, γ = 220 mJ/mol K^2)

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 θ_p

CeRuSi (θ_p = -81 K)

CeRuSiH (θ_p = -18 K)

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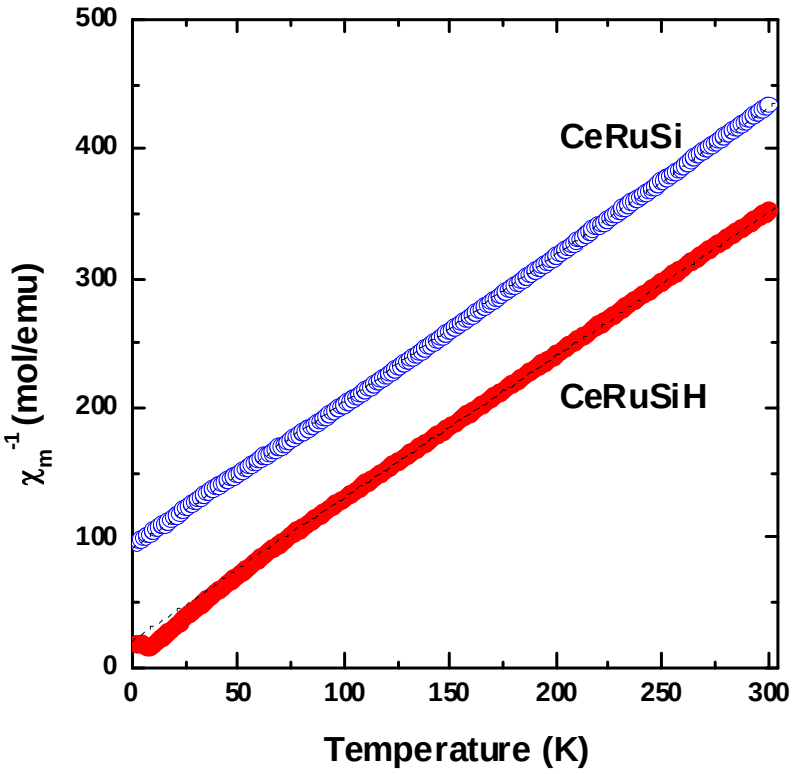
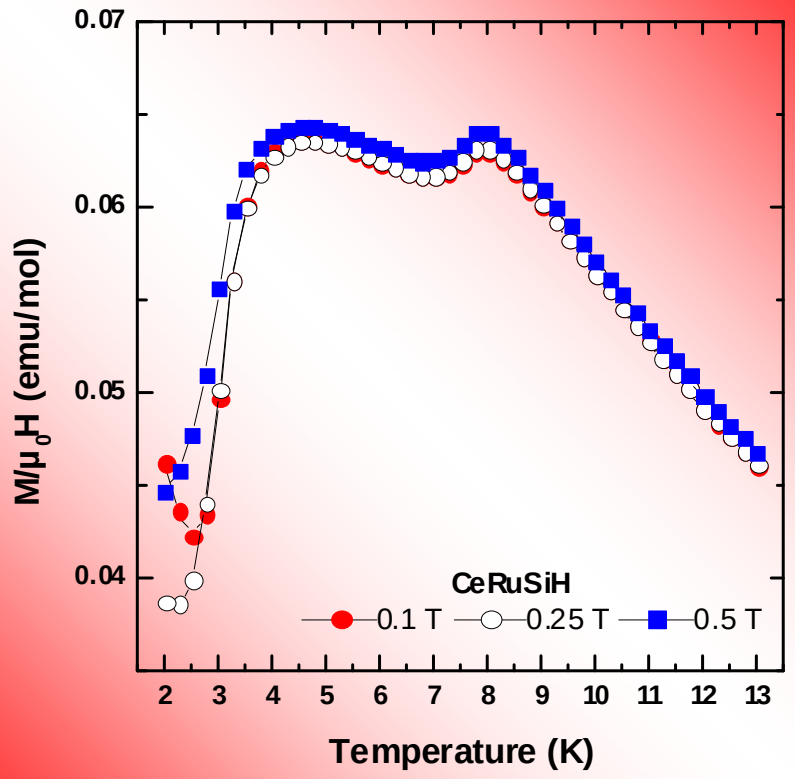
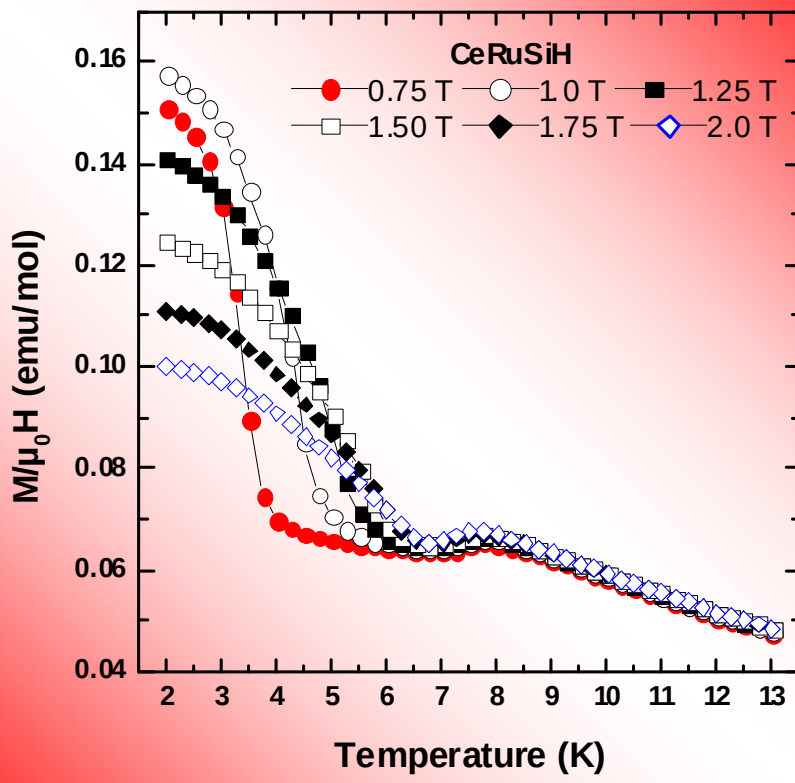
Decrease of the Kondo effect



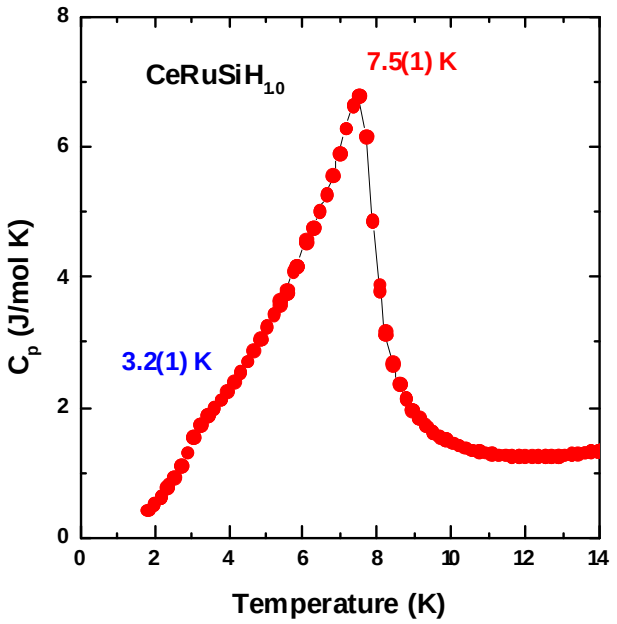
CeRuSi → CeRuSiH : transition from non magnetic to antiferromagnetic ordering (complex magnetic phase diagram)

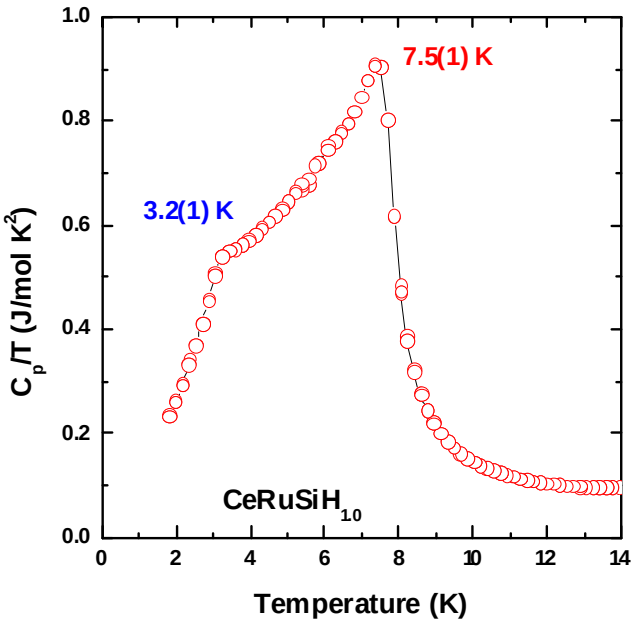




CeRuSiH shows two antiferromagnetic transitions at 7.5 K and 3.2 K. One (7.5 K) is independent to the magnetic field but the other (3.2 K) is strongly influenced.

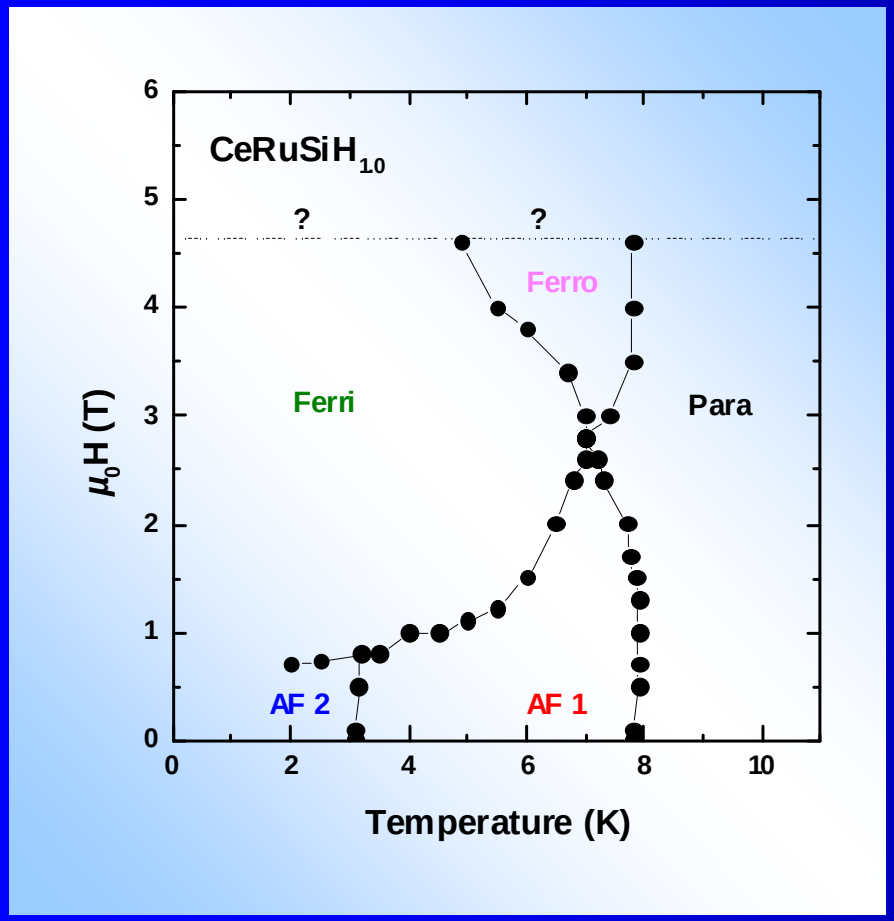
Specific heat measurements on $CeRuSiH_{1.0}$

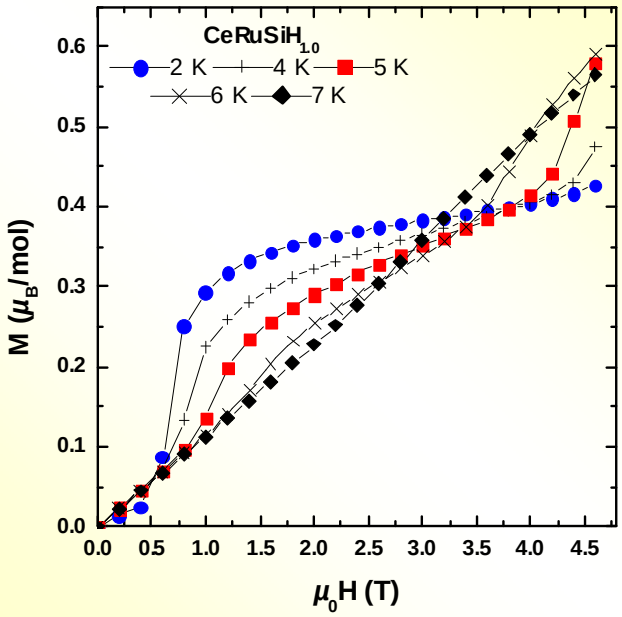




The two antiferromagnetic transitions are evidenced by this investigation.

$CeRuSiH_{1.0}$: complex magnetic phase diagram

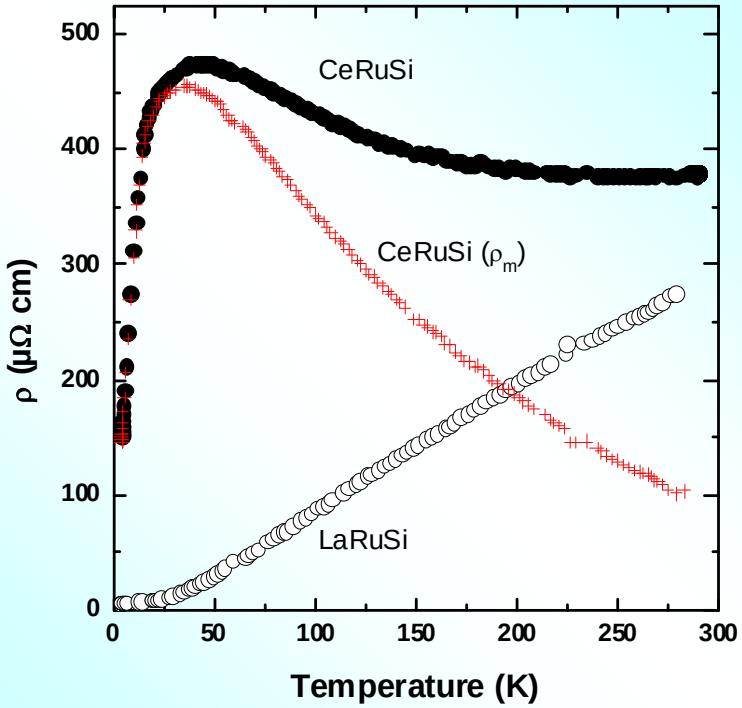


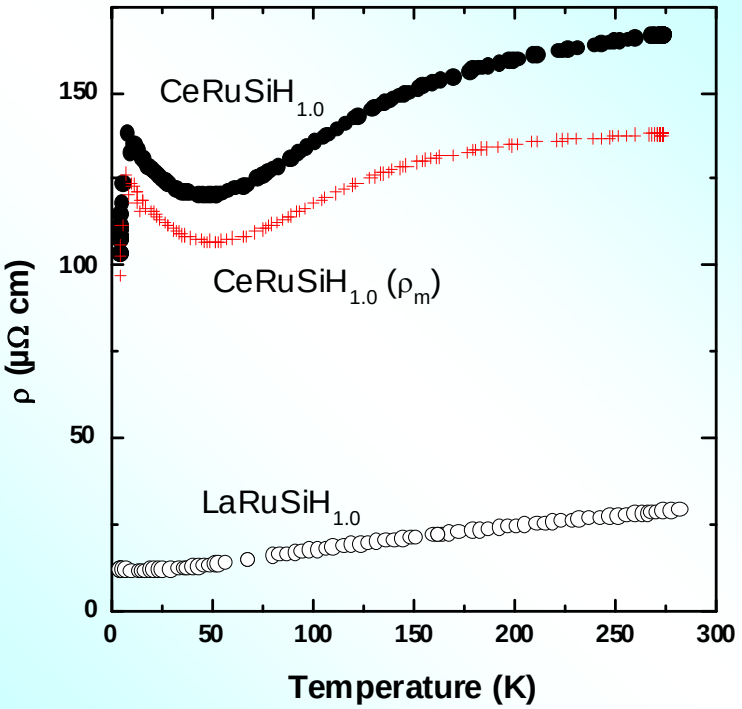


At 6 K, two transitions are induced by the field : AF1 - Ferri - Ferro.

At 2 K, only one is detected : AF2 - Ferri.

Electrical resistivity measurements on CeRuSi and $CeRuSiH_{1.0}$

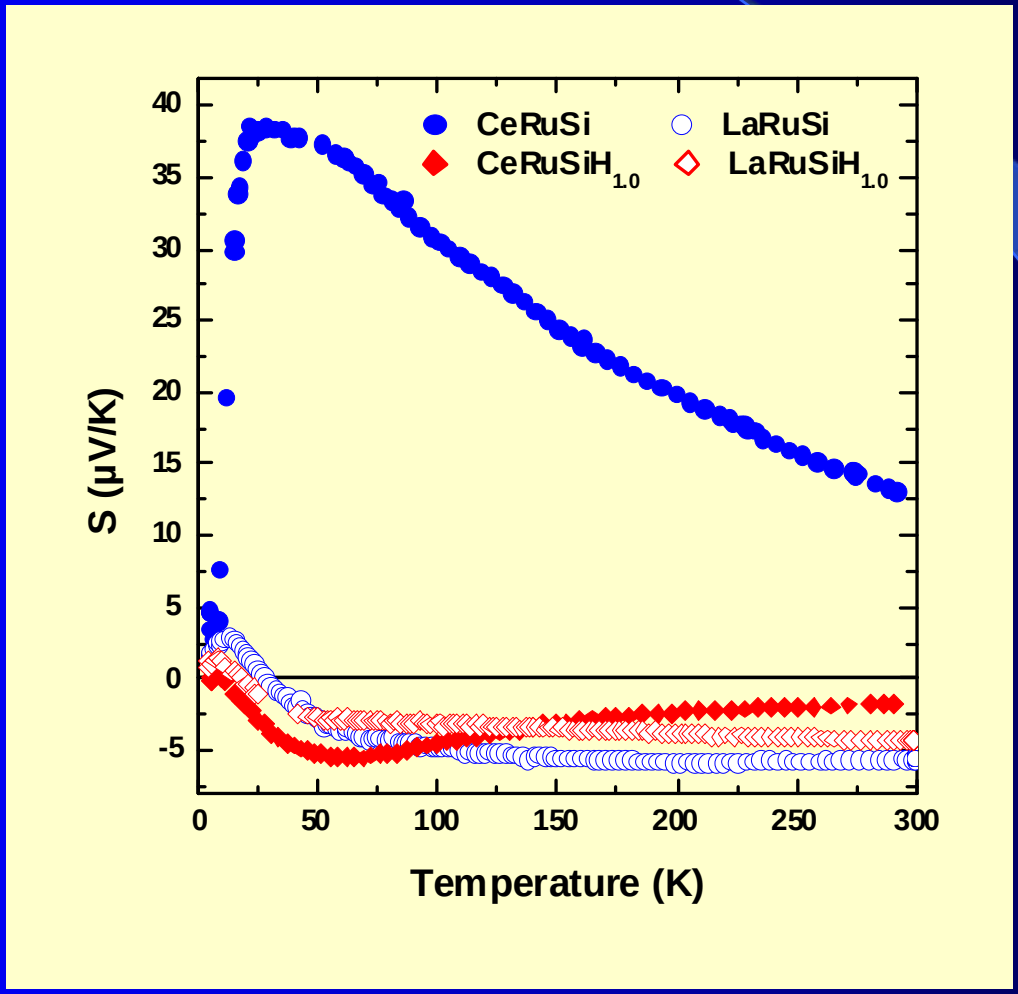




$-\rho_m = f(T)$ for CeRuSi shows a broad maximum near 36 K and follows above by a $\rho_m = -A \log T$ dependence (crystal field effect).

-Hydrogenation induces an increase of the metallic character (ρ_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

$CeCoSiH_{1.0}$
Int. valence
T_K = 130 K

$CeCoGeH_{1.0}$
Int. valence
T_K = 13.3 K

$CeRuSiH_{1.0}$
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 [Ce_4] pseudo-tetrahedral sites of CeCoSi, CeCoGe and CeRuSi.

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Competition between the increase of the unit cell volume and the occurrence of strong Ce – H bond (hybridization of 4f(Ce) states).

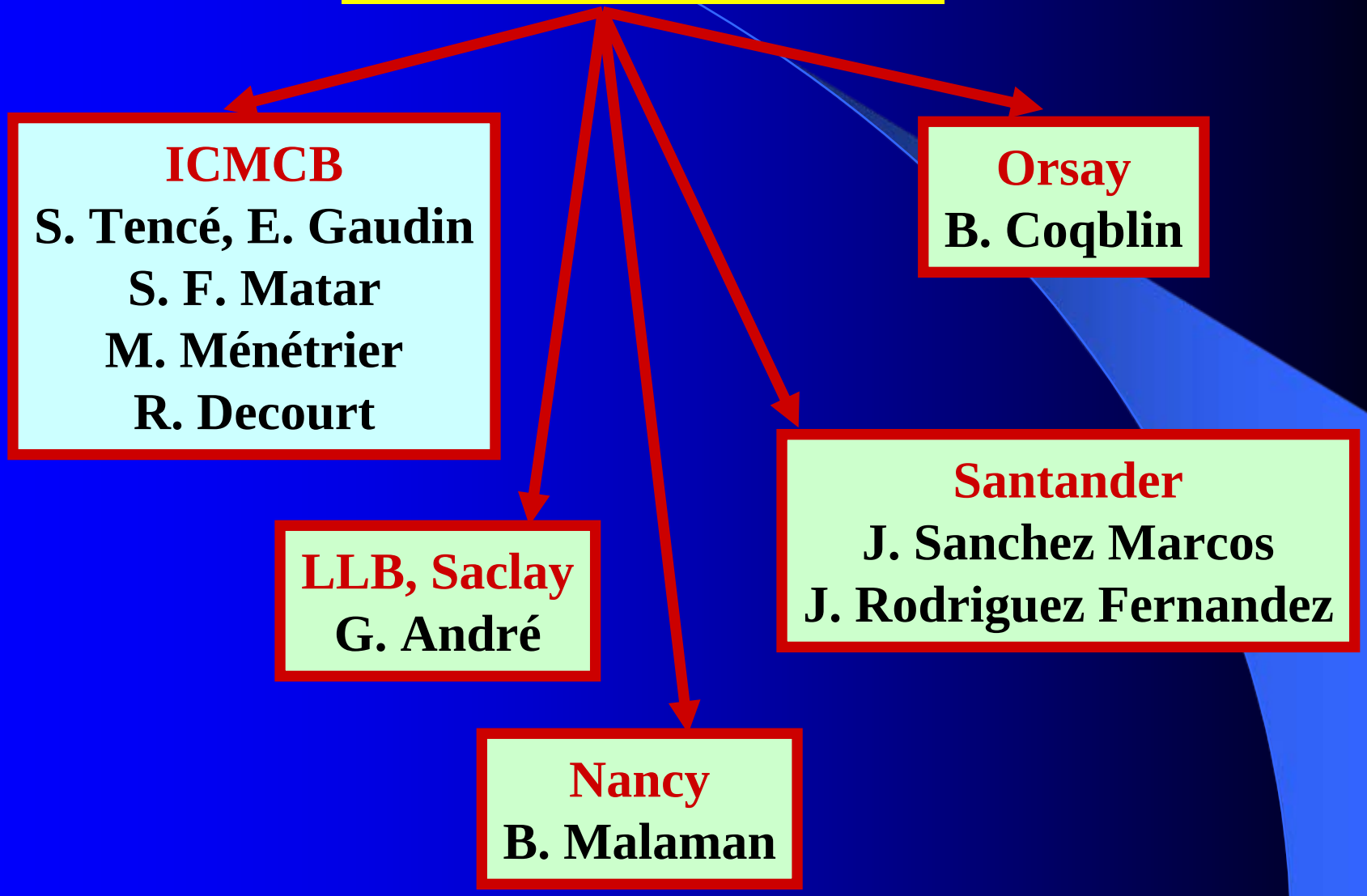
⇓

Various transitions:

antiferromagnetic (CeCoSi, CeCoGe) → spin fluctuations (CeCoSiH, CeCoGeH), chemical effect of H prevails over the unit cell expansion effect.

non magnetic (CeRuSi) → antiferromagnetic (CeRuSiH), opposite effect.

Acknowledgements



Thanks you for your attention