Mesure du pouvoir thermoélectrique des phases intermédiaires stables à 900°C dans les systèmes ternaires Ce-Fe-Si et U-Fe-Si.

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3. Departamento de Química, Instituto Tecnológico e Nuclear/CFMC-UL, P-2686-953 Sacavém, Portugal

Thermoelectrical power of the intermediate phases of the Ce-Fe-Si and U-Fe-Si ternary systems,

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Motivation : heavy fermion thermoelectricity

Ce- & U- based intermetallics

Competing interactions

- unstable valence : Ce $^{3+/4+}$, U $^{3+/4+}$
- long range RKKY : localized *f*- ē
- crystal field effect
- Kondo effects
- heavy fermion behavior …..

hybridisation *f*-states and *s*-, *p*-, *d*- states of the ligands

complicated *S*(T) [1,2]

- interatomic distances
- chemical substitutions
- pressure

[1] D. Jaccard, J. Sierro in: P. Wachter, H. Boppart (Eds) Valence Instabilities, North-Holland, 1982 p 409.
[2] A.K. Bhattachajee, B. Coqblin, Phys. Rev. B., 13 (1976) 3441

Remarkable feature of the Ce-Fe and U-Fe compounds

- ***R***Fe_2 : ***R*** = Y, Ce, Gd and U ⟹ C15, cubic Laves phases

	RFe_2	YFe_2 [3]	$GdFe_2$ [3]	$CeFe_2$ [4]	UFe_2 [5]
	Tc (K)	545	785	230	160
neutron diffraction and XMCD experiments	μ_m (μ_B/Fe)	1.5	1.8	1.2	0.6
	μ_m (μ_B/*R*)	-	7.5	0.2	0.1

Strong hybridization between 4*f* or 5*f* and 3*d* electrons [6]

[3] H. Kirchmayr, C.A. Poldy, in K.A. Gschneidner, L. Eyring (Eds), Handbook on the Physics and Chemistry of Rare Earth, chap.14, North-Holland, 1979.

[4] L. Paolasini, G.H. Lander, S.M. Shapio, R. Caciuffo, L. Lebech, L.P. Regnault, B. Roessli, J.M. fournier, Phys. Rev. B, 54 (1996) 7222

[5] M. Wulff, G.H. Lander, B. Lech, A. Delapalme, Phys. Rev. B, 39 (1989) 4719.

[6] M.M.S. Brooks, O. Erikson, B. Johanson, J.JM. Franse, P.H. Frings, J. Phys. F., 18 (1988) L33.

transport properties of $CeFe_2$

- ρ (T) and *S* (T) : idiosyncratic features [7]

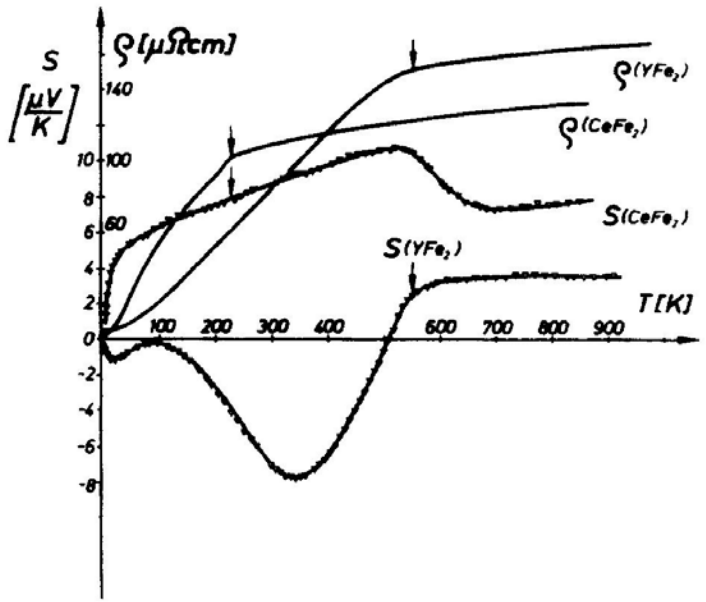


Fig. 2. Temperature dependence of the electrical resistivity and the thermopower of $CeFe_2$ and YFe_2 in the temperature range from 4 K up to 1000 K.

+ subsequent experiments
- pressure
- H(T)
- alloying….

↓

electronic instability

↓

hybridization between Ce - 4*f* and Fe - 3*d* electrons

Project : Systematic investigations of the crystal-chemistry and electronic properties of the intermediate phases of the Ce - & U – Fe – Si ternary systems

[7] E. Gratz, E. Bauer, H. Nowotny, A.T. Burkov, M.V. Vedernikov, Solid State Comm., 69 (1989) 1007.

Outline :

Part 1: The Ce-Fe-Si ternary system

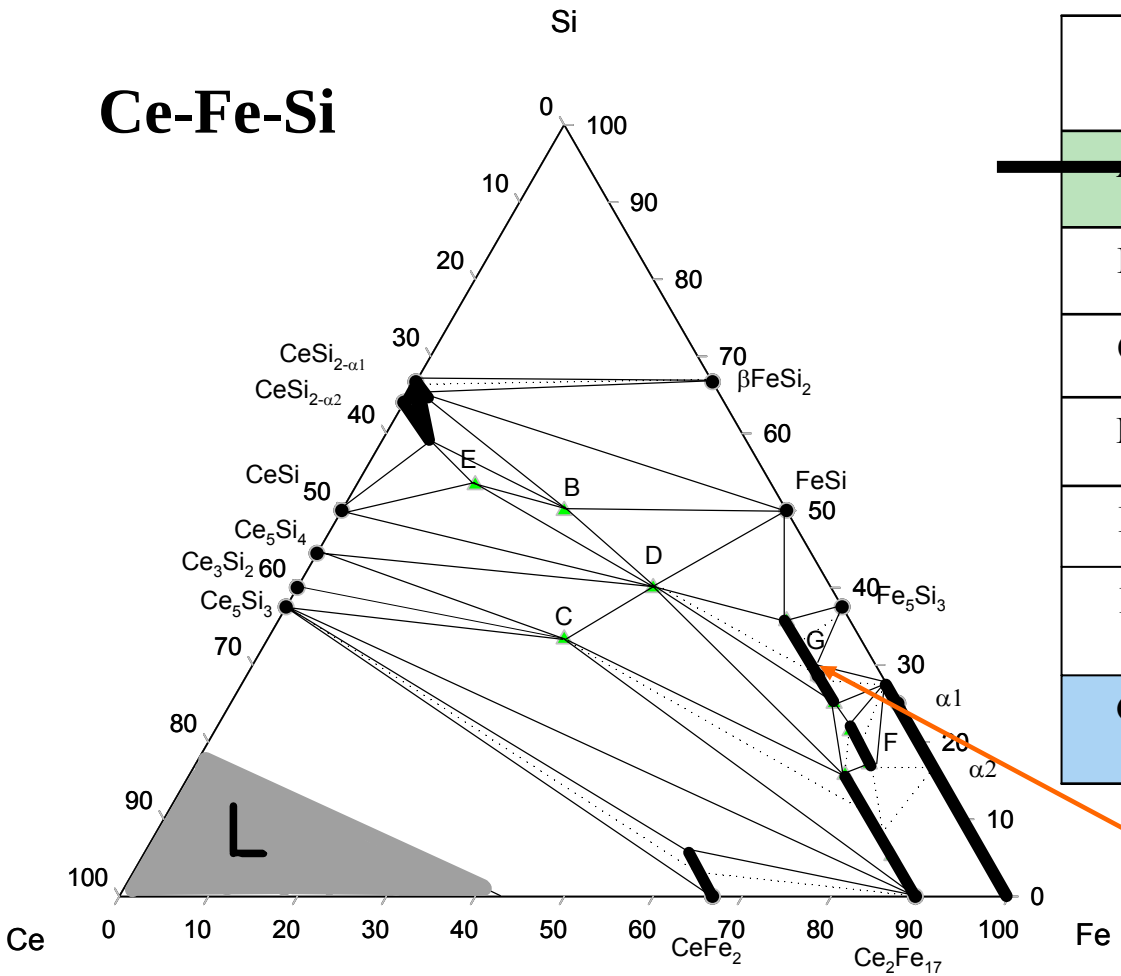
1. the isothermal section at 900°C
2. the new compound
3. the magnetic properties of the ternary compounds
4. the electrical resistivity behavior
5. the thermoelectrical power

Part 2 : the U-Fe-Si ternay system

1. the isothermal section
2. the new compounds and their electronic properties
3. transport properties of the ternary compounds

Part 3: conclusion

Isothermal section at 900°C



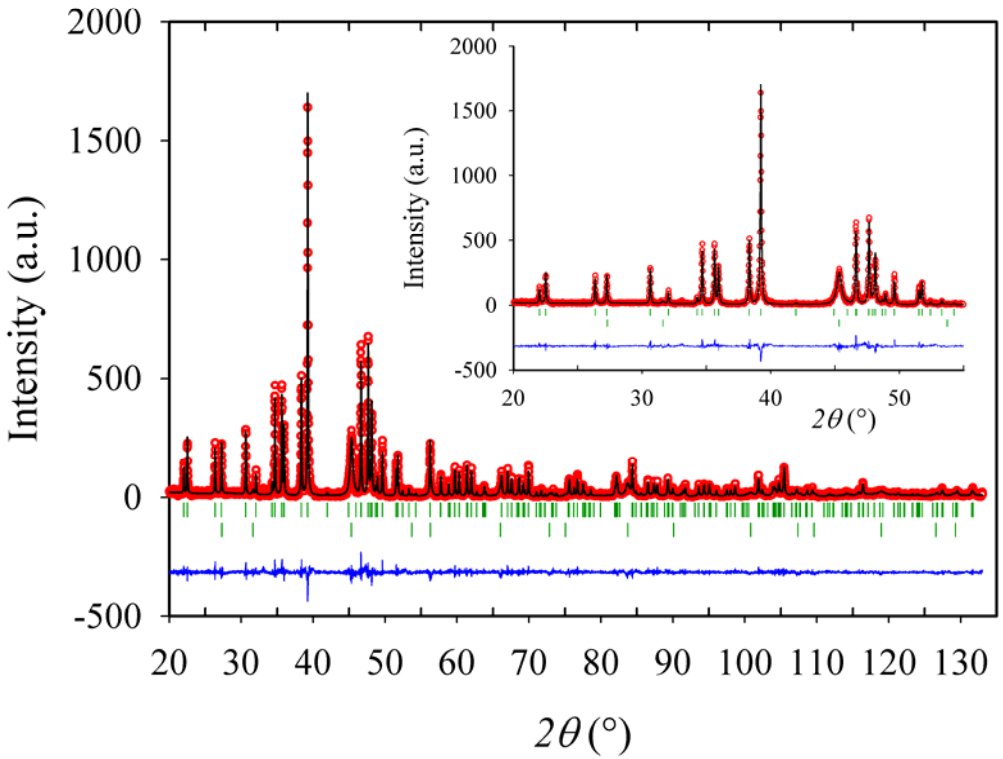
	phase	Pearson code	Structure type
~~A~~	~~Ce_2FeSi_3~~	~~*hP3*~~	~~AlB_2~~
B	$CeFeSi_2$	*oC16*	$CeNiSi_2$
C	CeFeSi	*tP6*	Cu_2Sb
D	$CeFe_2Si_2$	*tI10*	$CeAl_2Ga_2$
E	$Ce_5Fe_2Si_8$	*hP3*	AlB_2
F	$CeFe_{13-x}Si_x$ $2.4<x<2.6$	*cF112*	$NaZn_{13}$
G	$CeFe_{13-y}Si_y$ $3.5<y<5$	*tI56*	$Ce_2Ni_{17}Si_9$

$CeFe_{13-y}Si_y$ $3.5<y<5$

G: peritectoïd reaction
Tt < 1200°C

D. Berthebaud et al., J Alloys Compd., in press.

Rietveld Refinement of $CeFe_9Si_4$

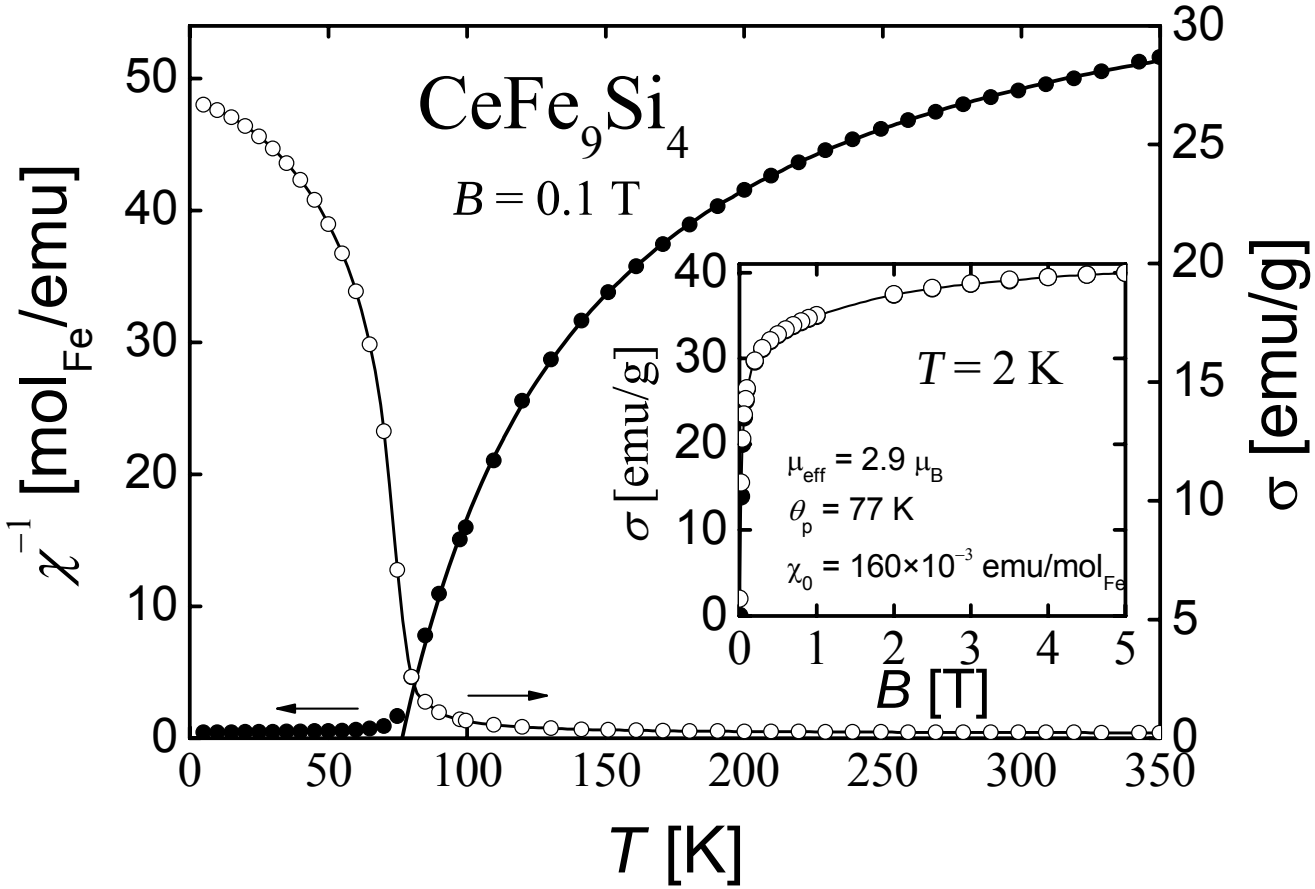


Formula		**$CeFe_9Si_4$ ($Ce_2Ni_{17}Si_9$-type)**
Space group		***I4/mcm (No. 140)***
Lattice parameters (Å)	**a :** **c :**	**7.892(1)** **11.666(1)**
***R-factors* (%)**	**R_B :** ***Rp*** ***Rexp*** ***Rwp*** **χ^2**	**5.83** **15.6** **22.9** **19.0** **1.46**

D8 Bruker diffractometer

Sol-X detector, monochromatized CuKα1 radiation

Magnetic properties of the ternary phases

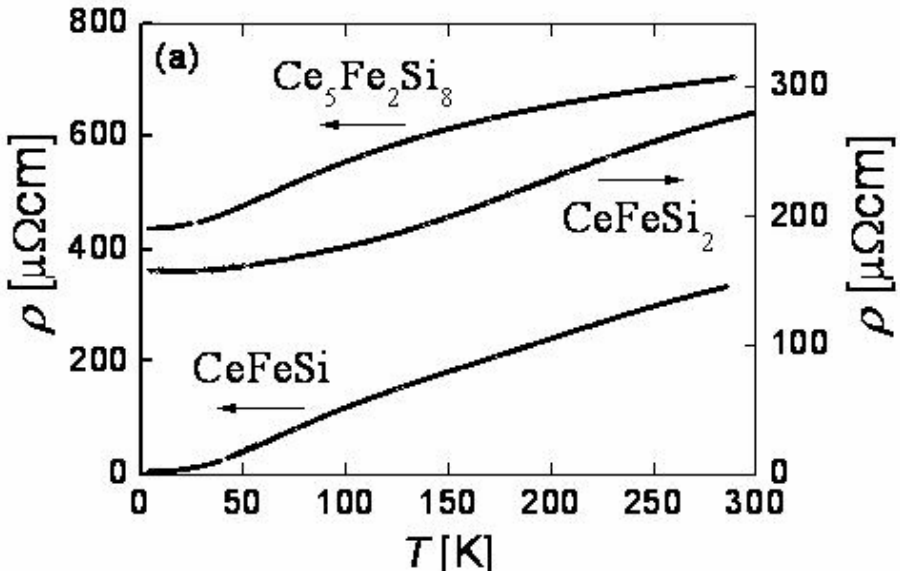


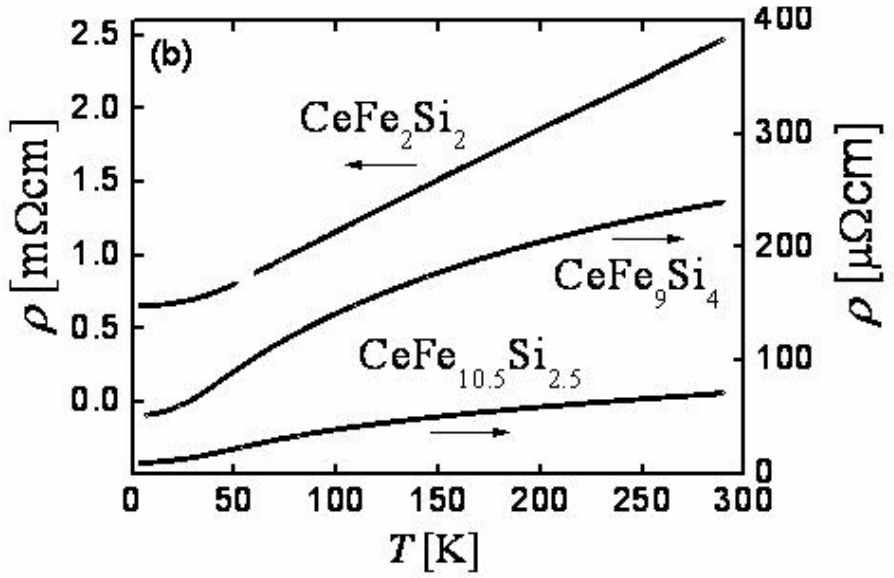
Ferromagnet : $CeFe_{13-x}Si_x$, x = 2,4 (Tc = 202 K) [8]

Pauli paramagnet : $CeFeSi$, $CeFeSi_2$, $CeFe_2Si_2$, $Ce_5Fe_2Si_8$

[8] Y. Zhao, J. Liang, W. Tang, Y. Guo, G. Rao, J. Appl. Phys., 78 (1995) 2866.

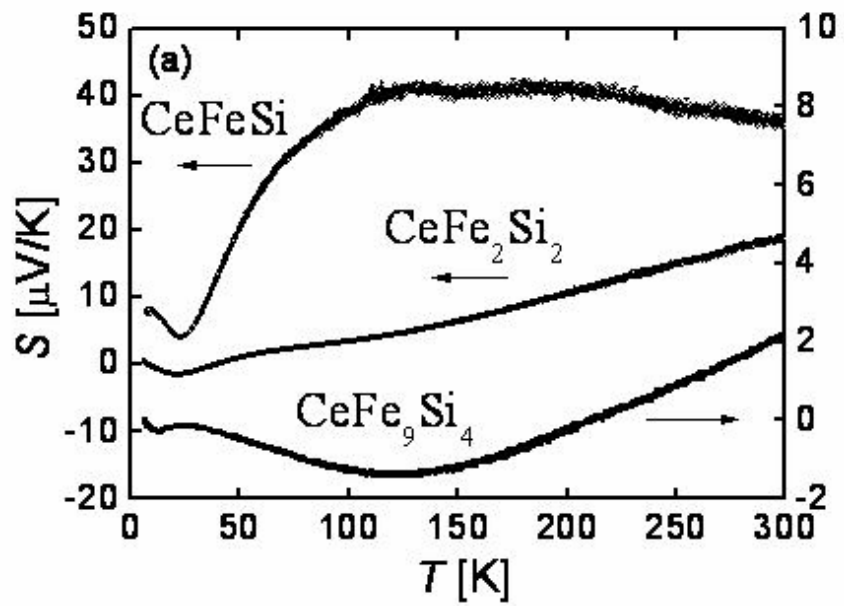
$\rho(T)$ of Ce-Fe-Si ternary compounds

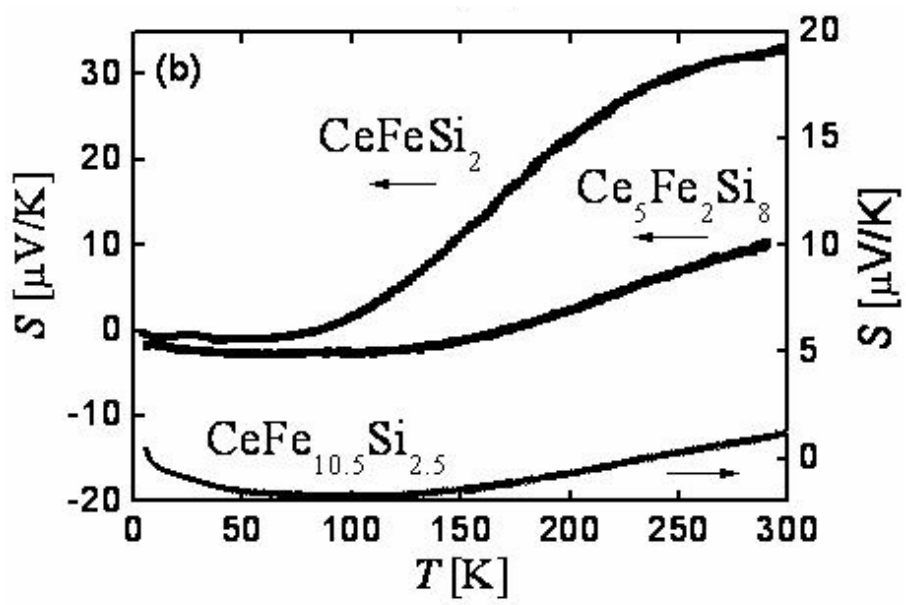




Metallic or semi-metallic behaviors

S(T) of Ce-Fe-Si ternary compounds

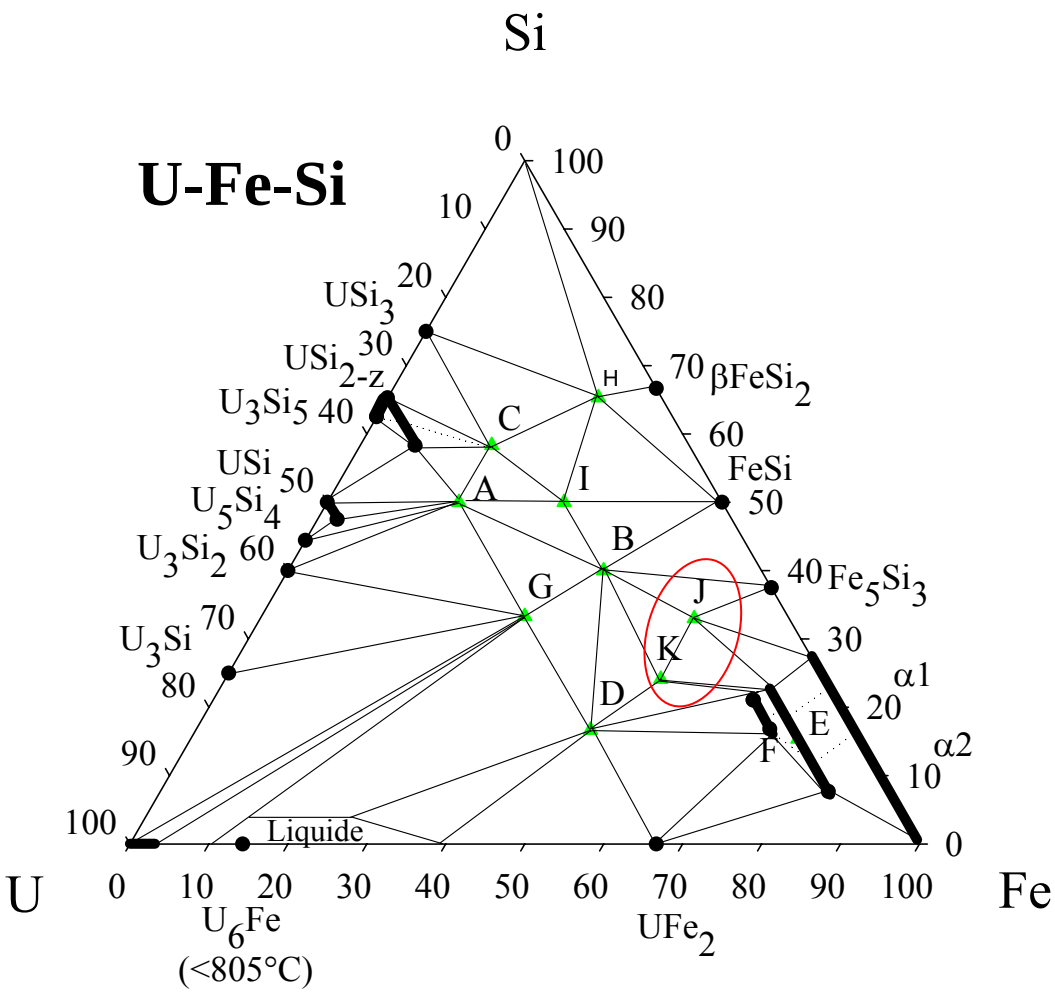




modest values of the thermoelectrical power

CeFeSi (S =40μV/K à 150K) et $CeFeSi_2$ (S = 30μV/K à 300K)

Isothermal section at 900°C

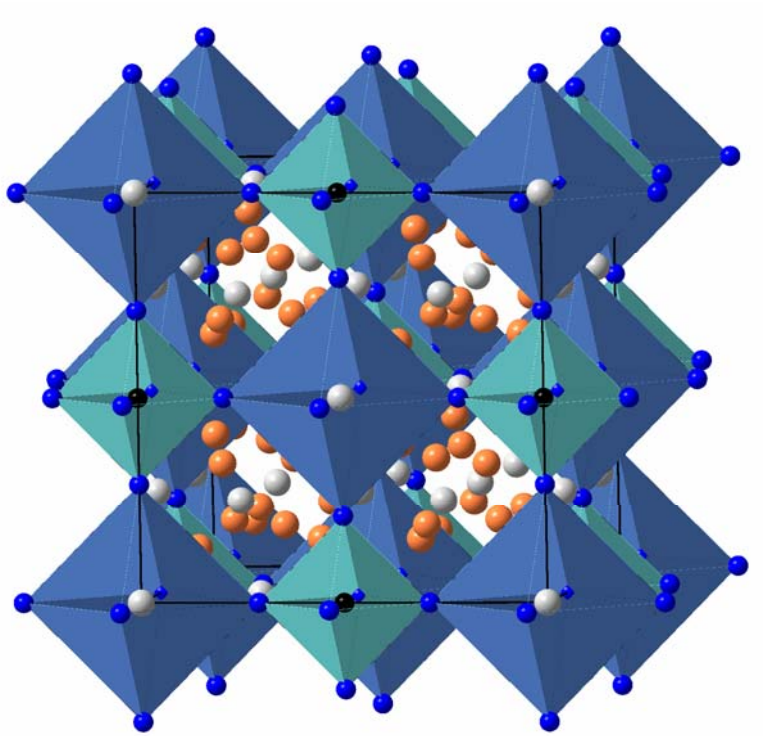


	Phase	Pearson code	Type structural
A	U_2FeSi_3	hP3	AlB_2
B	UFe_2Si_2	tI10	Al_4Ba
C	$U_3Fe_2Si_7$	oC24	$U_3Fe_2Si_7$
D	U_2Fe_3Si	hP12	$MgZn_2$
E	$UFe_{12-x}Si_x$ $1<x<3$	tI26	$ThMn_{12}$
F	$U_2Fe_{17-x}Si_x$ X=3.2 à 4	hP38	Th_2Ni_{17}
G	UFeSi	oP12	TiNiSi
H	$U_{1.2}Fe_4Si_{9.7}$	hP30	$Er_{1.2}Fe_4Si_{9.7}$
I	$U_2Fe_3Si_5$	mS40	$Lu_2Co_3Si_5$
J	UFe_5Si_3	tP9	UFe_5Si_3
K	$U_6Fe_{16}Si_7$	cF116	$Mg_6Cu_{16}Si_7$

$U_6Fe_{16}Si_7$ & $U_6Fe_{16}Si_7C$

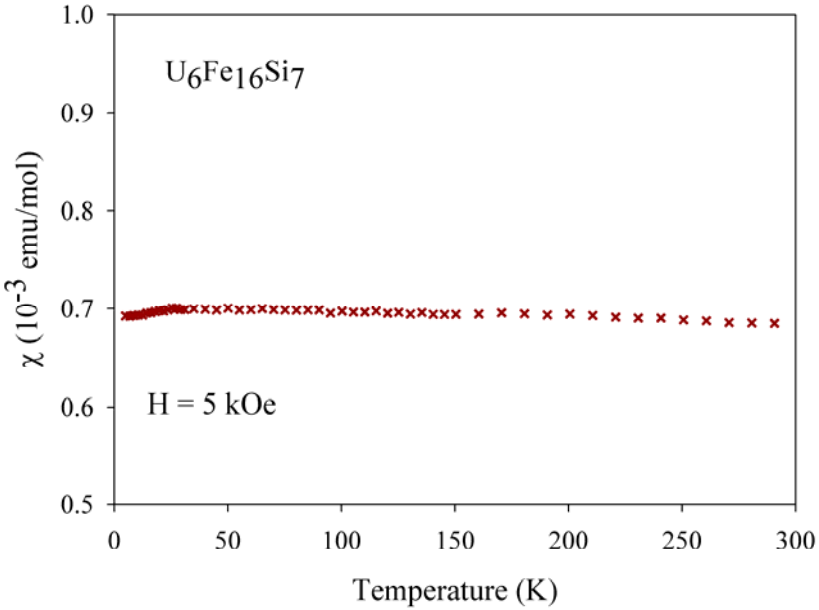
$U_6Fe_{16}Si_7$
Cubic, $Fm\bar{3}m$, a = 11.7206(5)Å
$Th_6Mn_{23} \Rightarrow Mg_6Cu_{16}Si_7$

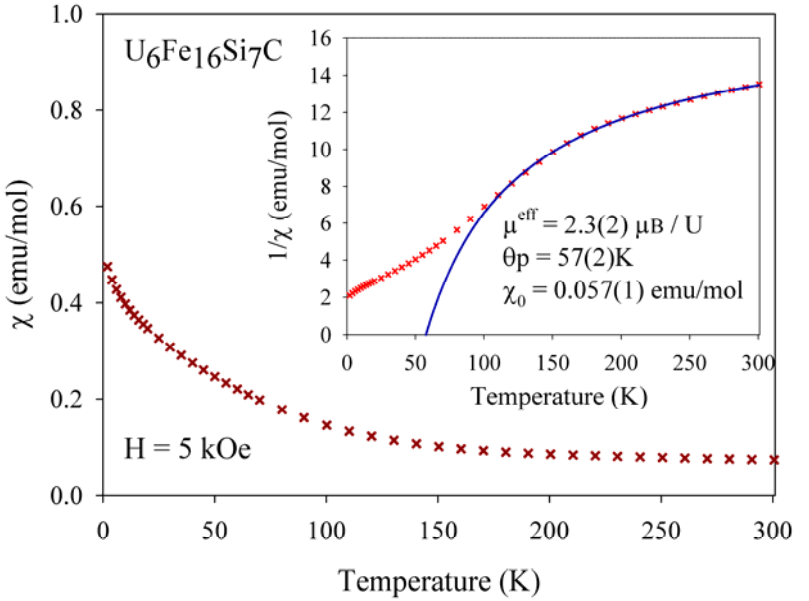
$U_6Fe_{16}Si_7C$
Cubic, $Fm\bar{3}m$, a = 11.7814(2)Å
Ir_4Sc_{11} ($Ir_7IrSc_{16}Sc_6$) $\Rightarrow Zr_6Zn_{23}Si$



Perspective view of the crystal structure of $U_6Fe_{16}Si_7C$

Magnetic properties of $U_6Fe_{16}Si_7$ & $U_6Fe_{16}Si_7C$

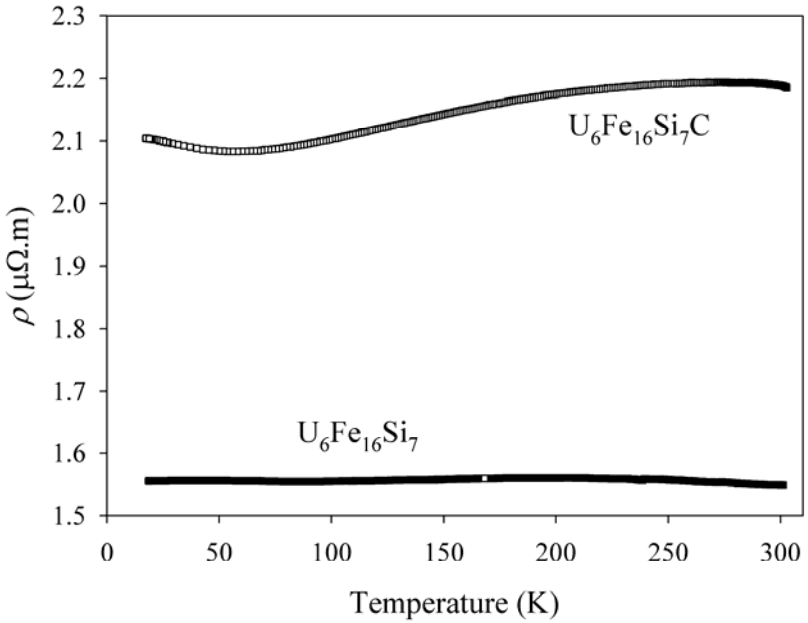


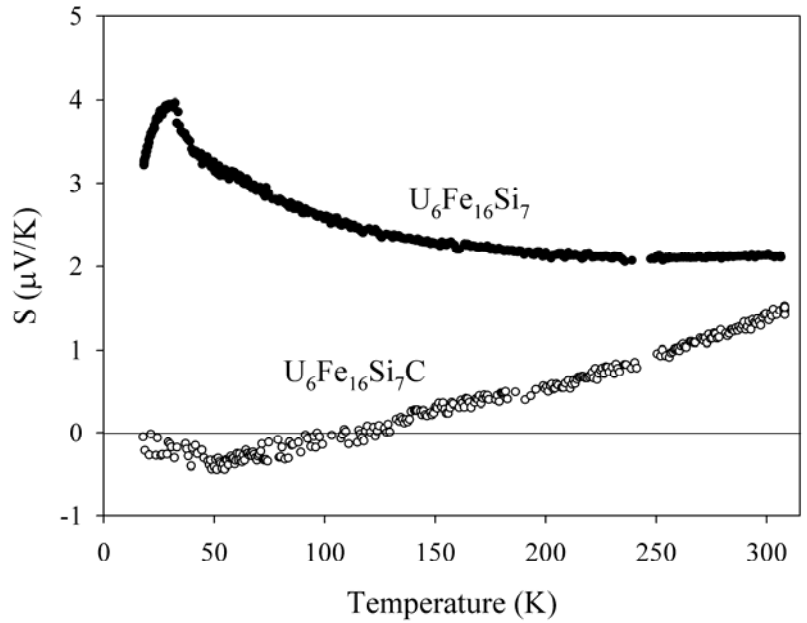


$U_6Fe_{16}Si_7$:
- Pauli paramagnet
- delocalized system

$U_6Fe_{16}Si_7C$:
- reduced magnetic moment on U atoms
- partially localized system

Transport properties of $U_6Fe_{16}Si_7$ & $U_6Fe_{16}Si_7C$



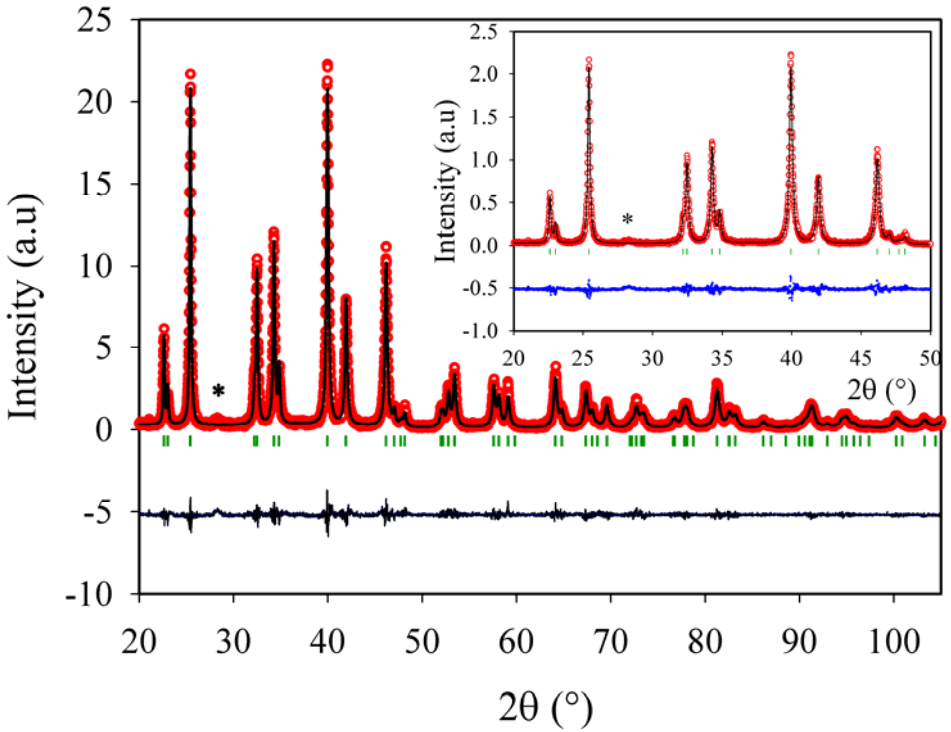


$\Rightarrow$ metallic behavior

$\Rightarrow$ few μV/K

UFe_5Si_3

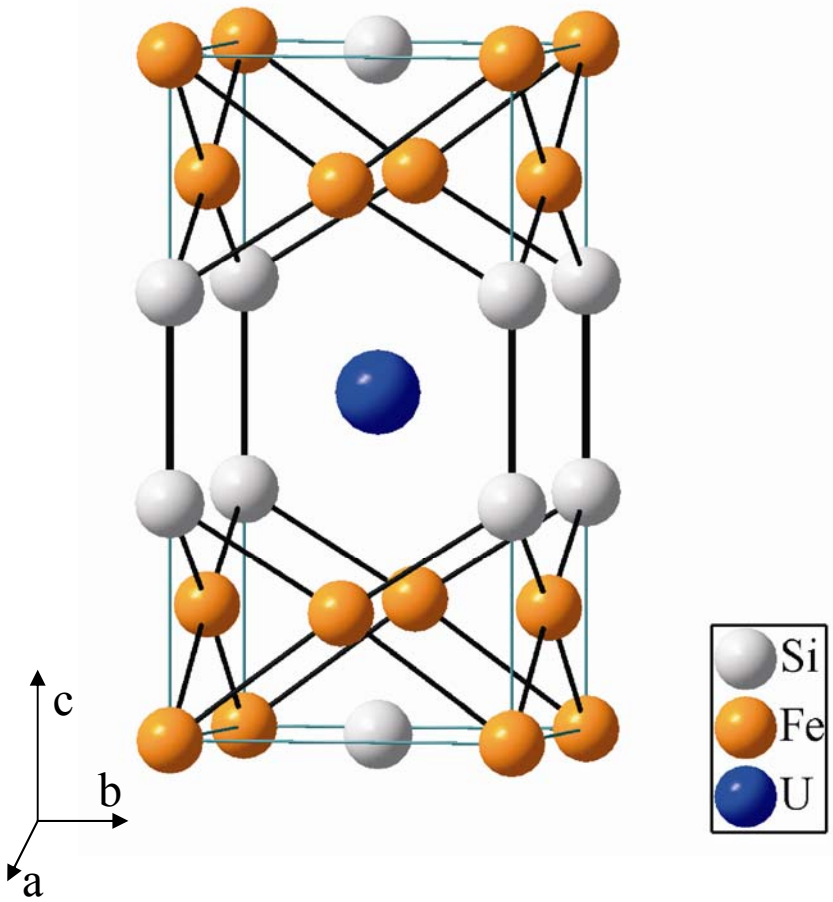
- Peritectoïd formation : $UFe_2Si_2 + Fe_3Si \rightarrow UFe_5Si_3$
- Synthesis : rapid solidification of the melt (splat cooling)
  annealing at 900°C for 10 days



Formula		UFe_5Si_3
Space group		*P4/mmm (No. 123)*
Parameters (Å)	a : c :	3.9296(5) 7.7235(1)
R-factors (%)	R_B : *R*p *R*exp *R*wp χ^2	2.93 8.93 12.5 10.9 1.32

D8 Bruker diffractometer
Sol-X detector, monochromatized CuKα1 radiation

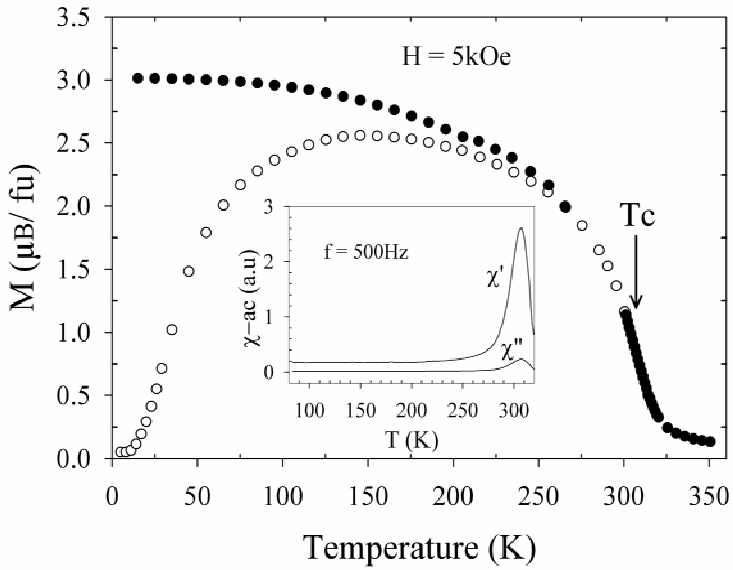
Crystal Structure & Magnetic behavior of UFe_5Si_3

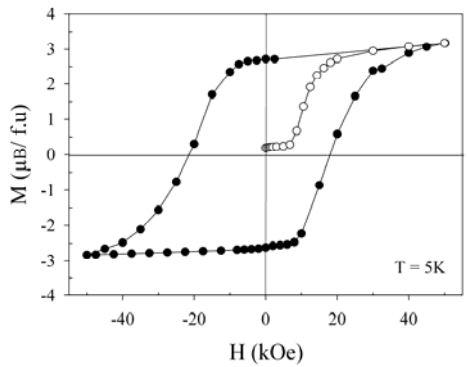


d(Fe-Fe) = 2.44 Å

d(Fe-Fe)*iron* = 2.48 Å

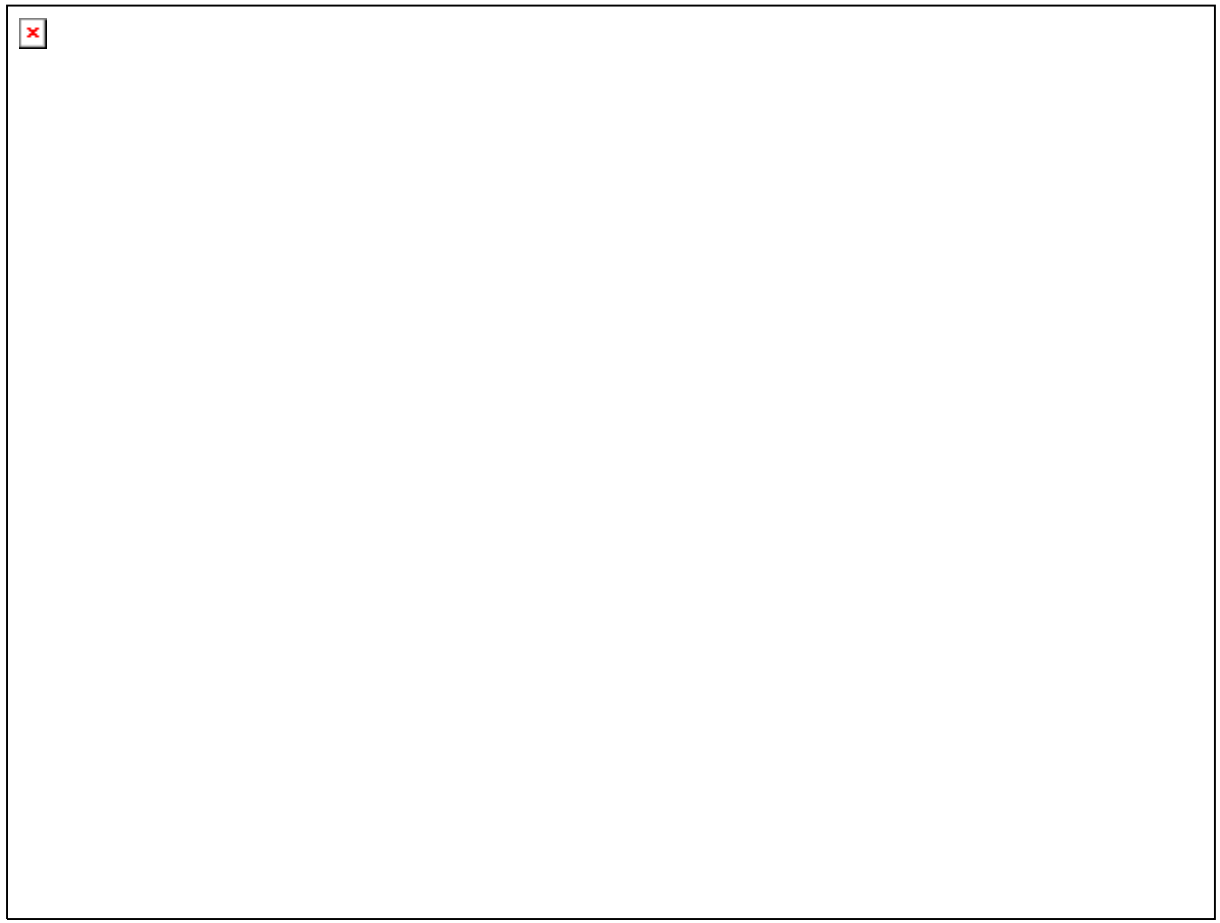
Ferromagnet : Tc = 310(2) K





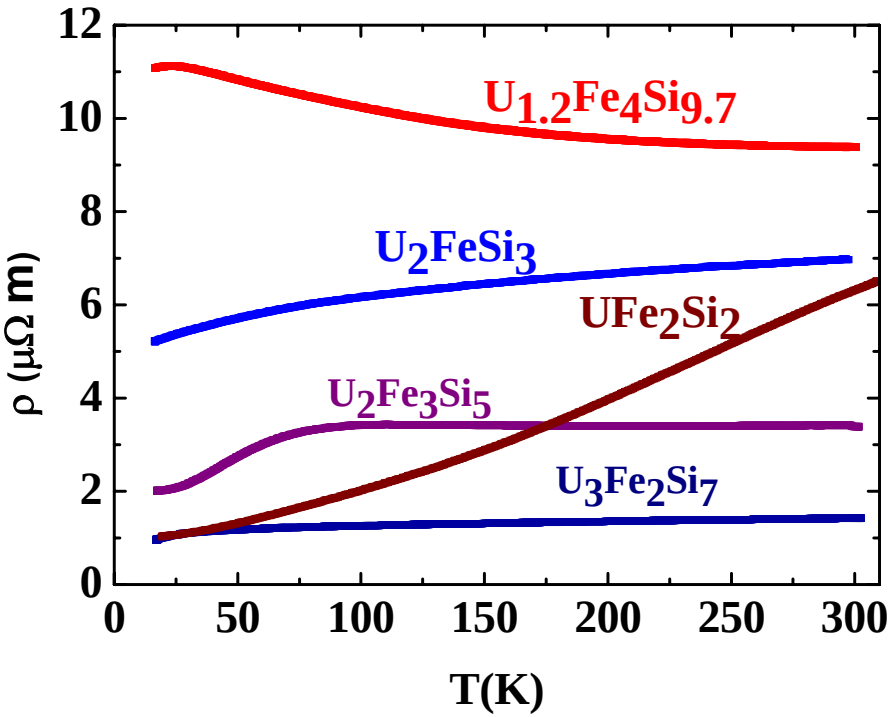
σs = 3μB/ f.u.

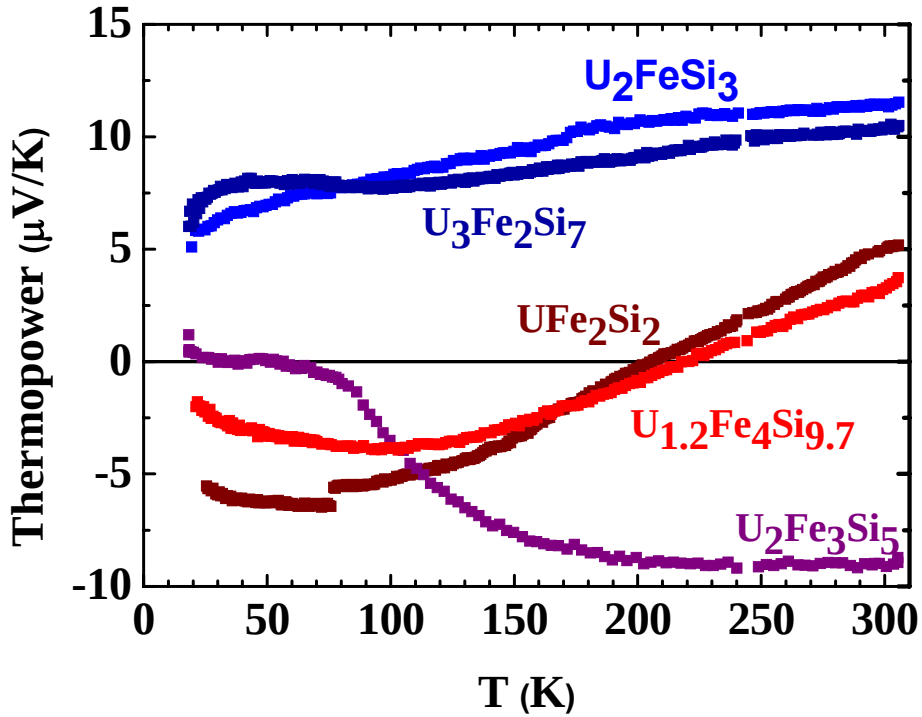
Transport properties of UFe_5Si_3



- $\rho(T) = \rho 0 + AT^2$, $T < 120K$
- S(T) : anomaly at T = 70K $\Rightarrow$ Kondo scattering ?

Transport properties of U-Fe-Si ternary compounds



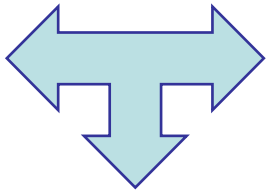


- metallic or semi-metallic behaviors
- modest values of the thermoelectrical power

Conclusion : U & Ce – Fe – Si compounds

Initerant :

(Ce &U)FeSi,
(Ce&U)Fe_2Si_2
$CeFeSi_2$,
$CeFe_9Si_4$
$Ce_5Fe_2Si_8$,
U_2FeSi_3,
$U_6Fe_{16}Si_7$
$U_2Fe_5Si_3$,
$U_2Fe_3Si_7$,
$UFe_{10}Si_2$



partially localized :

$U_6Fe_{16}Si_7C$
$U_{1.2}Fe_4Si_{9.7}$

U and Ce, *f* electrons hybridize with *s*-, *p*- or *d*- electrons of Si or Fe

metallic or semi-metallic behaviors,
modest values of thermoelectrical power,
(CeFeSi, 40µV/K about 150 K)

- no simple relation between ρ(T) and S(T)
- hybridization of *f* and *s*-, *p*- or *d*- electrons and S(T)

Future : Ge-compounds

⇒ to move the system toward localization of the *f* electrons

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