

STRUCTURAL AND ELECTRICAL PROPERTIES OF NEW SILICIDES :  
 $\text{ThCo}_x\text{Si}_{2-x}$  ( $0 \leq x \leq 1$ ) AND  $\text{ThTSi}$  ( $T = \text{Ni}, \text{Pt}$ )

Wang Xian Zhong\*, Wee Lam Ng\*\*, B. Chevalier\*, J. Etourneau\*  
and P. Hagenmuller\*

\* Laboratoire de Chimie du Solide du C.N.R.S.  
Université de Bordeaux I  
351 cours de la Libération, 33405 Talence cedex, France.

\*\* Department of Chemistry, University of Malaya, Pontai Valley  
Kuala Lumpur, Malaysia

(Received July 12, 1985; Communicated by P. Hagenmuller)

ABSTRACT

New silicides have been prepared in ternary systems : thorium-transition element ( $T = \text{Co}, \text{Ni}, \text{Pt}$ )-silicon. With cobalt compounds  $\text{ThCo}_x\text{Si}_{2-x}$  ( $0 \leq x \leq 1$ ) a structural change occurs with the sequence  $\alpha\text{-ThSi}_2$  (tetr.)  $\rightarrow \beta\text{-ThSi}_2$  (hex)  $\rightarrow \alpha\text{-ThSi}_2$  (tetr.) as  $x$  increases. It has been clearly shown that  $\text{ThPtSi}$  is isostructural with  $\text{LaPtSi}$  (i.e. of ordered  $\alpha\text{-ThSi}_2$  type). However structure refinement from X-ray powder measurements is not conclusive to decide whether Si and T atoms are ordered or disordered in  $\text{ThTSi}$  ( $T = \text{Co}, \text{Rh}, \text{Ir}, \text{Ni}$ ) compounds of  $\alpha\text{-ThSi}_2$  type.  $\text{ThNiSi}$ ,  $\text{ThPtSi}$  and the cobalt poor and rich compounds have clearly been found to be superconducting above 2K.

The dependence of the superconducting transition temperature  $T_{\text{cr}}$  on crystal structure is well illustrated by the two allotropic varieties of thorium disilicides (1,2). The tetragonal  $\alpha\text{-ThSi}_2$  form (Cc type and  $I4_1/amd$  space group) has been found to be superconducting at a clearly higher temperature ( $T_{\text{cr}} = 3.16\text{K}$ ) than that observed ( $T_{\text{cr}} = 2.41\text{K}$ ) for the hexagonal  $\beta\text{-ThSi}_2$  form (C32 type and  $P6/mmm$  space group). This enhanced superconductivity of the  $\alpha$ -modification has also been observed in some rare earth disilicides and digermanides (3,4). More recently in a study of a series of solid solutions derived from  $\alpha\text{-ThSi}_2$  and with formula  $\text{ThT}_x\text{Si}_{2-x}$  ( $T = \text{Rh}$  or  $\text{Ir}$ ) it was shown that  $T_{\text{cr}}$  varies in a complex manner with  $x$  (5). The transition temperature is rapidly dropped by replacement of Si by Rh or Ir for  $0 < x < 0,25$  and falls below 1.6K for  $0,25 < x < 0,75$ . Then  $T_{\text{cr}}$  rises abruptly to a maximum value as  $x$  approaches unity and the corresponding compounds  $\text{ThRh}_{0,96}\text{Si}_{1,04}$  ( $T_{\text{cr}} = 6.45\text{K}$ ) and  $\text{ThIrSi}$  ( $T_{\text{cr}} = 6.50\text{K}$ ) have the highest superconducting

transition temperatures so far reported for materials isostructural with  $\alpha$ -ThSi<sub>2</sub>. For the sake of both completeness and comparison we have investigated here the solid solutions ThCoSi<sub>x</sub>Si<sub>2-x</sub> (0 < x < 1) and the equiatomic silicides ThNiSi and ThPtSi.

#### EXPERIMENTAL PROCEDURE

Compounds of the desired composition have been prepared by conventional arc melting techniques in a continuous flow of purified argon. The powder constituent elements (Th, Co, Ni, Pt, Si) of ultra pure grade have been pressed into pellets, weighting each 300 mg, and placed on a cold copper block inside a tri-arc furnace. The weight loss of the samples after several meltings was negligible and the reported nominal compositions are considered to be accurate to  $\pm 1\%$ . After melting, the samples were annealed at 950°C for eight days.

The homogeneity and the composition of the samples have been checked after melting and after annealing by X-ray microprobe analysis. In addition the samples were identified by X-ray powder diffraction using a Guinier camera (CuK $\alpha$  radiation). The lattice parameters were determined by a least-square refinement method using silicon as an internal standard.

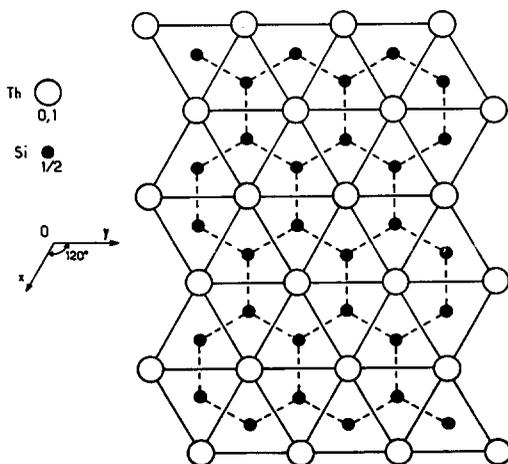
The samples were tested for superconductivity down to 1.7K by performing a.c. resistivity measurements using a four-probe technique

#### RESULTS AND DISCUSSION.

##### Structural aspect

##### The ThCoSi<sub>x</sub>Si<sub>2-x</sub> system

Before describing the study of the ThCoSi<sub>x</sub>Si<sub>2-x</sub> system it is worthwhile mentioning that the allotropic transformation of thorium disilicide,  $\beta$ -ThSi<sub>2</sub>  $\leftrightarrow$   $\alpha$ -ThSi<sub>2</sub>, is reversible and occurs in the temperature range 1250-1350°C.



The main difference between the two polymorphic structures concerns the arrangement of the silicon atoms. In  $\beta$ -ThSi<sub>2</sub> (Fig.1) silicon atoms form a layer structure similar to that of graphite, whereas a three-dimensional silicon network is present in the  $\alpha$ -ThSi<sub>2</sub> phase (Fig.2).

FIG. 1  
Projection of the structure of  $\beta$ -ThSi<sub>2</sub> onto the yOz plane

The two forms have a common elementary building unit : a silicon centered trigonal prism of Th atoms labelled  $[\text{Th}_3\text{SiTh}_3](6)$ . Those trigonal prisms are packed alternatively up and down resulting in infinite prism rows which are connected with infinite zig-zag chains of silicon atoms. While the prism rows are all perpendicular to the  $xOy$  plane in  $\alpha\text{-ThSi}_2$  (Fig.1), they are alternatively perpendicular and parallel to the  $xOy$  plane in  $\alpha\text{-ThSi}_2$  (Fig.2).

As cobalt atoms replace progressively the silicon atoms in  $\text{ThSi}_2$ , the resulting solid-solution  $\text{ThCo}_x\text{Si}_{2-x}$  exhibits a structural change and five regions can be distinguished as  $x$  increases (Fig.3 and Table I)

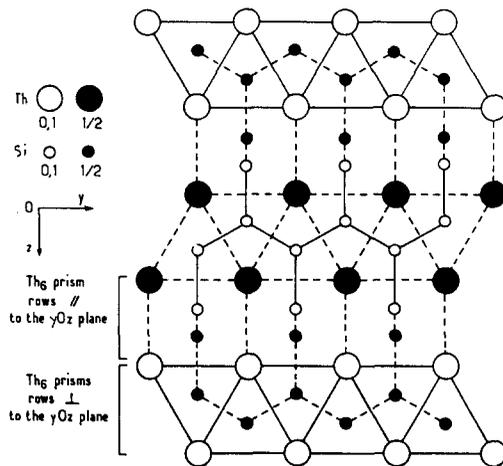


FIG.2  
Projection of the structure of  $\alpha\text{-ThSi}_2$   
onto the  $yOz$  plane

- For  $0 < x < 0.40$ , all samples obtained are single phases having the tetragonal  $\alpha$ -type structure with decreasing  $c/a$  ratio.
- For  $0.40 < x < 0.45$ , a mixture of two phases with  $\alpha$ - and  $\beta$ -type structures appears.
- For  $0.45 < x < 0.70$ , all materials prepared are single phases having the hexagonal  $\beta$ -type structure with decreasing  $c/a$  ratio.
- For  $0.70 < x < 0.85$ , two phases corresponding again to the  $\alpha$ - and  $\beta$ -type structures can be identified.
- For  $0.85 < x < 1$ , the samples prepared are single phases isostructural with  $\alpha\text{-ThSi}_2$ .

The explanation of why particular structural types are formed is generally a complex problem which cannot be solved easily. Nevertheless, some remarks can be made concerning the structural changes in the  $\text{ThCo}_x\text{Si}_{2-x}$  system

Two parameters can govern the structural changes : the size of the transition element and the variation of the valence electron concentration as silicon atoms are replaced by the transition elements. In order to show the influence of the size of the transition elements on the structure of the compounds, we may compare three systems for which transition elements belonging to the same column of the periodic Table, bring the same number of outer electrons :  $\text{ThCo}_x\text{Si}_{2-x}$ ,  $\text{ThRh}_x\text{Si}_{2-x}$  and  $\text{ThIr}_x\text{Si}_{2-x}$ .

As indicated previously a structural change with the sequence  $\alpha\text{-ThSi}_2 + \beta\text{-ThSi}_2 \rightarrow \alpha\text{-ThSi}_2$  has been observed as  $x$  increases for cobalt compounds, while the  $\alpha\text{-ThSi}_2$  type structure is kept with Rh and Ir in the entire composition range  $0 \leq x \leq 1$  (5). The  $\alpha\text{-ThSi}_2$ -type structure is stabilized by transition elements such as Rh and Ir whose sizes are larger than that of silicon. The rhodium or iridium substitution gives rise to an increase of the Si-Si and Si-Rh or Si-Ir distances along the  $c$ -axis, leading to an increase of both  $c/a$  ratio and unit cell volume (5). On the contrary, the cobalt substitution, which involves a decrease of both  $c/a$  ratio and unit cell volume (Fig.3 and Table I) of the

TABLE I

Crystallographic data and superconducting transition temperatures for the annealed samples  $\text{ThCo}_x\text{Si}_{2-x}$  ( $0 \leq x \leq 1$ ) (\* broad transition - see Fig.5).

x in $\text{ThCo}_x\text{Si}_{2-x}$	$\alpha\text{-ThSi}_2$ type			$\beta\text{-ThSi}_2$ type			$T_{\text{cr}}$ (K)
	a(Å)	c(Å)	$\frac{c}{a}$	a(Å)	c(Å)	$\frac{c}{a}$	
0	4.127	14.194	3.440				3.16
0.05	4.119	14.121	3.428				2.38
0.10	4.107	14.061	3.424				2.18
0.15	4.114	14.019	3.408				
0.30	4.117	13.976	3.395				
0.35	4.110	13.999	3.406				
0.40	4.091	13.985	3.418		trace		
0.42	4.204	14.003	3.412	4.031	4.200	1.042	
0.45		trace		4.030	4.197	1.041	
0.50				4.043	4.189	1.036	~ 2K*
0.55				4.050	4.162	1.028	
0.65				4.056	4.136	1.020	
0.70	4.068	14.091	3.464	4.070	4.100	1.007	
0.75	4.074	14.094	3.459		trace		
0.80	4.078	14.119	3.463		trace		
0.85	4.078	14.122	3.463		trace		
0.925	4.084	14.133	3.461				2.70
1	4.077	14.115	3.462				2.84

$\alpha\text{-ThSi}_2$  type structure, leads to occurrence of the hexagonal  $\beta\text{-ThSi}_2$  type in the composition range  $0.45 < x < 0.70$ . A similar structural change has also been observed in the analogous  $\text{PrNi}_x\text{Si}_{2-x}$  system (7). However, while at rising x the c/a ratio increases with nickel and decreases with cobalt, the unit cell volumes decrease whatever the substituent. At first sight it seems that decrease of the unit cell volume of the  $\alpha\text{-ThSi}_2$  type structure favors appearance of the  $\beta\text{-ThSi}_2$  type.

For a cobalt content  $x \geq 0.70$  the  $\beta\text{-ThSi}_2$  type structure becomes less stable and the  $\alpha\text{-ThSi}_2$  type structure forms again. At that composition more than one silicon atom out of three are replaced by the smaller cobalt atoms and the hexagons containing both Co and Si become distorted to such an extent that the  $\beta\text{-ThSi}_2$  structure is destroyed.

In order to determine the exact position of the Co and Si atoms for the equiatomic compound  $\text{ThCoSi}$  of the  $\alpha\text{-ThSi}_2$  type, the intensities of the lines of the X-ray powder diagram have been calculated in two eventualities: (i) for Co and Si atoms randomly distributed between Si sites of the  $\alpha\text{-ThSi}_2$  structure ( $I_{4_1}/amd$ ) (ii) for an ordered arrangement of the cobalt and silicon atoms on the silicon sites of the  $\alpha\text{-ThSi}_2$  structure type with a corresponding lowering of the space group symmetry from  $I_{4_1}/amd$  down to  $I_{4_1}md$ ; such an ordered structure corresponds to the  $\text{LaPtSi}$ -type in which each Pt atom has three Si close neighbors and vice-versa (Fig.4).

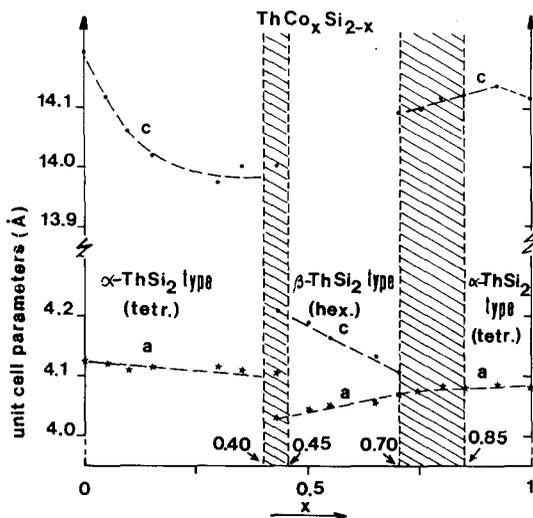


FIG. 3

Variation of the lattice parameters vs. composition for the  $\text{ThCo}_x\text{Si}_{2-x}$  compounds after annealing at  $950^\circ\text{C}$  for 8 days.

As shown in Table II, the comparison between observed and calculated intensities does not allow us to conclude if Co and Si atoms are ordered or occupy the Si sites of  $\alpha\text{-ThSi}_2$  at random.

It is worthwhile noticing that the crystal structure of the  $\text{ThCoSi}$  silicide differs from that of other equiatomic compounds  $\text{RECoSi}$  ( $\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}$ ) which crystallize in the  $\text{PbFCl}$  type (8).

The equiatomic silicides  $\text{ThNiSi}$  and  $\text{ThPtSi}$ .

$\text{ThNiSi}$  crystallizes in the  $\alpha\text{-ThSi}_2$  type but, as for  $\text{ThCoSi}$ , no clear evidence has been found for an ordering between Ni and Si on the silicon sites. On the contrary an ordered structure isotypic with  $\text{LaPtSi}$  has been observed for  $\text{ThPtSi}$ . These results have been verified by comparing observed powder diagram intensities with calculated ones (Table II). An ordered structure of  $\text{LaPtSi}$ -type has also been found for similar compounds such as  $\text{RENiSi}$  ( $\text{RE} = \text{Ce}, \text{Pr}, \text{Nd}$ ) (7) and  $\text{REPtSi}$  ( $\text{RE} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Gd}$ ) (9,10).

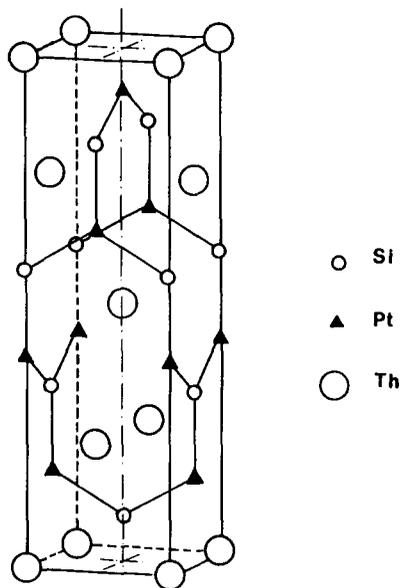


FIG. 4

Structure of  $\text{ThPtSi}$  ( $\text{LaPtSi}$  type)

TABLE II

Comparison of calculated and observed line intensities for ThPtSi and ThCoSi

h k l	ThPtSi			ThCoSi		
	I <sub>obs</sub>	I <sub>calc</sub> ordering	I <sub>calc</sub> disordering	I <sub>obs</sub>	I <sub>calc</sub> ordering	I <sub>calc</sub> disordering
1 0 1	79	81	11	360	386	383
0 0 4	113	123	60	282	231	229
1 0 3	460	449	336	647	523	516
1 1 2	1000	1000	1000	1000	1000	1000
1 0 5	519	473	531	468	415	418
2 0 0	358	340	399	391	298	301
1 1 6	-	1	0	129	88	88
1 0 7	217	215	246		187	188
2 1 1	39	20	35	>371	{ 101	100
0 0 8	24	22	9		34	34
2 0 4	89	69	34	>263	{ 134	133
2 1 3	172	155	116	253	179	178
2 1 5	290	247	278	251	213	214
1 0 9	45	43	35	-	53	53
2 2 0	113	108	127	128	92	93
2 1 7	163	157	180		136	137
3 0 1	-	4	1	>166	{ 20	20
2 0 8	43	34	14		54	53
2 2 4	31	27	13	>153	{ 53	53
3 0 3	34	31	24	37	36	36
1 1 10	126	100	97		90	90
3 1 2	194	184	185	>309	{ 178	178
3 0 5	58	56	64		48	49
1 0 11	-	2	1	> 67	{ 14	14
2 1 9		{ 42	34	47	52	53
0 0 12	>79	{ 28	33	-	52	53
3 0 7	43	42	49			

### Electrical properties

#### The silicides $\text{ThCo}_x\text{Si}_{2-x}$ ( $0 \leq x \leq 1$ )

The electrical properties of the  $\text{ThCo}_x\text{Si}_{2-x}$  compounds have been studied on annealed samples (950°C for 8 days). Contrary to the equiatomic silicides ThRhSi and ThIrSi which may also have an  $\alpha\text{-ThSi}_2$  type structure, ThCoSi is not transformed into the  $\beta\text{-ThSi}_2$  form in the annealing conditions reported above.

Only the  $\text{ThCo}_x\text{Si}_{2-x}$  solid solutions with the  $\alpha\text{-ThSi}_2$  type structure, have been found clearly to be superconducting above 1.7K in the composition ranges  $0 \leq x < 0.15$  and  $0.85 < x \leq 1$  (Fig.5 and Table I).

The silicides with  $\beta\text{-ThSi}_2$  structure show broad superconducting transitions as shown by the variation of the electrical resistivity vs temperature (Fig.5). The width of the transition range remains unchanged whatever the annealing conditions.

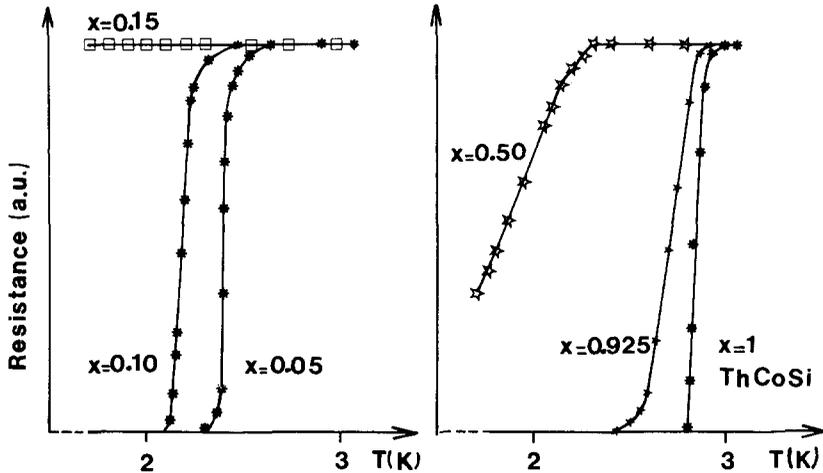


FIG.5

Resistance vs temperature for various  $\text{ThCoSi}_{2-x}$  annealed samples  
(8 days at  $950^\circ\text{C}$ )

The poorest cobalt compounds exhibit superconducting transition temperatures which decrease as  $x$  increases, from this point of view they behave as the silicides  $\text{ThTSi}_{2-x}$  ( $T = \text{Rh}$  or  $\text{Ir}$ ). Although an increase of  $T_{\text{cr}}$  with  $x$  has been observed for the cobalt rich compounds, nevertheless the  $T_{\text{cr}}$  values remain lower than that of  $\alpha\text{-ThSi}_2$  ( $T_{\text{cr}} = 3.16$  K) (Table I).

#### The silicides ThNiSi and ThPtSi

The equiatomic compounds ThNiSi and ThPtSi exhibit sharp superconducting transitions respectively at 2K and 2.98K (Fig.6).

#### Conclusions

Contrary to  $\text{ThRhSi}_{2-x}$  and  $\text{ThIrSi}_{2-x}$  compounds the  $\text{ThCoSi}_{2-x}$  silicides exhibit a structural change in the composition range  $0 < x < 1$ . The structures which are observed as  $x$  increases correspond to the sequence:  $\alpha\text{-ThSi}_2$  type  $\rightarrow$   $\beta\text{-ThSi}_2$  type  $\rightarrow$   $\alpha\text{-ThSi}_2$  type. Structural changes have also been reported for other silicides  $\text{REThSi}_{2-x}$  containing a rare earth and a 3d element ( $T = \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{Ag}$ ) (7,11). As indicated in Table III, the equiatomic silicides  $\text{MTSi}$  ( $M = \text{Th}$  or rare earths and  $T = \text{Co}, \text{Rh}, \text{Ir}, \text{Ni}, \text{Pt}$ ) crystallize in a structural type which depends strongly on the nature of the M element. ThPtSi is isostructural with the equiatomic rare earth compounds in which Si and Pt atoms are ordered on the Si sites (LaPtSi-type). For thorium compounds containing Co, Rh, Ir or Ni atoms a refinement of the structures from X-ray powder measurements does not allow us to conclude on the existence or absence of ordering between silicon and transition element atoms

TABLE III

Structural types of the equiatomic ternary thorium and rare earth silicides MTSi (\* this work) ● LaPtSi (ordered  $\alpha$ -ThSi<sub>2</sub>), □ PbFCl, ☑ TiNiSi, ☒ SrSi<sub>2</sub>, or ZrOS  
 O no conclusive results from structure refinement on powder.

M \ T	Co(3d)	Rh(4d)	Ir(5d)	Ni(3d)	Pt(5d)
Th	O *	O(5)	O(5)	O *	● *
La	□ (8)	☒ (12)	☒ (9,12)	-	● (9)
Ce	□ (8)			● (7)	● (9)
Pr	□ (8)			● (7)	● (9)
Nd	□ (8)		☒ (12)	● (7)	● (9)
Sm	□ (8)			-	● (9)
Eu				-	
Gd		☒ (13)	☒ (9)	☒ (9)	● (9)
Tb		☒ (13)	☒ (15)	☒ (9)	☒ (9)
Dy		☒ (13)	☒ (15)	☒ (9)	☒ (9)
Ho		☒ (13)	☒ (15)	☒ (9)	☒ (9)
Er		☒ (13)	☒ (9)	☒ (9)	☒ (9)
Tm					☒ (9)
Yb					(9)
Lu				☒ (9)	☒ (9)
Y		☒ (13)	☒ (9)	☒ (9)	☒ (9)

TABLE IV

Valence electron concentration (VEC), crystallographic data and superconducting transition temperature ( $T_{cr}$ ) for equiatomic ternary silicides ThTSi.

Silicides	VEC	a ° (Å)	c ° (Å)	V ° <sup>3</sup> (Å <sup>3</sup> )	$d_{T-Si}$ (Å)	$T_{cr}$ (K)
ThCoSi	5.66	4.077	14.115	234.62	2.351	2.84
ThRh <sub>0.96</sub> Si <sub>1.04</sub>	5.66	4.129	14.280	243.45	2.381	6.45
ThIrSi	5.66	4.143	14.270	244.94	2.386	6.5
ThNiSi	6	4.073	14.099	233.89	2.349	2
ThPtSi	6	4.154	14.582	251.62	2.404	2.98

The superconducting properties of the  $\text{ThT}_x\text{Si}_{2-x}$  compounds with  $T = \text{Co}, \text{Rh}, \text{Ir}, \text{Ni}, \text{Pt}$ , are sensitive to the nature of the transition element as shown in Table IV. For a same valence electron concentration (VEC) the superconducting transition is lower with the 3d-elements than with the 4d and 5d elements. Such an observation has already been made for other compounds such as  $\text{Sc}_M\text{Si}_{10}$  ( $M = \text{Co}, \text{Rh}, \text{Ir}$ ) (14). On the other hand the lowest  $T_{cr}$  values are observed for compounds having the smallest unit cell volumes and hence the shortest T-Si distances.

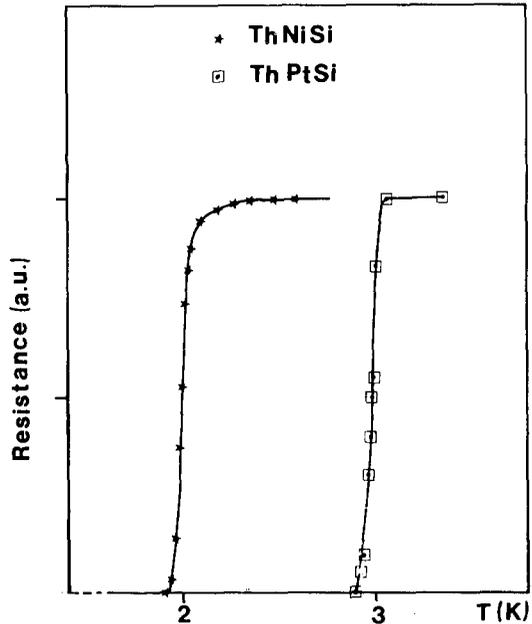


FIG.6

Electrical resistance vs temperature for  
ThNiSi and ThPtSi

#### REFERENCES

- 1 - G.F. Hardy and J.K. Hulm, Phys. Rev., 93, 1004, 1954.
- 2 - A. Brown, Acta Cryst., 14, 860, 1961.
- 3 - B.T. Matthias, E. Corenzwit and W.H. Zachariasen, Phys. Rev., 112, 89, 1958.
- 4 - W.E. Henry, C. Betz and H. Muir, Bull. Amer. Phys. Soc., 7, 474, 1962.
- 5 - P. Lejay, B. Chevalier, J. Etourneau, J.M. Tarascon and P. Hagenmuller, Mat. Res. Bull., 18, 67, 1983.
- 6 - E. Parthé in " Propriétés thermodynamiques, physiques et structurales des dérivés semi-métalliques ", Colloques Internationaux du CNRS, p.157, 1967.

- 7 - I. Mayer and I. Felner, *J. of Solid State Chemistry*, 7, 292, 1973.
- 8 - O.I. Bodak, E.I. Gladyshevskii and P.T. Kripyakevich, *J. Struct. Chem. (USSR)*, 11, 283, 1970.
- 9 - E. Hovestreydt, N. Engel, K. Klepp, B. Chabot and E. Parthé, *J. Less Common Metals*, 85, 247, 1982.
- 10- K. Klepp and E. Parthé, *Acta Cryst.*, B38, 1105, 1982.
- 11- E. Parthé in " Les éléments des terres rares " - Colloques Internationaux du CNRS N°180 - Tome I, p. 61, 1969.
- 12- B. Chevalier, A. Cole, P. Lejay, M. Vlasse, J. Etourneau and P. Hagenmuller, *Mat. Res. Bull.*, 41, 801, 1982.
- 13- B. Chevalier, A. Cole, P. Lejay, M. Vlasse, J. Etourneau and P. Hagenmuller, *Mat. Res. Bull.*, 17, 251, 1982.
- 14- H.F. Braun and C.V. Segre, *Solid State Comm.*, 35, 735, 1980.
- 15- B. Chevalier, P. Lejay, B. Lloret, Wang-Xian-Zhong, J. Etourneau et P. Hagenmuller, *Ann. Chim. Fr.* 9, 987, 1984.