ELSEVIER

Journal of Alloys and Compounds 227 (1995) 32–36

Journal of
ALLOYS
AND COMPOUNDS

Structure of "$TaCo_4Si_3$", a new silicide closely related to the $Y_{13}Pd_{40}Sn_{31}$ stannide

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Received 26 January 1995

Abstract

A new ternary compound "$TaCo_4Si_3$" has been studied using single-crystal X-ray diffraction data. The crystal structure is closely related to that of $Y_{13}Pd_{40}Sn_{31}$ with space group *P6/mmm* and $Z=21$, $a=b=17.141(3)$ Å, $c=7.906(2)$ Å, $D_x=9.14$ g cm^{-3}, μ (MoKα) $=54.5$ mm^{-1}, $F(000)=4924$, $R=0.049$ for 308 contributing unique reflections and 36 refined parameters. In the five compounds, $Y_{13}Pd_{40}Sn_{31}$, $Li_{13}Ni_{40}Si_{31}$, $Sc_{12.7}Ni_{40.7}Ge_{31}$, $NbCo_4Si_3$ and $TaCo_4Si_3$, the structures can be described as a stacking along the *c*-axis of two elemental "Zr_4Al_3" and "$CaCu_5$"-type blocks, but the nature and the *z*-coordinate of the atom on the 2(e) site (0 0 *z*) are not well determined. In the case of $TaCo_4Si_3$, these uncertainties are solved.

Keywords: Silicides

1. Introduction

Over the last few years, the oxidation behaviour of both niobium alloys and protective silicide coatings of niobium alloys has again been the subject of important research [1]. This is why we have recently reconsidered a previous study of the Nb–T–Si (when T ≡ V, Cr, Mn, Fe, Co, Ni) systems [2,3], and thus carried out a complete structural characterization of the ternary phase "$TaCo_4Si_3$". Our study has been made easier by the crystallographic data of $Y_{13}Pd_{40}Sn_{31}$ published by Cenzual and Parthé [4] and those of $Li_{13}Ni_{40}Si_{31}$ and $Sc_{12.7}Ni_{40.7}Ge_{31}$ recently reported by Bodak et al. [5]. The space group as well as the cell parameters of these three compounds are close to those of $TaCo_4Si_3$ and they suggest similar structural relationships.

Let us mention the most important structural features of $Y_{13}Pd_{40}Sn_{31}$. Its structure has been described as an intergrowth of three kinds of structural segments (Fig. 1). The first is characteristic of ternary ordering variants of the $CaCu_5$ type (i.e. $PrNi_2Al_3$ and $CeCo_3B_2$) [6,7]. It can be noted that the $CeCo_3B_2$-type structure is adopted by some ternary silicides such as RRh_3Si_2 and RRu_3Si_2 (R ≡ RE, Y) [8]. The second unit has an atomic arrangement similar to that of YPd_2Sn with $MnCu_2Al$-structure type (Heusler phase) [9].The third segment is a column of Pd centred Sn prisms and Sn centred Pd prisms along [001]. Their dimensions and atomic environment are close to those found in the ZrNiAl structure [10], an ordered variant of Fe_2P. Moreover, as noticed by the authors, some doubts remain concerning the occupancies of some atomic sites where Pd and Sn atoms can be exchanged.

In order to obtain the best refinement of the structure of both $Li_{13}Ni_{40}Si_{31}$ and $Sc_{12.7}Ni_{40.7}Ge_{37}$, Bodak et al. proposed a structural variant of $Y_{13}Pd_{40}Sn_{31}$ where new atomic positions are introduced with partial occupancy (Table 1) [5]. Moreover, after careful analysis of Table 1, it appears that the atoms located along the six-fold axis (Y, Li, Ni) exhibit unusually strong temperature factor values.

2. Experimental details

Small needle-like single crystals of $TaCo_4Si_3$ and $NbCo_4Si_3$ were obtained from powder by gas transport in a sealed quartz tube under the following conditions: alloy powder composition $Ta(Nb)_{20}Co_{45}Si_{35}$; temperature of evaporation zone 1223 K; temperature of deposition zone 1313 K; transport agent I_2 (1.25 mg cm^{-3}). The conditions for data collection on a NONIUS CAD 4 automatic diffractometer and structure refinement are listed in Table 2.

In a first step, taking into account inaccuracies concerning the "isostructural" silicide and germanide, only 20 atomic sites of $Y_{13}Pd_{40}Sn_{31}$ (i.e. all except the 00*z* sites) were retained for a first least-squares refinement of both $NbCo_4Si_3$

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SSDI 0925-8388(95)01615-5

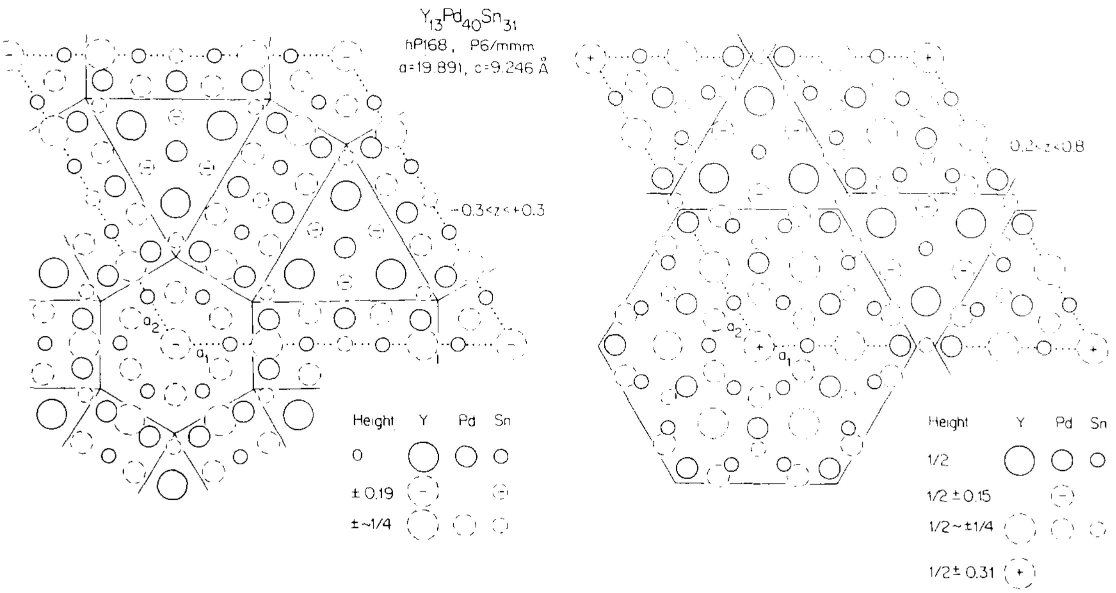

Fig. 1. [0001] projection of the structure of $Y_{13}Pd_{40}Sn_{31}$ [4]; hexagon, slab of "$CaCu_5$" type; rectangle, slab of "BiF_3" type (Heusler phase); triangle, columns of trigonal prisms.

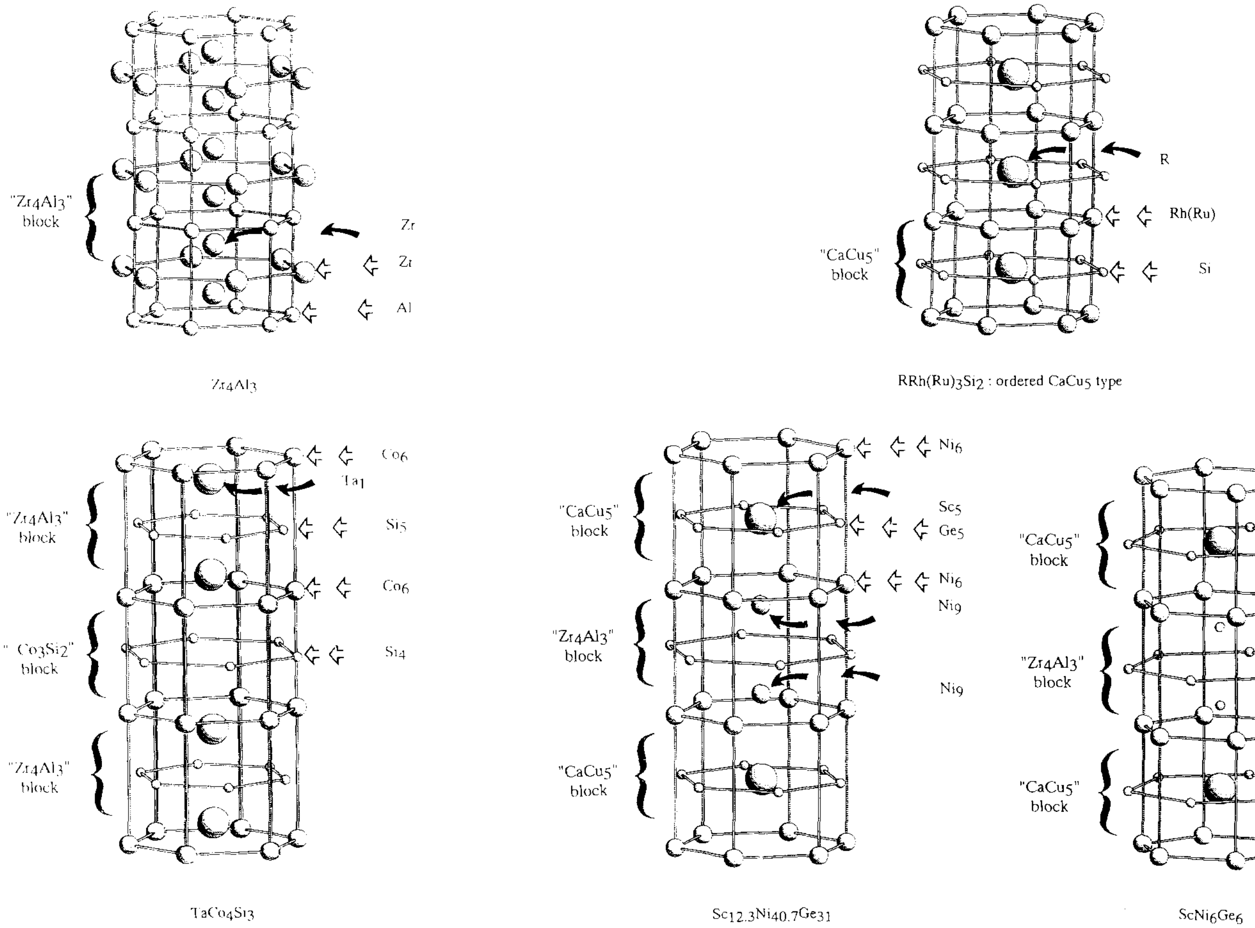

Fig. 2. Stacking of "Zr_4Al_3" and "$CaCu_5$" blocks along the six-fold axis in the structures of $TaCo_4Si_3$, $Sc_{12.3}Ni_{40.7}Ge_{31}$ and $ScNi_6Ge_6$.

Table 1
Atomic coordinates, thermal parameters and occupancy factors of $Y_{13}Pd_{40}Sn_{31}$, $Li_{13}Ni_{40}Si_{31}$, $Sc_{12.3}Ni_{40.7}Ge_{31}$ and $TaCo_4Si_3$; M ≡ Y, Li, Sc, Ta; M′ ≡ Pd, Ni, Co; B ≡ Sn, Si, Ge; *t* occupancy factor

	$Y_{13}Pd_{40}Sn_{31}$ [4]					$Li_{13}Ni_{40}Si_{31}$ [5]				
	x	y	z	t	U (Å^2)	x	y	z	t	B (Å^2)
M1	0	0	0.194	1	5	0	0	0.27	1	2
M2	0.2433	$2x$	0	1	2.3	0.234	$2x$	0	1	1
M3	0.5761	$2x$	1/2	1	1.3	0.574	$2x$	1/2	1	1
M4	0.2712	0	0.2895	1	1.6	0.28	0	0.314	1	1
M5										
M′1	1/3	2/3	0	1	0.9	1/3	2/3	0.064	0.5	0.6
M′2	0.4225	0	1/2	1	0.9	0.4204	0	1/2	1	0.6
M′3	0.5452	$2x$	0	1	0.8	0.5424	$2x$	0	1	0.6
M′4	0.1410	$2x$	1/2	1	0.5	0.1424	$2x$	1/2	1	0.6
M′5	0.2603	$2x$	0.348	1	0.9	0.265	$2x$	0.3372	1	1.1
M′6	0.0884	$2x$	0.2419	1	1.4	0.0938	$2x$	0.2337	1	1.2
M′7	0.0857	0.3209	0	1	0.9	0.0859	0.3157	0	1	0.7
M′8	0.1058	0.4476	0.2211	1	0.8	0.1014	0.444	0.2254	1	0.9
B1	1/3	2/3	1/2	1	0.7	1/3	2/3	0.459	0.5	0.4
B2	1/2	0	0.2584	1	0.6	1/2	0	0.266	1	0.8
B3	0.3862	0	0	1	0.8	0.3831	0	0	1	0.9
B4	0.1621	0	0	1	0.9	0.1613	0	0	1	0.9
B5	0.1459	0	1/2	1	1.0	0.1480	0	1/2	1	0.8
B6	0.6073	$2x$	0.1869	1	0.4	0.6045	$2x$	0.174	1	0.7
B7	0.1776	$2x$	0.2333	1	0.6	0.1791	$2x$	0.2378	1	2.2
B8	0.1264	0.4111	1/2	1	0.7	0.1335	0.4189	1/2	1	0.8

	$Sc_{12.3}Ni_{40.7}Ge_{31}$ [5]					"$TaCo_4Si_3$"				
	x	y	z	t	B (Å^2)	x	y	z	t	B (Å^2)
M1						0	0	0.309(2)	0.78(5)	0.6(3)
M2	0.244	$2x$	0	1	0.7	0.2442(2)	$2x$	0	1	0.3(1)
M3	0.576	$2x$	1/2	1	0.7	0.5770(2)	$2x$	1/2	1	0.4(1)
M4	0.2721	0	0.2942	1	0.7	0.2711(2)	0	0.3035(4)	1	0.4(1)
M5	0	0	1/2	0.64	0.7					
M′1	1/3	2/3	0	1	0.3	1/3	2/3	0	1	0.5(2)
M′2	0.42	0	1/2	1	0.9	0.418(1)	0	1/2	1	0.3(2)
M′3	0.5434	$2x$	0	1	0.6	0.5436(5)	$2x$	0	1	0.2(2)
M′4	0.1420	$2x$	1/2	1	0.9	0.1403(7)	$2x$	1/2	1	0.3(3)
M′5	0.2609	$2x$	0.3455	1	0.7	0.2621(4)	$2x$	0.343(1)	1	0.6(2)
M′6	0.0883	$2x$	0.2389	1	1.6	0.0919(5)	$2x$	0.232(2)	1	1.5(2)
M′7	0.0859	0.3220	0	1	0.9	0.0886(8)	0.3249(8)	0	1	0.4(2)
M′8	0.1052	0.4491	0.2236	1	0.9	0.1012(5)	0.4449(5)	0.2310(9)	1	0.5(1)
M′9	0	0	0.17	0.67	1.4				1	
B1	1/3	2/3	1/2	1	0.8	1/3	2/3	1/2	1	2.3(1)
B2	1/2	0	0.2663	1	0.6	1/3	0	0.262(4)	1	0.1(1)
B3	0.3856	0	0	1	0.8	0.387(2)	0	0	1	0.9(5)
B4	0.1656	0	0	1	0.9	0.163(3)	0	0	1	2.1(8)
B5	0.1457	0	1/2	1	0.9	0.138(2)	0	1/2	1	0.5(1)
B6	0.6063	$2x$	0.1841	1	0.8	0.604(1)	$2x$	0.186(3)	1	0.4(3)
B7	0.178	$2x$	0.2301	1	0.9	0.178(1)	$2x$	0.235(4)	1	0.6(4)
B8	0.1273	0.4718	1/2	1	0.8	0.128(2)	0.408(2)	1/2	1	0.5(4)

and $TaCo_4Si_3$ [11]. In this hypothesis, the R factors were respectively $R = 0.14$ and $R = 0.09$. Then the "difference" Fourier syntheses revealed along the c-axis several peaks in the case of niobium silicide (000, 000.3, 000.5) and only one (000.31) in the case of tantalum silicide.

In the case of $NbCo_4Si_3$, it has been impossible to determine with accuracy both the nature and the position of the atom(s) along the c-axis, the best refinement ($R = 0.09$) yielding unusually short interatomic distances and too high individual isotropic thermal factor values.

Table 2
"$TaCo_4Si_3$" and "$NbCo_4Si_3$": summary of data collection and structure refinement

	"$NbCo_4Si_3$"	"$TaCo_4Si_3$"
Molar mass (g)	4331.4	5535
Average crystal diameter (μm)	≈ 100	≈ 40
Symmetry (μm)	Hexagonal	Hexagonal
a (Å)	17.180(20)	17.141(3)
c (Å)	7.918(7)	7.906(2)
V (Å^3)	2023.9	2011.9
Z	2	2
ρ_{cal} (g cm^{-3})	7.11	9.14
Space group	$P6/mmm$	$P6/mmm$
Radiation	Mo Kα (1500 W)	Mo Kα (1500 W)
Monochromator	Graphite	Graphite
Scan mode	θ, ω	θ, ω
Take-off angle (deg)	3.5	3.5
Recording limits (deg)	$\theta < 25$	$\theta < 25$
Linear absorption coefficient μ (cm^{-1})	9.5	54.5
Numbers of reflections		
recorded	837	958
considered ($\sigma(I)/I < 0.3$)	283	308
$F(000)$	1091	4924
Number of parameters	36	36
Final R value	0.090	0.049
Microprobe analysis (at.%)	$Nb_{14.5}Co_{49.3}Si_{36.2}$	$Ta_{14.5}Co_{49.30}Si_{36.2}$
Formula after refinement		$Ta_{15.2}Co_{47.8}Si_{37}$

On the contrary, in the case of $TaCo_4Si_3$, the occurrence of a Ta atom (M1) at the atomic coordinates 0, 0, 0.31 has led to a better R factor ($R = 0.06$). A least refinement of the coordinates and the occupancy factors of the 21 atomic sites has improved the reliability factor ($R = 10.049$), the corresponding composition being close to that derived from microprobe analysis ($Ta_{14.5}Co_{49.3}Si_{36.2}$ at%), with a partial occupancy of the single Ta 2(e) site. The different refined parameters are listed in Table 1.

3. Discussion

The structure of the new silicide, $TaCo_4Si_3$, can be considered a variant of the $Y_{13}Pd_{40}Sn_{31}$, $Li_{13}Ni_{40}Si_{31}$ and $Sc_{12.7}Ni_{40.7}Ge_{31}$ structures. Moreover, the existence of $Ta_{13}Co_{40}Si_{31}$ "validates" in a way the structural description related in the introduction of Ref. [4]. It is particularly true for the "Fe_2P block", since TaCoSi belongs to the Co_2P-type structure which is closely related to the Fe_2P-type structure and where metallic prisms are built from four Ta atoms and two Co atoms [12]. In addition, it can be noted that in the Ti–Fe–Si system, where an isostructural phase $Ti_{13}Co_{40}Si_{31}$ has been identified [3], an equiatomic TiFeSi ternary compound crystallizes with a structure resulting from a slight orthorhombic deformation of hexagonal Fe_2P [13].

Consequently, the four structures described in detail in Table 1 are all characterized by the same framework even if two positions (1/3 2/3 z) with z close to 0 and 0.5 are only half occupied in $Li_{13}Ni_{40}Si_{31}$, while in the other compounds the "equivalent" atomic sites 1/3 2/3 0(1/2) are completely filled.

This framework, of formula $M_{24}M'_{80}B_{62}$, generates hexagonal antiprism channels along the six-fold axis ($M'B_6$) with different, even uncertain filling. Nevertheless, in the case of the Ta phase, the uncertainty concerning both the atom type and the atomic position on the six-fold axis seem to have been removed.

One Ta atom is located in the hexagonal antiprism built from six Si atoms (B5) and six Co atoms (M'6) (Fig. 2), while Y in the $Y_{13}Pd_{40}Sn_{31}$ stannide is at the centre of the neighbouring antiprism built from six Sn atoms (B4) and six Pd atoms (M_6').

The largest atom, Ta or Y, is situated out of the hexagonal plane of Si or Sn, forming Ta–Ta ($d = 3.023$ Å) and Y–Y ($d = 3.587$ Å) dumbbells. Thus, this part of the structure seems more related to the Zr_4Al_3-type structure than to the $CeCo_3B_2$-type structure (ordered $CaCu_5$ type). Actually, along the six-fold axis there is alternate stacking of both "$Ta_2Co_2Si_3$" (Zr_4Al_3 type) and "Co_3Si_2" blocks (Fig. 2).

However, in the case of the $Sc_{12.7}Ni_{40.7}Ge_{31}$ germanide, an intergrowth of two slabs, respectively an "$ScNi_3Ge$" slab (ordered $CaCu_5$ block) and an "Ni_4Ge_3" slab (Zr_4Al_3 block), induces an atomic arrangement characteristic of the $ScNi_6Ge_6$ structure, which is a variant of the $HfFe_6Ge_6$-type structure [14]. In this structure the Ge atoms constituting the dumbbells would be exchanged with Ni atoms (Fig. 2).

The geometrical features of $TaCo_4Si_3$ and related phases described above give perhaps a rudimentary answer to the question raised by the residual electronic densities (000 and 001/2) in the $NbCo_4Si_3$ study. The structure of this ternary niobium silicide could result from a more complex intergrowth of both $CaCu_5$ and Zr_4Al_3 "units", inducing a superstructure, not detected by conventional X-ray studies (Weissenberg photographs) because of small contributions of the concerned atoms to the measured intensities.

Finally, in the MM'_6B_6 compounds, the existence of many structural parts resulting from an intergrowth of "$HfFe_6Ge_6$" and "$ScFe_6Ge_6$" segments supports this hypothesis [15].

Acknowledgments

We wish to thank Dr J.M. Claude and the Service Commun de microanalyse de l'Université de Nancy I as well as the Service Commun de diffractométrie automatique. This study was supported by the DRET organization under Contract 91/176.

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