

Synthesis and Structure of NbPdSi

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The new silicide NbPdSi was prepared by melting the elements in an arc-furnace. Well-shaped single crystals were obtained by annealing the sample in an induction furnace. The structure of NbPdSi has been studied by X-ray powder and single crystal diffractometer data: TiNiSi type, *Pnma*, $Z = 4$, $a = 643.0(1)$, $b = 376.7(1)$, $c = 744.4(2)$ pm, $wR2 = 0.0330$, 346 F^2 values, and 20 variables. The palladium and silicon atoms build up a three-dimensional [PdSi] network where each palladium atom has a strongly distorted tetrahedral silicon coordination at Pd–Si ranging from 242 to 250 pm. The niobium atoms fill channels left in the [PdSi] network.

Key words: Silicide, Intermetallics, Crystal Chemistry

Introduction

Equiatomic $TT'Si$ silicides (T and T' are transition metals) have intensively been investigated in recent years with respect to their superconducting behaviour [1–5, and ref. therein]. The highest transition temperature (10.3 K) has been observed for Zr–RhSi [6]. An interesting system is the 3.5 K superconductor TaPtSi, where the superconductivity can be suppressed by niobium substitution within the solid solutions $Ta_{1-x}Nb_xPtSi$ [3]. Most of the $TT'Si$ silicides crystallize with the orthorhombic TiNiSi type [7]. Herein we report on the preparation and structure refinement of the new silicide NbPdSi, which adopts the same orthorhombic structure.

Experimental Section

Synthesis

Stoichiometric amounts of niobium pieces (< 1 mm, Serva, 99.9%), palladium powder (ca. 200 mesh, Merck, 99.9%), and silicon pieces (6N, Wacker) were ground and mixed in an agate mortar. The mixture was cold-pressed into a pellet ($\varnothing 6$ mm) and subsequently melted into ingots inside an arc-melting furnace [8] operated with an INVERTEC

Table 1. Crystal data and structure refinement for NbPdSi.

Empirical formula	NbPdSi
Molar mass [g/mol]	227.40
Unit cell dimensions [pm] (Guinier powder data)	$a = 643.0(1)$ $b = 376.7(1)$ $c = 744.4(2)$ $V = 0.1803 \text{ nm}^3$
Space group	<i>Pnma</i>
Pearson symbol, Z	oP12, 4
Calculated density [g/cm ³]	8.38
Crystal size [μm^3]	$30 \times 50 \times 60$
Transmission ratio (max/min)	1.26
Absorption coefficient [mm ⁻¹]	16.4
$F(000)$	404
θ Range [°]	4 to 32
Range in hkl	$\pm 9, \pm 5, \pm 11$
Total no. reflections	1902
Independent reflections	346 ($R_{\text{int}} = 0.0374$)
Reflections with $I > 2\sigma(I)$	337 ($R_{\text{sigma}} = 0.0161$)
Data/parameters	346 / 20
Goodness-of-fit on F^2	1.240
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0168$; $wR2 = 0.0327$
R indices (all data)	$R1 = 0.0174$; $wR2 = 0.0330$
Extinction coefficient	0.039(2)
Largest diff. peak and hole [$e/\text{\AA}^3$]	1.14 and -0.96

V 130 TIG welding generator under an argon atmosphere of ca. 800 mbar. The argon was previously purified before over titanium sponge (870 K), silica gel and molecular sieves. The button was remelted three times to ensure homogeneity. The resulting ingot was sealed in an evacuated quartz tube and annealed in a high-frequency (HF) furnace (Hüttinger TIG 2.5/300) setup, further described by Niepmann *et al.* [9]. Inside the induction coil the ingot was first brought to its melting point, after which a steady temperature of about 100 degrees below the melting point was held for one hour. After cooling the sample to room temperature, the ingot was broken into smaller pieces and into powder using a steel mortar.

X-ray imaging plate data and structure refinement

The purity of the sample was checked through a powder pattern using a Guinier camera (equipped with an image plate system Fujifilm, BAS-1800) with Cu-K α_1 radiation and α -quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The orthorhombic lattice parameters (Table 1) were obtained by a least-squares refinement of the powder data. The correct indexing of the diffraction lines was ensured by an intensity calculation [10] using the positional parameters obtained from the structure refinement.

Irregularly shaped single crystals of NbPdSi were selected from the annealed sample and examined by Laue photographs on a Buerger precession camera (equipped with an imaging plate system Fujifilm BAS-1800) in order to establish suitability for intensity data collection which was car-

Table 2. Atomic coordinates and anisotropic displacement parameters (pm^2) for NbPdSi. All atoms lie on the Wyckoff site $4c$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + \dots + 2hka^*b^*U_{12}]$. U_{eq} is defined as a third of the trace of the orthogonalized U_{ij} tensor. $U_{12} = U_{23} = 0$. The occupancy parameters were obtained in a different series of least-squares cycles.

Atom	Occup.	x	y	z	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
Nb	100.3(3)	0.97285(4)	1/4	0.66635(4)	59(2)	67(2)	66(2)	-1(1)	64(1)
Pd	99.6(3)	0.35186(3)	1/4	0.43743(3)	66(1)	63(1)	68(1)	1(1)	65(1)
Si	100.5(8)	0.73283(14)	1/4	0.37093(12)	70(4)	60(4)	71(4)	2(3)	67(2)

Nb:	2	Si	268.4	Pd:	1	Si	242.0
	1	Si	268.7		2	Si	242.5
	2	Si	276.0		1	Si	249.9
	2	Pd	291.6		2	Pd	283.6
	1	Pd	297.4		2	Nb	291.6
	2	Pd	298.2		1	Nb	297.4
	1	Pd	305.0		2	Nb	298.2
	2	Nb	313.1		1	Nb	305.0
	2	Nb	344.8	Si:	1	Pd	242.0
					2	Pd	242.5
					1	Pd	249.9
					2	Nb	268.4
					1	Nb	268.7
					2	Nb	276.0

Table 3. Interatomic distances (pm) in NbPdSi calculated with the powder lattice parameters. Standard deviations are all equal or smaller than 0.1 pm.

ried out at r. t. by use of a Stoe IPDS-II diffractometer with graphite monochromatized Mo- K_{α} radiation. A numerical absorption correction was applied to the data. All relevant crystallographic details are listed in Table 1.

The systematic extinctions of the data set were compatible with space group $Pnma$, in agreement with our previous investigation on NbIrSi [5]. The atomic parameters of the latter silicide were taken as starting values and the structure was refined using SHELXL-97 (full-matrix least-squares on F_0^2) [11] with anisotropic atomic displacement parameters for all atoms. As a check for the correct composition, the occupancy parameters were refined in separate series of least-squares cycles. All sites were fully occupied within less than two standard uncertainties. In the last cycles the ideal occupancies were assumed again. A final difference Fourier synthesis revealed no significant residual peaks (see Table 1). The refined positional parameters and interatomic distances are listed in Tables 2 and 3. Further details on the structure refinements are available*.

The bulk sample and the single crystal measured on the diffractometer were analyzed by EDX using a LEICA 420 I scanning electron microscope with elemental niobium, palladium, and SiO_2 as standards. The crystal mounted on a quartz fibre was first coated with a thin carbon film. The EDX analyses (33 ± 2 at.-% Nb : 34 ± 2 at.-% Pd : 33 ± 2 at.-% Si) revealed no impurity elements and was in good agreement with the ideal composition.

*Details may be obtained from: Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No. CSD-416177.

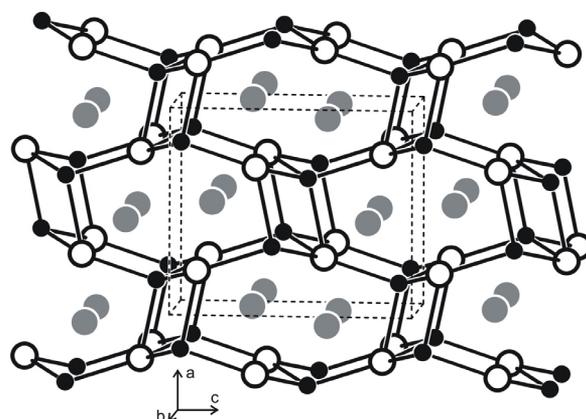


Fig. 1. View of the NbPdSi structure approximately along the y axis. Niobium, palladium, and silicon atoms are drawn as medium grey, filled, and open circles, respectively. The three-dimensional [PdSi] network is emphasized.

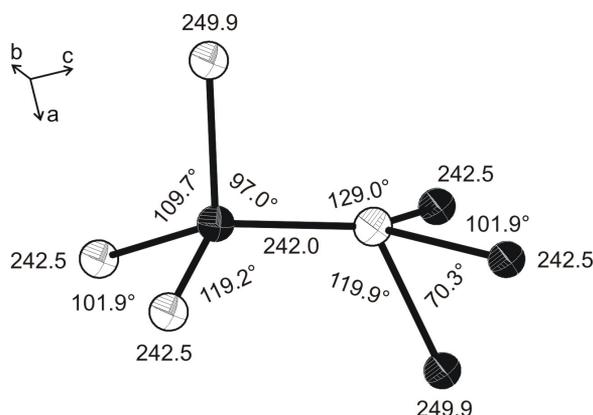


Fig. 2. Cutout of the three-dimensional [PdSi] network of NbPdSi. Palladium and silicon atoms are drawn as filled and open circles, respectively. Relevant bond distances and angles are indicated.

Discussion

The equiatomic silicide NbPdSi is isotypic with TiNiSi [7], and can furthermore be considered as a ternary ordered version of the Co_2Si structure [12]. Two distinct metal positions, here niobium and palla-

dium, cause an ordering of the transition metals due to their different sizes (metallic radii: $r_{\text{Nb}} = 143$, $r_{\text{Pd}} = 138$ pm [13]). As in the TiNiSi structure, the larger of the transition metals (titanium resp. niobium) has five Si neighbours and the smaller (nickel resp. palladium) only four as shown in Figs 1 and 2. The NbPdSi structure belongs to the large family of intermetallic compounds that are structurally derived from the AlB_2 type [14]. The palladium and silicon atoms build up fully ordered Pd_3Si_3 hexagons. The latter are strongly puckered (Fig. 1), and consequently we observe also interlayer Pd–Si interactions.

The Pd–Si distances within the three-dimensional [PdSi] network range from 242 to 250 pm, close to the sum of the covalent radii of 245 pm [13]. We can thus assume a considerable degree of Pd–Si bonding in this silicide. A cutout of the [PdSi] network is shown in Fig. 2. Although one observes quite similar Pd–Si distances, some of the Pd–Si–Pd and Si–Pd–Si angles substantially deviate from the tetrahedral angle. The palladium atoms show a relatively short Pd–Pd dis-

tance of 284 pm, only slightly longer than in *fcc* palladium (275 pm) [15]. We can thus assume weak Pd–Pd bonding interactions.

The situation is different for the niobium atoms. The Nb–Si (268–276 pm) and Nb–Pd (292–305 pm) distances are all longer than the sums of the covalent radii of 251 (Nb + Si) and 262 (Nb + Pd) pm [13]. The shorter Nb–Nb distances of 313 pm are comparable with *bcc* niobium (8×286 and 4×330 pm) [15]. This comparison of the interatomic distances strongly underlines the description with the three-dimensional [PdSi] network. This picture is consistent with recent electronic structure calculations on a variety of silicides within the TiNiSi family of compounds [16].

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