Structure determination of niobium palladium arsenide, $Nb_5Pd_4As_4$, from a $5 \times 5 \times 5\,\mu m^3$ crystal with synchrotron radiation

Meitian Wang,[a] Arthur Mar,[a,*] and Elizabeth J. MacLean[b]

[a] *Department of Chemistry, University of Alberta, Edmonton, Alta., Canada T6G 2G2*
[b] *CLRC Daresbury Laboratory, Daresbury, Warrington WA4 4AD, UK*

Abstract

Niobium palladium arsenide, $Nb_5Pd_4As_4$, is the second phase found in the Nb–Pd–As system. It was synthesized by direct reaction of the elements and its crystal structure was determined from X-ray diffraction data obtained with synchrotron radiation on a $5 \times 5 \times 5\,\mu m^3$ single crystal at 150 K. $Nb_5Pd_4As_4$ is isostructural to $Nb_5Pd_4P_4$ and adopts the $Nb_5Cu_4Si_4$-type structure (tetragonal, space group $I4/m$, $Z = 2$, $a = 10.4457(17)\,\text{Å}$, $c = 3.7868(6)\,\text{Å}$). The structure can be described as being built up of As-centered trigonal prisms whose vertices are Nb and Pd atoms, or as chains of octahedral Nb_6 clusters embedded in As_8 cubes parallel to chains of edge-sharing tetrahedral Pd_4 clusters. Extended Hückel calculations show that metal–metal bonding constitutes the most important contribution to the stability of the structure, and that the Pd atoms are close to being zero-valent.
© 2003 Elsevier Science (USA). All rights reserved.

Keywords: Arsenide; Niobium; Palladium; Crystal structure; Synchrotron radiation

1. Introduction

Although structural information can be extracted from powder X-ray diffraction data, it is always preferable to analyze single-crystal X-ray diffraction data whenever possible because of the greater precision that can be obtained. The high intensity of modern synchrotron radiation sources, along with the high sensitivity of CCD-based detectors, is now enabling very small crystals to be examined [1,2].

In the (Nb, Ta)–Pd–(P, As, Sb) system, the only compounds known thus far are $Nb_5Pd_4P_4$ [3] and Nb_9PdAs_7 [4]. Interest in these compounds stems from the desire to understand the role of metal–metal bonding in metal-rich pnictides and to systematize the poorly investigated crystal chemistry of the Pd systems in contrast to the analogous Ni systems. Reported here are the synthesis, structure, and bonding of the ternary arsenide $Nb_5Pd_4As_4$, isostructural to $Nb_5Pd_4P_4$. Because of difficulties in growing large single crystals of $Nb_5Pd_4As_4$, the original intention was to collect powder diffraction data for the purpose of structure determina-

tion. However, we were successful in extracting from the powder sample a single crystal of dimensions $5 \times 5 \times 5\,\mu m^3$, on which X-ray diffraction data were collected with the use of synchrotron radiation.

2. Experimental

2.1. Synthesis

A 0.25-g mixture of Nb powder (99.8%, Cerac), Pd powder (99.95%, Cerac), and As powder (99.99%, Alfa-Aesar) in the ratio 5:4:4 was loaded into an alumina tube jacketed by a fused-silica tube. The tube was evacuated and heated at 600°C for 1 day and 1000°C for 3 days, resulting in a quantitative yield of $Nb_5Pd_4As_4$ in the form of a black powder, as determined by the powder X-ray diffraction pattern obtained on an Enraf-Nonius FR552 Guinier camera (Cu$K\alpha_1$ radiation; Si standard).

2.2. Structure determination

X-ray diffraction data were collected on a Bruker AXS SMART CCD area-detector diffractometer [5] at the microcrystal diffraction facility on station 9.8 of the

*Corresponding author. Fax: +1-780-492-8231.
E-mail address: arthur.mar@ualberta.ca (A. Mar).

Synchrotron Radiation Source, CLRC Daresbury Laboratory [6,7]. The crystal was mounted on the end of a two-stage glass fiber with perfluoropolyether oil, and cooled by a Cryostream nitrogen-gas stream [8]. The wavelength was calibrated by measurement of the unit cell parameters of a standard crystal of known structure. Data collection proceeded through three series of ω-rotation exposure frames with different crystal orientation ϕ angles. Reflection intensities were integrated using standard procedures [9], allowing for the plane-polarized nature of the primary synchrotron beam. Corrections were applied semiempirically for absorption and incident beam decay [9]. Unit cell parameters were refined from the observed ω angles of all strong reflections in the complete data set [9]. The structure was solved by direct methods and refined by least-squares methods on all unique measured F^2 values [10]. The centrosymmetric space group $I4/m$ was chosen on the assumption that $Nb_5Pd_4As_4$ is isostructural to $Nb_5Pd_4P_4$ [3]. Technical details are given in Table 1. Final values of the positional and displacement parameters are given in Table 2. Interatomic distances are listed in Table 3. Further data, in the form of a CIF, have been sent to Fachinformationszentrum Karlsruhe, Abt. PROKA, 76344 Eggenstein-Leopoldshafen, Germany, as supplementary material No. CSD-412866 and

Table 1
Crystal data for $Nb_5Pd_4As_4$

Formula	$Nb_5Pd_4As_4$
Formula mass (amu)	1189.83
Temperature (K)	150(2)
Radiation	Synchrotron, $\lambda = 0.6880\,\text{Å}$
Space group	$C_{4h}^5 - I4/m$ (No. 87)
a (Å)	10.4457(17)
c (Å)	3.7868(6)
V (Å^3)	413.19(12)
Z	2
ρ_{calcd} (g cm^{-3})	9.563
μ (mm^{-1})	30.964
Crystal dimensions (mm)	$0.005 \times 0.005 \times 0.005$
Transmission factors	0.861–0.861
2θ limits	$5.34° \leqslant 2\theta \leqslant 57.78°$
Data collected	$-14 \leqslant h \leqslant 14, -14 \leqslant k \leqslant 10,$ $-5 \leqslant l \leqslant 4$
No. of data collected	1483
No. of unique data, including $F_o^2 < 0$	339 ($R_{int} = 0.0113$)
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	313
No. of variables	21
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)^a$	0.026
$R_w(F_o^2)^b$	0.069
Goodness of fit	1.122
$(\Delta\rho)_{max}, (\Delta\rho)_{min}$ (e Å^{-3})	1.987, −1.723

$^a R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

$^b R_w(F_o^2) = \left[\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4 \right]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (0.0405p)^2 + 14.4413p]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $Nb_5Pd_4As_4$

Atom	Wyckoff position	x	y	z	U_{eq} (Å^2)^a
Nb(1)	2a	0	0	0	0.0044(3)
Nb(2)	8h	0.30972(8)	0.38055(8)	0	0.0042(2)
Pd	8h	0.40547(7)	0.11028(6)	0	0.0038(2)
As	8h	0.06659(9)	0.24482(9)	0	0.0033(2)

$^a U_{eq}$ is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected interatomic distances (Å) in $Nb_5Pd_4As_4$

Nb(1)–As	2.6502(10) ($\times 4$)	Nb(2)–Nb(1)	3.0154(7) ($\times 2$)
Nb(1)–Nb(2)	3.0154(7) ($\times 8$)	Nb(2)–Nb(2)	3.3189(12) ($\times 2$)
Nb(2)–As	2.6400(9) ($\times 2$)	Nb(2)–Nb(2)	3.5469(14) ($\times 2$)
Nb(2)–As	2.7723(9) ($\times 2$)	Pd–As	2.4415(8) ($\times 2$)
Nb(2)–As	2.9086(13)	Pd–As	2.4959(12)
Nb(2)–Pd	2.9406(9) ($\times 2$)	Pd–Pd	2.8616(8) ($\times 4$)
Nb(2)–Pd	2.9951(12)	Pd–Pd	3.0344(14)
Nb(2)–Pd	3.0554(11)		

Table 4
Extended Hückel parameters

Atom	Orbital	H_{ii} (eV)	ζ_{i1}	c_1	ζ_{i2}	c_2
Nb	5s	−9.04	1.89			
	5p	−5.13	1.85			
	4d	−9.94	4.08	0.6401	1.64	0.5516
Pd	5s	−7.51	2.19			
	5p	−3.86	2.15			
	4d	−12.53	5.98	0.55	2.61	0.67
As	4s	−16.22	2.23			
	4p	−12.16	1.89			

can be obtained by contacting FIZ (quoting the article details and the corresponding CSD numbers).

2.3. Band structure

A tight-binding extended Hückel band structure calculation was performed on $Nb_5Pd_4As_4$ with the use of the EHMACC suite of programs [11,12]. The atomic parameters were taken from literature values [4] and are listed in Table 4. Properties were extracted from the band structure using 128 k points in the irreducible portion of the Brillouin zone.

3. Results and discussion

$Nb_5Pd_4As_4$ is the second phase found in the Nb–Pd–As system, in which Nb_9PdAs_7 was recently discovered [4]. It is isostructural to the phosphides $Nb_5Ni_4P_4$
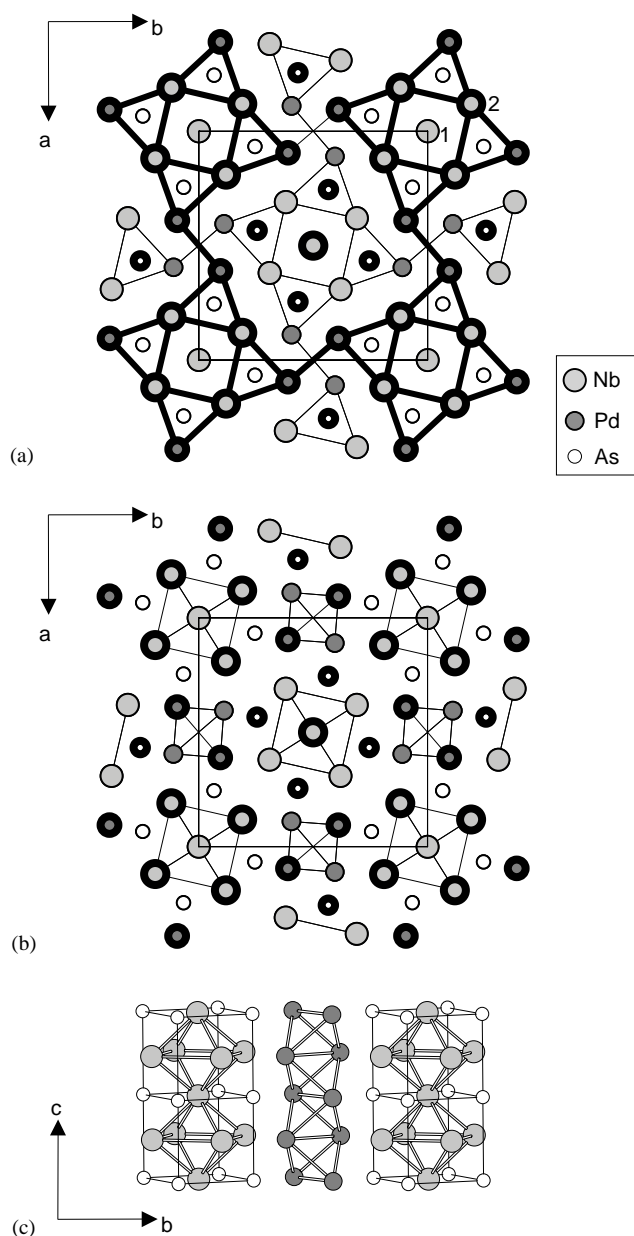
Fig. 1. Projection down the *c*-axis of the structure of $Nb_5Pd_4As_4$, in terms of (a) As-centered trigonal prisms or (b) Nb_6 octahedra and Pd_4 tetrahedra. Atoms marked with heavy rims are displaced by $\frac{1}{2}$ the *c* unit repeat. The chains of Nb_6As_8 and Pd_4 clusters are shown in (c).

[13,14], $Ta_5Ni_4P_4$ [14], and $Nb_5Pd_4P_4$ [3], which belong to the $Nb_5Cu_4Si_4$ structure type [15]. Fig. 1 shows different representations of the $Nb_5Pd_4As_4$ structure. In common with many transition-metal pnictides whose metal-to-pnicogen ratio is close to 2:1, the structure can be described through pnicogen-centered trigonal prisms as building blocks. Fig. 1a shows how such As-centered trigonal prisms, each with four Nb and two Pd atoms at the vertices, are connected to form tetramers; the center of each tetramer contains an additional Nb atom. The tetramers are then connected together through Pd–Pd bonds. This viewpoint draws out the relationship to

Nb_9PdAs_7, whose structure can also be built up of As-centered trigonal prisms [4]. Figs. 1b and c portray the structure of $Nb_5Pd_4As_4$ in the more customary fashion as consisting of two types of chains aligned along the *c* direction: one contains As_8 cubes embedding octahedral Nb_6 clusters compressed along the *c* direction and sharing opposite corners, and the other contains edge-sharing Pd_4 tetrahedra. This viewpoint emphasizes the relationship to other structures built up of one-dimensional corner-shared M_6X_8 clusters, so that the Nb_5Cu_4 Si_4-type structure is sometimes described as being a filled Ti_5Te_4-type structure [16]. Neither description is completely satisfactory, of course. The first description neglects some Nb–Nb bonds, the second description neglects Nb–Pd bonds but overemphasizes the long As–As distances (> 3.7 Å) (Fig. 1c), and both descriptions neglect the presence of Nb–As and Pd–As bonds.

Similar to the analysis for Nb_9PdAs_7 [4], examination of the relative electronegativities suggests that any electron transfer will occur predominantly from Nb to As in the formation of Nb–As bonds. Assuming full electron transfer, the resulting formulation $(Nb^{2.4+})_5(Pd^0)_4(As^{3-})_4$ then implies that there are 2.6 valence electrons remaining on each Nb atom available for additional metal–metal bonding. Such a formulation also suggests that the Pd atoms can enter as guests into a hypothetical host structure "Nb_5As_4" that corresponds to the Ti_5Te_4-type structure. (Although Nb_5As_4 is unreported, the analogues Ta_5As_4 [17,18], Nb_5Sb_4 [19,20], and Ta_5Sb_4 [21] are known.) To evaluate the bonding more accurately, the band structure of $Nb_5Pd_4As_4$ was calculated. Fig. 2 shows the density of states (DOS) curve and its atomic projections. Consistent with expectations, there remain many unfilled Nb $4d$ states above the Fermi level whereas the Pd $4d$ and As $4p$ states are almost completely filled below the Fermi level ($\varepsilon_f = -9.72$ eV). Fig. 3 shows the crystal orbital overlap population (COOP) curves for various contacts. The dominant contribution to the stability of $Nb_5Pd_4As_4$ is the formation of Nb–Nb and Nb–As bonds, as these are the interactions that are optimized through complete occupation of all the bonding levels and no antibonding levels (Figs. 3a and c). In the structural description emphasizing chains of Nb_6 clusters, the range of intrachain Nb–Nb distances of 3.0154(7)–3.3189(12) Å corresponds to a Mulliken overlap population (MOP) of 0.197 whereas the longer interchain Nb–Nb distance of 3.5469(14) Å still has a substantial MOP value of 0.095. The Nb–As bonds of 2.6400(9)–2.9086(13) Å are strong (MOP 0.353). The remaining types of bonds are not optimized, since some antibonding levels have to be occupied. This lends support to the idea that the Pd atoms can be viewed as guests inserted into a "Nb_5As_4" matrix, similar to a proposal made for the Ni atoms in $Nb_5Ni_4P_4$ [13]. Although weak, the Nb–Pd bonds of 2.9406(9)–3.0554(11) Å

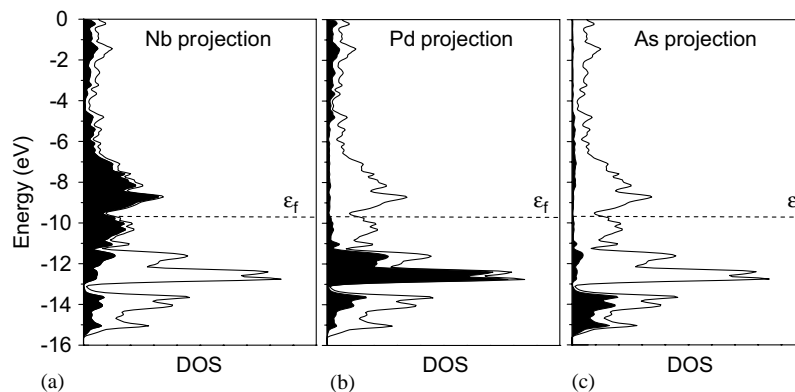Fig. 2. Contributions of (a) Nb, (b) Pd, and (c) As (shaded regions) to the total density of states (DOS) (line) for $Nb_5Pd_4As_4$. The horizontal line marks the Fermi level ($\varepsilon_f = -9.72$ eV).
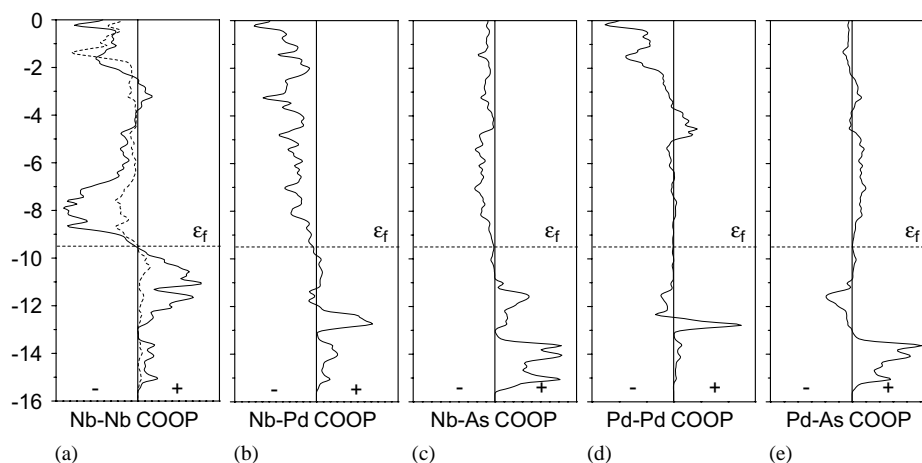

Fig. 3. Crystal orbital overlap population (COOP) curves for (a) Nb–Nb (solid line, intracluster; dashed line, intercluster), (b) Nb–Pd, (c) Nb–As, (d) Pd–Pd, and (e) Pd–As interactions in $Nb_5Pd_4As_4$.

(MOP 0.070) can be considered as originating from a Lewis acid–base interaction between early and late transition metals [22]. The Mulliken charges are found to be $+0.32$ for Nb, -0.25 for Pd, and -0.15 for As. It may seem surprising that Pd carries the most negative charge, but this reflects its similar electronegativity compared to As ($\chi_{Pauling} = 2.2$ for both elements). Situations involving weakly electronegative ligands, relative to the transition metals, have been previously discussed [23,24]. The Pd atoms can be regarded as being essentially closed shell, with a d^{10} configuration to a first approximation. Correspondingly, formation of the Pd–As bonds of 2.4415(8)–2.4959(12) Å (MOP 0.211) requires some antibonding levels to be filled (Fig. 3e). The weak Pd–Pd bonds of 2.8616(8)–3.0344(14) Å (MOP 0.027) originate from d^{10}–d^{10} interactions [25] that mix in contributions from 5s and 5p states so that there is a small net stabilization of bonding despite the occupation of antibonding states, as shown in the COOP curve (Fig. 3d). A closer

inspection of the integrated atomic orbital projections of the DOS suggests that the configuration of Pd in the compound is $4d^{9.63}\,5s^{0.35}\,5p^{0.27}$. A possible interpretation is that the weak Pd–Pd bonding arises primarily from dispersion interactions between essentially d^{10} cores with a small degree of covalent interactions between 5s and 5p orbitals. The band structure of $Nb_5Pd_4As_4$ resembles those of $Nb_5Pd_4P_4$ [26] and $Nb_5Ni_4P_4$ [13]. Although MOP values cannot be compared directly between different types of contacts, the Nb–Nb and Nb–pnicogen interactions are always the most important in all three structures. The MOP values for the Ni–Ni or Pd–Pd contacts are always small but positive, supporting the proposal of d^{10}–d^{10} interactions.

This work has further demonstrated the feasibility of synchrotron radiation in single-crystal X-ray diffraction analysis to obtain accurate structural information on samples that would otherwise be dismissed as powder. The description of $Nb_5Pd_4As_4$ as being derived from inserting essentially neutral Pd atoms as guests suggests

that it may be worth targeting the preparation of the host structure "Nb_5As_4", as well as other stuffed $M_5M'_4Pn_4$ compounds.

Acknowledgments

References

[1] J.J. Pluth, J.V. Smith, D.Y. Pushcharovsky, E.I. Semenov, A. Bram, C. Riekel, H.-P. Weber, R.W. Broach, Proc. Natl. Acad. Sci. USA 94 (1997) 12263.

[2] P.C. Burns, J.J. Pluth, J.V. Smith, P. Eng, I. Steele, R.M. Housley, Am. Mineral. 85 (2000) 604.

[3] M. Wang, R. McDonald, A. Mar, Inorg. Chem. 39 (2000) 4936.

[4] M. Wang, A. Mar, Inorg. Chem. 40 (2001) 5365.

[5] SMART, Version 5.054, Bruker AXS Inc., Madison, WI, 1998.

[6] R.J. Cernik, W. Clegg, C.R.A. Catlow, G. Bushnell-Wye, J.V. Flaherty, G.N. Greaves, I. Burrows, D.J. Taylor, S.J. Teat, M. Hamichi, J. Synchrotron Radiat. 4 (1997) 279.

[7] W. Clegg, M.R.J. Elsegood, S.J. Teat, C. Redshaw, V.C. Gibson, J. Chem. Soc., Dalton Trans. (1998) 3037.

[8] J. Cosier, A.M. Glazer, J. Appl. Crystallogr. 19 (1986) 105.

[9] SAINT, Version 6.02a, Bruker AXS Inc., Madison, WI, 2000.

[10] G.M. Sheldrick, SHELXTL, Version 5.10, Bruker AXS Inc., Madison, WI, 1998.

[11] M.-H. Whangbo, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 6093.

[12] R. Hoffmann, Solids and Surfaces: A Chemist's View of Bonding in Extended Structures, VCH Publishers, New York, 1988.

[13] F. Charki, S. Deputier, P. Benard-Rocherulle, R. Guérin, M. Bouayed, A. Le Beuze, J.Y. Saillard, Solid State Sci. 1 (1999) 607.

[14] R. Berger, P. Phavanantha, M. Mongkolsuk, Acta Chem. Scand., Ser. A 34 (1980) 77.

[15] E. Ganglberger, Monatsh. Chem. 99 (1968) 549.

[16] A. Simon, Angew. Chem., Int. Ed. Engl. 20 (1981) 1.

[17] R. Dronskowski, A. Simon, P. Plambeck-Fischer, Z. Kristallogr. 198 (1992) 101.

[18] S. Rundqvist, B. Carlsson, C.-O. Pontchour, Acta Chem. Scand., Ser. A 23 (1969) 2188.

[19] H. Boller, H. Nowotny, Monatsh. Chem. 95 (1964) 1272.

[20] S. Furuseth, A. Kjekshus, Acta Chem. Scand. 18 (1964) 1180.

[21] S.K. Kang, G.J. Miller, Acta Crystallogr., Sect. C 55 (1999) 483.

[22] L. Brewer, P.R. Wengert, Metall. Trans. 4 (1973) 83.

[23] K.-S. Lee, H.-J. Koo, D. Dai, J. Ren, M.-H. Whangbo, Inorg. Chem. 38 (1999) 340.

[24] H.-J. Koo, M.-H. Whangbo, Inorg. Chem. 38 (1999) 2204.

[25] P. Pyykkö, Chem. Rev. 97 (1997) 597.

[26] M. Wang, A. Mar, unpublished results.