




## Article

# The crystal structure of arsenopalladinite, Pd<sub>8</sub>As<sub>2.5</sub>Sb<sub>0.5</sub>, and its relation to mertieite-II, Pd<sub>8</sub>Sb<sub>2.5</sub>As<sub>0.5</sub>

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### Abstract

The crystal structure of arsenopalladinite, Pd<sub>8</sub>As<sub>2.5</sub>Sb<sub>0.5</sub>, from the Kaarreoja River, Inari commune, Finnish Lapland, Finland, was solved to  $R_1 = 0.0451$  on the basis of single-crystal X-ray diffraction data. The mineral is triclinic, space group  $P\bar{1}$ . The unit-cell parameters are:  $a = 7.3344(7)$ ,  $b = 7.3870(8)$ ,  $c = 7.5255(7)$  Å,  $\alpha = 98.869(8)$ ,  $\beta = 102.566(8)$ ,  $\gamma = 119.096(11)^\circ$ ,  $V = 331.19(7)$  Å<sup>3</sup> and  $Z = 2$ . The crystal structure of arsenopalladinite consists of an alternation of layers made by pnictogen (As, Sb) and layers made by palladium atoms stacked along the  $c$  axis. Arsenic and (As, Sb) nets exhibit a triangular topology ( $A$  and  $D$  nets), whereas palladium layers show triangular or pentagon-triangular nets ( $B$  and  $C$  nets). The unit-cell contains 6 layers, with the  $ABCDCBA$  stacking sequence. Although arsenopalladinite shows characteristics very similar (nets of the same topology) to the closely-related mineral mertieite-II, Pd<sub>8</sub>Sb<sub>2.5</sub>As<sub>0.5</sub>, it has a different stacking sequence.

**Keywords:** arsenopalladinite, crystal structure, pnictogen nets, palladium nets

(Received 20 May 2020; accepted 10 August 2020; Accepted Manuscript published online: 28 August 2020; Associate Editor: František Laufek)

### Introduction

Arsenopalladinite was discovered in the residual concentrates from gold washing at Itabira, Minas Gerais, Brazil. It was reported firstly with the Pd<sub>3</sub>As stoichiometry and with a hexagonal unit cell of  $a = 6.80$ ,  $c = 3.48$  Å (Claringbull and Hey, 1957). Later, Clark *et al.* (1974) determined that concentrates contained three palladium arsenide–antimonide minerals: arsenopalladinite; atheneite, (Pd,Hg)<sub>3</sub>As; and isomertieite, (Pd,Cu)<sub>5</sub>(Sb,As)<sub>2</sub>. The grains defined originally as hexagonal arsenopalladinite actually turned out to be atheneite. Clark *et al.* (1974) redefined the arsenopalladinite formula as Pd<sub>5</sub>(As,Sb)<sub>2</sub>. The unit-cell was found to be triclinic:  $a = 7.399$ ,  $b = 14.063$ ,  $c = 7.352$  (Å),  $\alpha = 92^\circ 03'$ ,  $\beta = 118^\circ 57'$  and  $\gamma = 95^\circ 54'$  (Clark *et al.*, 1974).

A few years later, Cabri *et al.* (1977) studied arsenopalladinite from Itabira, Minas Gerais, Brazil and from the Stillwater Complex, Montana, and revised the chemical formula to Pd<sub>8</sub>(As,Sb)<sub>3</sub>. Furthermore, the As:Sb ratio in arsenopalladinite was found to be equal to 5:1 and the triclinic symmetry was confirmed.

Relations between mertieite-I, mertieite-II, isomertieite, stillwaterite and arsenopalladinite remained uncertain for a long time. The crystal structures of atheneite, isomertieite and mertieite-II have been recently elucidated. Atheneite was studied by Bindi (2010), who found that Hg atoms enter one of the As sites and redefined the mineral formula as Pd<sub>2</sub>(As<sub>0.75</sub>Hg<sub>0.25</sub>)

with  $Z = 3$ . The mineral was found to be hexagonal, with space group  $P\bar{6}2m$ ,  $a = 6.813(1)$ ,  $c = 3.4892(5)$  Å and  $V = 140.26(4)$  Å<sup>3</sup>.

The isomertieite formula was earlier revised as Pd<sub>11</sub>Sb<sub>2</sub>As<sub>2</sub> (Cabri and Laflamme, 1979, Cabri, 1981). Its crystal structure was refined recently in the space group  $Fd\bar{3}m$ , with  $a = 12.297(5)$  Å,  $V = 1859.3(2)$  Å<sup>3</sup> and  $Z = 8$  (Karimova *et al.*, 2016). The structure of mertieite-II, Pd<sub>8</sub>Sb<sub>2.5</sub>As<sub>0.5</sub>, was also studied recently (Karimova *et al.*, 2018). Mertieite-II is trigonal,  $R\bar{3}c$ , with  $a = 7.5172(3)$ ,  $c = 43.037(2)$  Å,  $V = 2106.1(2)$  Å<sup>3</sup>, and  $Z = 12$ . Here we report the first determination of the crystal structure of arsenopalladinite.

### Materials and methods

Arsenopalladinite crystals for the structural study were provided by Dr. Kari Kojonen, Geological Survey of Finland (GSF). Grains were collected from the black sands of gold placers from the Kaarreoja River, Inari commune, Finnish Lapland, Finland (68.65°N, 25.63°E).

The chemical composition was determined using a Cameca SX 100 electron microprobe (Table 1). The wavelength-dispersive spectroscopy analyses were performed with an operating voltage of 15 kV, a beam current of 20 nA, and a beam diameter of 1 µm. Pure Pd, Rh, Pt, cobaltite (for As), Sb<sub>2</sub>Te<sub>3</sub> (for Sb), chalcopyrite (for Cu and S) and hematite (for Fe) were used as standards.  $AsL\alpha$  (LIF diffracting crystal),  $PdL\alpha$  (LIF),  $SbL\alpha$  (PET),  $SK\alpha$  (PET),  $FeK\alpha$  (LIF),  $RhL\alpha$  (PET),  $PtL\alpha$  (LIF) and  $CuK\alpha$  (LIF) spectral lines were used.

The same crystal used for the chemical study was analysed by single-crystal X-ray diffraction at the XRD Centre of Research Park of St. Petersburg State University. A hemisphere of three-dimensional data was collected at room temperature using an

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Cite this article: Karimova O.V., Zolotarev A.A., Johanson B.S. and Evstigneeva T.L. (2020) The crystal structure of arsenopalladinite, Pd<sub>8</sub>As<sub>2.5</sub>Sb<sub>0.5</sub>, and its relation to mertieite-II, Pd<sub>8</sub>Sb<sub>2.5</sub>As<sub>0.5</sub>. *Mineralogical Magazine* 84, 746–752. <https://doi.org/10.1180/mgm.2020.65>

**Table 1.** Representative\* analysis of arsenopalladinite (microprobe).

Element	Wt.%	Wt.%	Wt.%
As	16.18 (15.91–16.41)	16.13 (15.83–16.31)	16.13 (15.72–16.37)
Pd	77.67 (77.14–78.26)	77.68 (77.09–78.11)	77.46 (76.56–77.93)
Sb	5.41 (5.32–5.49)	5.45 (5.31–5.55)	5.44 (5.31–5.56)
Sum	99.45	99.53	99.23
Formula**	Pd <sub>8.11</sub> As <sub>2.40</sub> Sb <sub>0.49</sub>	Pd <sub>8.11</sub> As <sub>2.39</sub> Sb <sub>0.50</sub>	Pd <sub>8.11</sub> As <sub>2.40</sub> Sb <sub>0.50</sub>

\*Average analysis along the profiles.

\*\*Calculated with 11 atoms per formula unit.

**Table 2.** Crystal data and structure refinement for arsenopalladinite.

Crystal data	
Structural formula	Pd <sub>8</sub> As <sub>2.5</sub> Sb <sub>0.5</sub>
Crystal system	Triclinic
Space group	<i>P</i> 1
<i>a</i> (Å)	7.3344(7)
<i>b</i> (Å)	7.3870(8)
<i>c</i> (Å)	7.5255(7)
$\alpha$ (°)	98.869(8)
$\beta$ (°)	102.566(8)
$\gamma$ (°)	119.096(11)
<i>V</i> (Å <sup>3</sup> )	331.19(7)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	11.024
$\mu$ (mm <sup>-1</sup> )	35.472
Data collection	
Diffractometer	Xcalibur Eos
Radiation	MoK $\alpha$ ( $\lambda = 0.7107$ )
Temperature (K)	296(1)
2 $\theta$ range for data collection (°)	3 to 26
<i>R</i> <sub>int</sub> , <i>R</i> <sub>sigma</sub> (%)	5.45, 4.78
Refinement	
Reflections collected	4130
Independent reflections	1299
Observed reflections [ <i>F</i> <sub>o</sub> ≥ 4 $\sigma$ ( <i>F</i> <sub>o</sub> )]	1224
Data / restraints / parameters	1299/0/103
<i>S</i> (Goodness-of-fit on <i>F</i> <sup>2</sup> )	1.117
<i>R</i> [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0451, <i>wR</i> <sub>2</sub> = 0.1216
<i>R</i> (all data)	<i>R</i> <sub>1</sub> = 0.0479, <i>wR</i> <sub>2</sub> = 0.1241
$\Delta\rho$ (max)/(min) (e <sup>-</sup> /Å <sup>-3</sup> )	2.804/ -2.890

Xcalibur Eos diffractometer, which was operated at 50 kV and 40 mA (monochromatic MoK $\alpha$  X-radiation). The data were integrated and corrected by means of the *CrysAlisPro* (Agilent Technologies, 2012) program package, which was also used to

**Table 4.** Selected bond lengths (Å) for arsenopalladinite.

Pd1–As3	2.5394(4)	Pd2–As1	2.4558(5)	Pd3–As1	2.4280(2)
Pd1–As3	2.5700(3)	Pd2–As2	2.4660(2)	Pd3–As2	2.4816(5)
Pd1–Pd4	2.8971(3)	Pd2–Pd8	2.7344(4)	Pd3–Pd5	2.7660(2)
Pd1–Pd8	2.9080(3)	Pd2–Sb1	2.7460(4)	Pd3–Pd6	2.7692(3)
Pd1–Pd1	2.9101(2)	Pd2–Pd7	2.7952(5)	Pd3–As2	2.7784(3)
Pd1–Pd3	2.9220(6)	Pd2–Pd5	2.8197(3)	Pd3–As3	2.7969(4)
Pd1–Sb1	2.9498(3)	Pd2–Pd6	2.8841(5)	Pd3–Pd8	2.8091(3)
Pd1–Pd6	2.9502(5)	Pd2–Pd3	2.8851(3)	Pd3–Pd4	2.8730(4)
Pd1–Pd2	2.9641(2)	Pd2–Pd7	2.9049(3)	Pd3–Pd2	2.8851(3)
Pd1–As2	2.9760(4)	Pd2–As2	2.9104(3)	Pd3–Pd5	2.9021(5)
Pd1–Pd5	3.0714(6)	Pd2–Pd1	2.9641(2)	Pd3–Pd1	2.9220(6)
Pd1–Pd7	3.0739(3)	Pd2–Pd4	3.0512(3)	Pd3–Pd3	3.1570(3)
Pd4–As1	2.4464(3)	Pd5–As3	2.4543(2)	Pd6–As3	2.4920(6)
Pd4–As3	2.4761(2)	Pd5–As2	2.5100(2)	Pd6–As2	2.5923(3)
Pd4–Sb1	2.7755(6)	Pd5–Sb1	2.6594(3)	Pd6–Sb1	2.7584(3)
Pd4–Pd7	2.7832(4)	Pd5–Pd3	2.7660(2)	Pd6–Pd3	2.7692(3)
Pd4–Pd7	2.8301(5)	Pd5–Pd6	2.7930(3)	Pd6–Pd8	2.7738(4)
Pd4–Pd8	2.8472(3)	Pd5–Pd2	2.8197(3)	Pd6–Pd5	2.7930(3)
Pd4–Pd3	2.8730(4)	Pd5–Pd6	2.8552(3)	Pd6–Pd5	2.8552(3)
Pd4–Pd1	2.8971(3)	Pd5–Pd7	2.8646(4)	Pd6–As3	2.8833(3)
Pd4–As3	2.9091(2)	Pd5–Pd3	2.9021(5)	Pd6–Pd2	2.8841(5)
Pd4–Pd6	2.9260(4)	Pd5–Pd4	2.9453(3)	Pd6–Pd4	2.9260(4)
Pd4–Pd5	2.9453(3)	Pd5–Pd1	3.0714(6)	Pd6–Pd7	2.9412(3)
		Pd5–Pd1	3.2001(5)	Pd6–Pd1	2.9502(5)
Pd7–As3	2.4647(4)	Pd8–As2	2.3873(2)	As1–Pd3 ×2	2.4280(2)
Pd7–As2	2.4930(4)	Pd8–As1	2.5948(2)	As1–Pd4 ×2	2.4464(3)
Pd7–Sb1	2.7397(3)	Pd8–Pd2	2.7344(4)	As1–Pd2 ×2	2.4558(5)
Pd7–Pd4	2.7832(4)	Pd8–Pd6	2.7738(4)	As1–Pd8 ×2	2.5948(2)
Pd7–Pd2	2.7952(5)	Pd8–As3	2.8034(3)		
Pd7–Pd4	2.8301(5)	Pd8–Pd3	2.8091(3)	Sb1–Pd5 ×2	2.6594(3)
Pd7–Pd8	2.8379(3)	Pd8–Pd7	2.8379(3)	Sb1–Pd7 ×2	2.7397(3)
Pd7–Pd5	2.8646(4)	Pd8–Pd4	2.8472(3)	Sb1–Pd2 ×2	2.7460(4)
Pd7–Pd2	2.9049(3)	Pd8–As2	2.8792(6)	Sb1–Pd6 ×2	2.7584(3)
Pd7–Pd6	2.9412(3)	Pd8–Pd1	2.9080(3)	Sb1–Pd4 ×2	2.7755(6)
Pd7–Pd1	3.0739(3)	Pd8–Pd8	2.9226(5)	Sb1–Pd1 ×2	2.9498(3)
Pd7–Pd1	3.1568(3)	Pd8–Pd1	3.1231(4)		
As2–Pd8	2.3873(2)	As3–Pd5	2.4543(2)		
As2–Pd2	2.4660(2)	As3–Pd7	2.4647(4)		
As2–Pd3	2.4816(5)	As3–Pd4	2.4761(2)		
As2–Pd7	2.4930(4)	As3–Pd6	2.4920(6)		
As2–Pd5	2.5100(2)	As3–Pd1	2.5394(4)		
As2–Pd6	2.5923(3)	As3–Pd1	2.5700(3)		
As2–Pd3	2.7784(3)	As3–Pd3	2.7969(4)		
As2–Pd8	2.8792(6)	As3–Pd8	2.8034(3)		
As2–Pd2	2.9104(3)	As3–Pd6	2.8833(3)		
As2–Pd1	2.9760(4)	As3–Pd4	2.9091(2)		

apply empirical absorption correction using spherical harmonics, implemented in the *SCALE3 ABSPACK* scaling algorithm. The structure was solved by direct methods using *SHELXT* program

**Table 3.** Atomic coordinates and equivalent isotropic and anisotropic displacement parameters (Å<sup>2</sup>) for arsenopalladinite.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	<i>U</i> <sup>11</sup>	<i>U</i> <sup>22</sup>	<i>U</i> <sup>33</sup>	<i>U</i> <sup>23</sup>	<i>U</i> <sup>13</sup>	<i>U</i> <sup>12</sup>
Sb1	1 <i>a</i>	0	0	0	0.010(1)	0.0079(6)	0.0133(8)	0.0054(5)	0.0060(6)	0.0054(6)	0.0098(3)
Pd1	2 <i>i</i>	0.4357(2)	0.0567(2)	0.1593(2)	0.017(1)	0.0134(6)	0.0212(7)	0.0066(5)	0.0087(5)	0.0080(5)	0.0170(3)
Pd2	2 <i>i</i>	0.1814(2)	0.1226(2)	0.3907(2)	0.016(1)	0.0120(6)	0.0187(7)	0.0050(5)	0.0005(5)	0.0054(5)	0.0165(3)
Pd3	2 <i>i</i>	0.7896(2)	0.5003(2)	0.3932(2)	0.021(1)	0.0129(6)	0.0312(8)	0.0014(5)	0.0153(6)	0.0034(5)	0.0212(4)
Pd4	2 <i>i</i>	0.3778(2)	0.4168(2)	0.1520(2)	0.025(1)	0.0089(6)	0.0188(7)	0.0053(5)	−0.0045(6)	0.0059(6)	0.0252(4)
Pd5	2 <i>i</i>	0.0506(2)	0.7101(2)	0.7968(2)	0.023(1)	0.03119(8)	0.0159(7)	0.0045(5)	0.00449(6)	0.0287(7)	0.0225(4)
Pd6	2 <i>i</i>	0.9865(2)	0.3095(2)	0.8441(2)	0.023(1)	0.0120(6)	0.0189(7)	0.0091(5)	−0.0016(6)	−0.0002(6)	0.0226(4)
Pd7	2 <i>i</i>	0.7230(2)	0.8474(2)	0.2067(2)	0.024(1)	0.0317(8)	0.0171(7)	0.0061(6)	0.0060(5)	0.0028(6)	0.0237(4)
Pd8	2 <i>i</i>	0.4092(2)	0.7740(3)	0.3954(2)	0.025(1)	0.0447(9)	0.0295(8)	0.0254(7)	0.0200(6)	0.0314(7)	0.0247(4)
As1	1 <i>h</i>	½	½	½	0.012(1)	0.010(1)	0.016(1)	0.0057(9)	0.0051(9)	0.0045(9)	0.0125(5)
As2	2 <i>i</i>	0.1677(3)	0.8345(3)	0.5261(2)	0.014(1)	0.0165(8)	0.0159(8)	0.0067(6)	0.0080(7)	0.0114(7)	0.0141(4)
As3	2 <i>i</i>	0.3345(2)	0.6753(2)	0.0015(2)	0.014(1)	0.0085(7)	0.0237(9)	0.0085(7)	0.0027(7)	0.0047(6)	0.0137(4)

**Table 5.** The coordination number (CN) together with the average values of Pd–Pd and Pd–As/Sb distances ( $d_m$ ) around the different atoms in arsenopallanite.

Central atom	CN(Pd)*	$d_m$ (Å)	CN(As/Sb)**	$d_m$ (Å)
Pd1	8	2.8943	4	2.7588
Pd2	8	2.8014	4	2.6446
Pd3	8	2.7974	4	2.6212
Pd4	7	2.7917	4	2.6518
Pd5	9	2.8201	3	2.5412
Pd6	8	2.8016	4	2.6815
Pd7	9	2.8238	3	2.5658
Pd8	8	2.7725	4	2.6662
Sb	12	2.7715		
As1	8	2.4813		
As2	10	2.6474		
As3	10	2.6389		

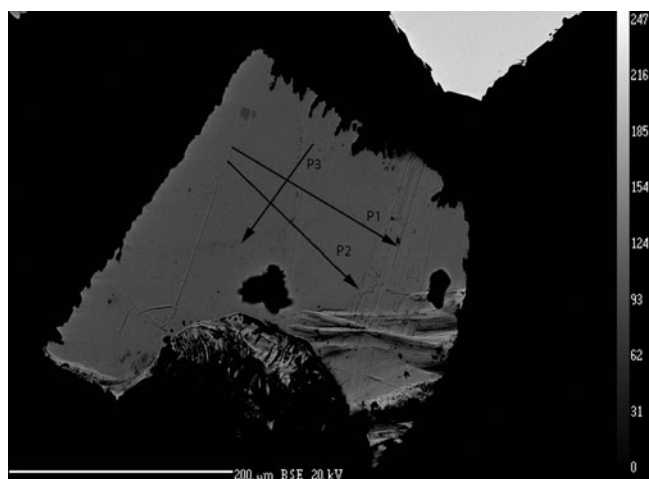
\*CN(Pd) is the number of nearest Pd neighbours;

\*\*CN(As/Sb) is the number of nearest As/Sb neighbours.

(Sheldrick, 2015a) in the frame of a *WinGX* programs package (Farrugia, 2012). Eight Pd, one Sb and three As sites were located in the structure. Refinement gave the full occupancies for As and Sb sites. The structure was refined to  $R_1 = 0.0451$  for 1224 unique observed reflections with  $|F_o| \geq 4\sigma F_o$  in an anisotropic approximation using *SHELXL* (Sheldrick, 2015b). The crystallographic data and selected refinement parameters are shown in Table 2. The final atomic coordinates and displacement parameters are listed in Table 3 and the selected interatomic distances are in Table 4. Table 5 shows the coordination numbers and the average values of the bond lengths. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

## Composition

The composition was obtained on the basis of 15 points along three lines across the crystal (Fig. 1). The mean analyses of each line are shown in Table 1. The element concentrations vary within very narrow limits (~1.5 wt.%). The average element contents (in wt.%) are: Pd 77.60, As 16.15, Sb 5.43. Minor amounts of S (0.01–0.09 wt.), Se (0.01–0.15 wt.), Pt (0.02–0.49 wt.%) and Cu (0.01–0.09 wt.%) were detected in

**Fig. 1.** SEM-BSE image of arsenopallanite,  $\text{Pd}_8\text{As}_{2.5}\text{Sb}_{0.5}$ .

some analyses. The empirical formula for arsenopallanite is  $\text{Pd}_{8.11}\text{As}_{2.39}\text{Sb}_{0.50}$ , calculated on the basis of 11 atoms per formula unit. The empirical formula calculated on the bases of 8 palladium atoms per formula unit is  $\text{Pd}_{8.00}\text{As}_{2.37}\text{Sb}_{0.49}$ .

## Crystal structure description

All palladium atoms occupy general positions in the structure (Wyckoff symbol  $2i$ ) (Table 3). One As atom is located on an inversion centre, at the Wyckoff position  $-1h$ , and the other two are in general positions  $2i$ . The antimony atoms site is located on another inversion centre – at the Wyckoff position  $1a$ .

The coordination polyhedra around all atoms are irregular (Fig. 2). The Pd and Sb sites have 12 neighbours (Tables 4, 5); the As1 site has 8 neighbours; As2 and As3 sites have 10 neighbours (Tables 4, 5). Interatomic distances in the structure vary significantly. The overall minimum Pd–As bond is 2.3873(2) Å. It is slightly less than the minimum palladium to arsenic distance in other Pd–As–Sb ternary minerals – mertieite-II and isomertieite are 2.488 and 2.465 Å, respectively (Karimova *et al.*, 2016; 2018). The characteristic feature of arsenopallanite is elongated Pd–As bonds to a maximum of 2.9760(4) Å. It is significantly longer than those bonds in mertieite-II and isomertieite are: 2.537 and 2.662 Å, respectively (Karimova *et al.*, 2016; 2018). The very long palladium to arsenic bonds (up to 3.380 Å) are also formed in the synthetic phase  $\text{Pd}_5\text{As}$  (Matkovic and Schubert, 1978). The Pd–Sb bonds lengths vary from 2.6594(3) Å to 2.9498(3) in arsenopallanite. This is in good agreement with those distances in isomertieite (2.708–2.894 Å, Karimova *et al.*, 2016). The palladium to antimony distances vary in wider limits in mertieite-II (2.602–3.340 Å, Karimova *et al.*, 2018), synthetic  $\text{Pd}_8\text{Sb}_3$  (2.594–3.303 Å, Marsh, 1994) and  $\text{Pd}_{20}\text{Sb}_7$  (2.600–3.303 Å, Wopersnow and Schubert, 1977).

The crystal structure of arsenopallanite is shown in Fig. 3. Atoms are located in layers stacked along the  $c$  axis, with palladium and pnictogen atoms (As and Sb) occupying different layers, respectively. The topology of the layers is described in Fig. 4. Antimony atoms site (Sb1) and one of the arsenic atom sites (As3) form a  $3^6$  triangular net (named the ‘A’ layer, Fig. 4). The next layer, ‘B’, is a distorted triangular net. It is formed by Pd2, Pd3 and Pd8 atomic sites. The next one, the ‘C’ layer, is pentagon–triangular net. It is formed by Pd1, Pd4, Pd5, Pd6 and Pd7 atomic sites. Finally, two arsenic atoms sites – As1 and As2 build a  $3^6$  triangular net (the ‘D’ layer). The A, B, C and D layers stack along the  $z$  direction of the unit cell (Fig. 3). The stacking sequence is: ABCDBCA. The unit cell contains 6 layers.

The crystal structure formula of arsenopallanite is  $\text{Pd}_{16}\text{As}_5\text{Sb}_1$  ( $Z=1$ ). It can be expressed in the form  $\text{Pd}_8\text{As}_{2.5}\text{Sb}_{0.5}$  ( $Z=2$ ), which is more suitable in order to compare it with other members of the mertieite mineral group.

## Discussion

The arsenopallanite unit cell reported here is the smallest, so-called reduced triclinic cell (Wolff, 2005). A larger unit cell was reported earlier in literature:  $a = 7.399$ ,  $b = 14.063$ ,  $c = 7.352$  (Å),  $\alpha = 92^\circ 03'$ ,  $\beta = 118^\circ 57'$ ,  $\gamma = 95^\circ 54'$  (Clark *et al.*, 1974, Cabri *et al.*, 1977, Cabri, 2002). These two cells are actually two possible choices describing the same crystal structure. The relation between them is shown in Fig. 5. The larger cell transforms into smaller one by transformation matrix  $(0 \ 0 \ \bar{1} / \bar{1} \ 0 \ 0 / \frac{1}{2} \ \frac{1}{2})$ .

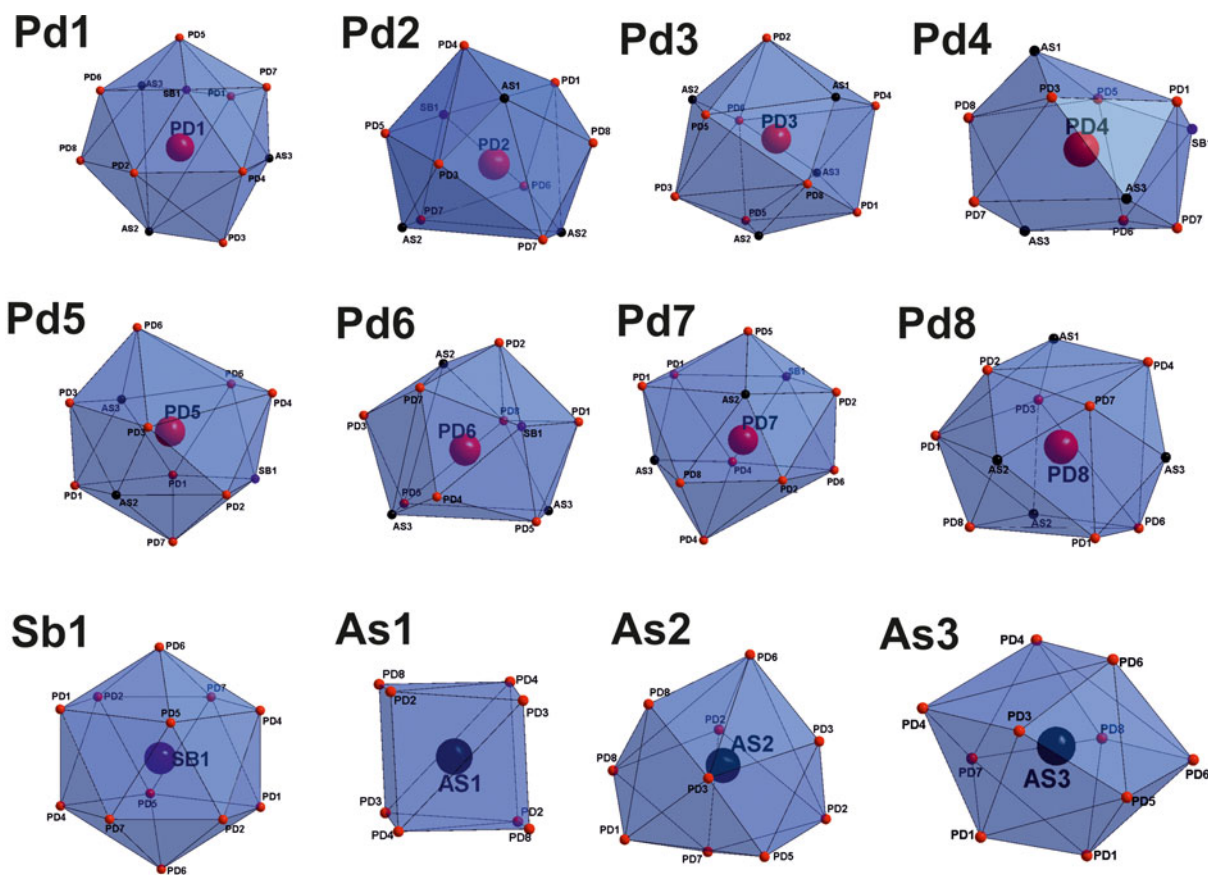


Fig. 2. Coordination polyhedra in the arsenopalladinite structure.

Pearson (1972) proposed describing the structures of metallic phases and intermetallic compounds in terms of atomic nets. The crystal structures of the minerals arsenopalladinite,  $Pd_8As_{2.5}Sb_{0.5}$ , and mertieite-II,  $Pd_8Sb_{2.5}As_{0.5}$ , have a close relation. The base of

the structure is the same in both cases. The structures are built up by layers of Pd and As/Sb atoms. The structural building unit is the same in both minerals. It is a package of 3 atomic layers: triangular pnictogen net + triangular Pd net + pentagon-triangular Pd net.

A key role in the structure stabilisation is played by the triangular nets of pnictogen atoms. The nets have identical  $-3^6$  topology in both minerals, but different plane symmetry. They are compared in Fig. 6. The plane symmetry of A and D nets in arsenopalladinite is  $p2$ . The plane symmetry of the pnictogen nets in mertieite-II is higher:  $p3m$  for the A net and  $p3$  for the D net. The nets contain several sites possibly hosting As and Sb atoms:  $T_1$ ,  $T_2$  and  $T_3$ . The arsenic and antimony distribution on positions at the nets are shown in Table 6. In the case of arsenopalladinite the  $T_1$  site is divided in two symmetry independent sites:  $T_1$  and  $T_1'$ . A common formula for both minerals can be expressed in a form:  $Pd_8T_{1.5}T_2T_{30.5}$ . Then, for mertieite-II it is  $Pd_8Sb_{1.5}Sb_1As_{0.5} = Pd_8T_{1.5}T_2T_{30.5}$  and for arsenopalladinite it is  $Pd_8As_1As_{0.5}Sb_{0.5} = Pd_8T_1T_{1'0.5}T_2T_{30.5}$ .

The pnictogen layers of two types alternate along the  $c$  axis in the structures of mertieite-II and arsenopalladinite (Fig. 7). Arsenopalladinite contains two pnictogen layers per unit cell, mertieite-II has 12.

Two adjacent layers stack on onto another likewise in classic close package structures. Two types of cavities are formed: hexagonal and tetragonal. Palladium atoms occupy all hexagonal and  $\frac{1}{2}$  of the tetragonal cavities (Fig. 8). Palladium atoms at the

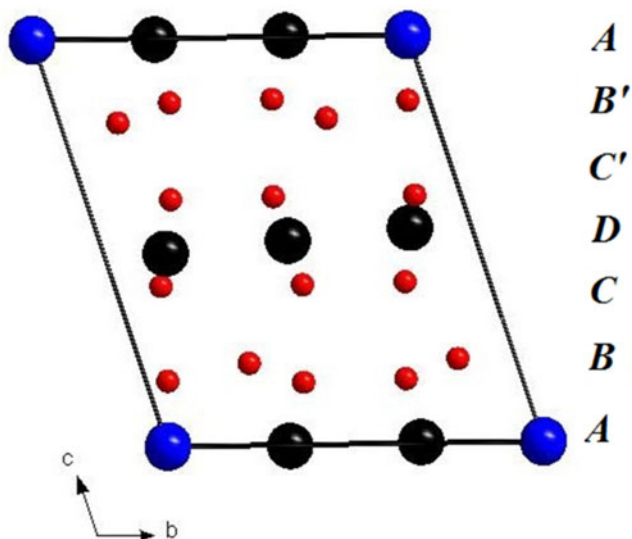


Fig. 3. The crystal structure of arsenopalladinite projected along the  $a$  axis. Blue circles are Sb atoms, black circles – As atoms and red circles – Pd atoms.



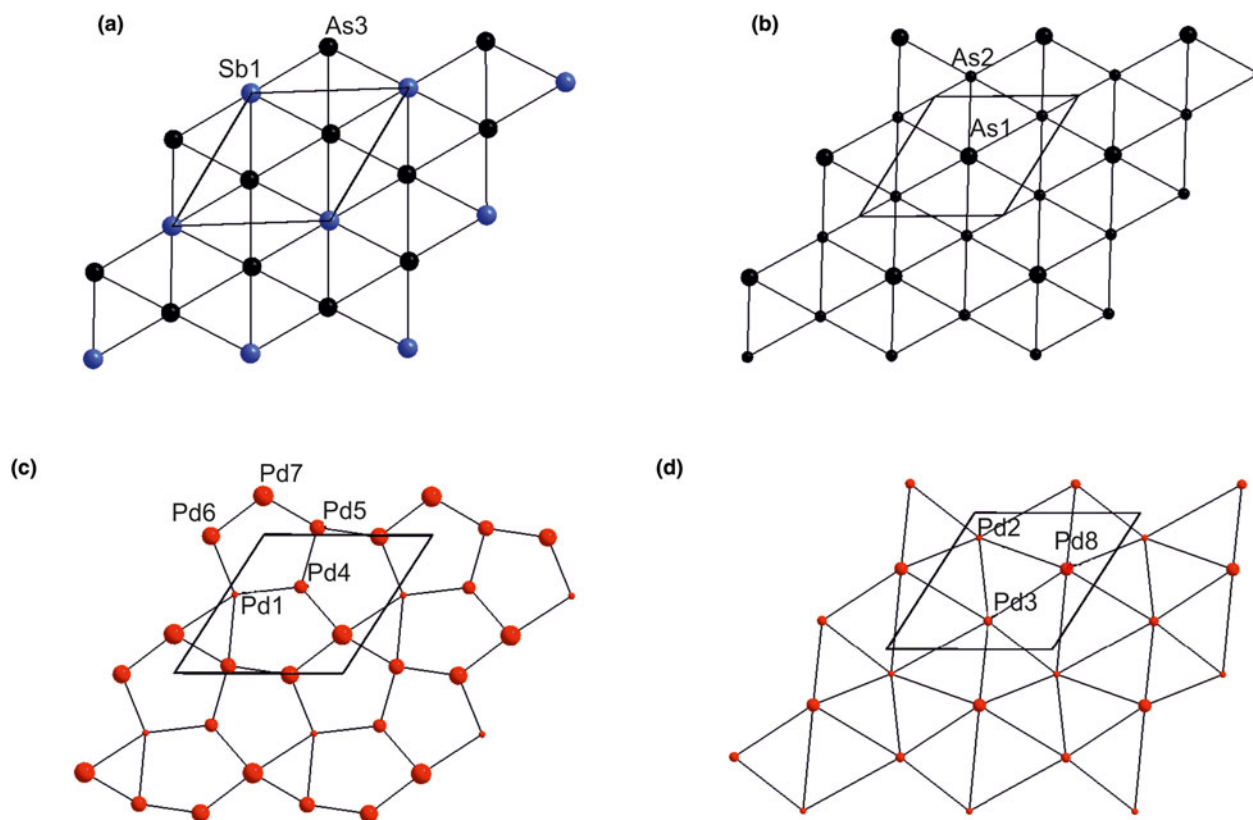


Fig. 4. Atomic nets in the crystal structure of arsenopalladinite. Colour codes as in Fig. 3.

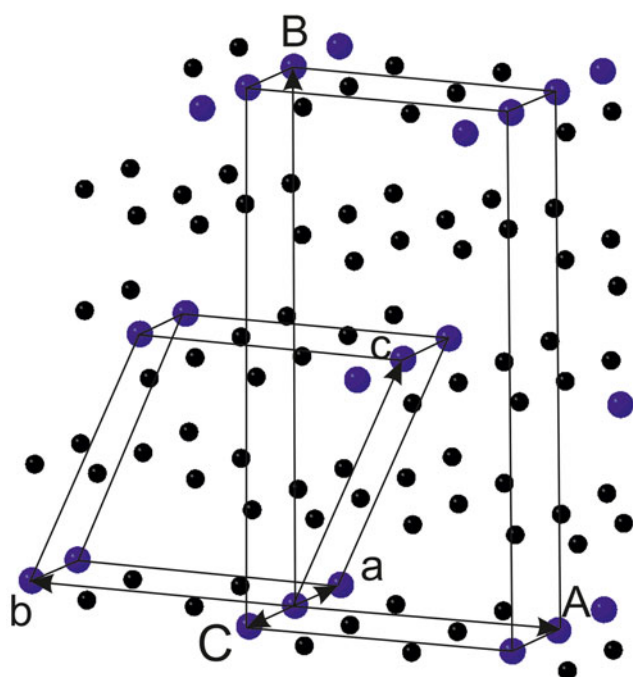


Fig. 5. Relation between two possible choices of the unit cell. Colour codes as in Fig. 3. Palladium atoms are omitted.

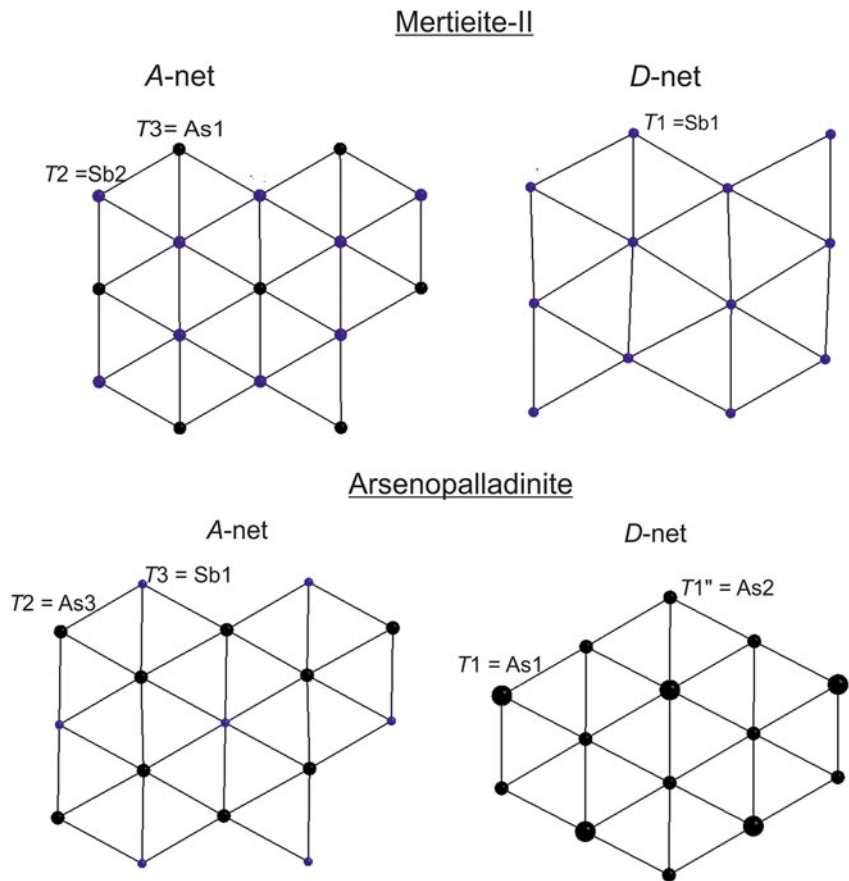
hexagonal cavities shift from the cavity centre. Thus, their coordination by As and Sb atoms reduces from six to three. So, the structure contains As and (As,Sb) tetrahedra, and triangles around Pd atoms.

The size of atoms is one of the factors that has an influence on the stability of a structure type (Pearson, 1972). The radius of arsenic, which has formed structure layers in arsenopalladinite, is smaller than those of antimony in mertieite-II: 1.39 and 1.59 Å, respectively (metallic radii, Pearson, 1972). When the smaller arsenic substitutes antimony in the structure layers, an adaptation of interatomic distances leads to atom shifts from the symmetry sites and so a change of structure symmetry.

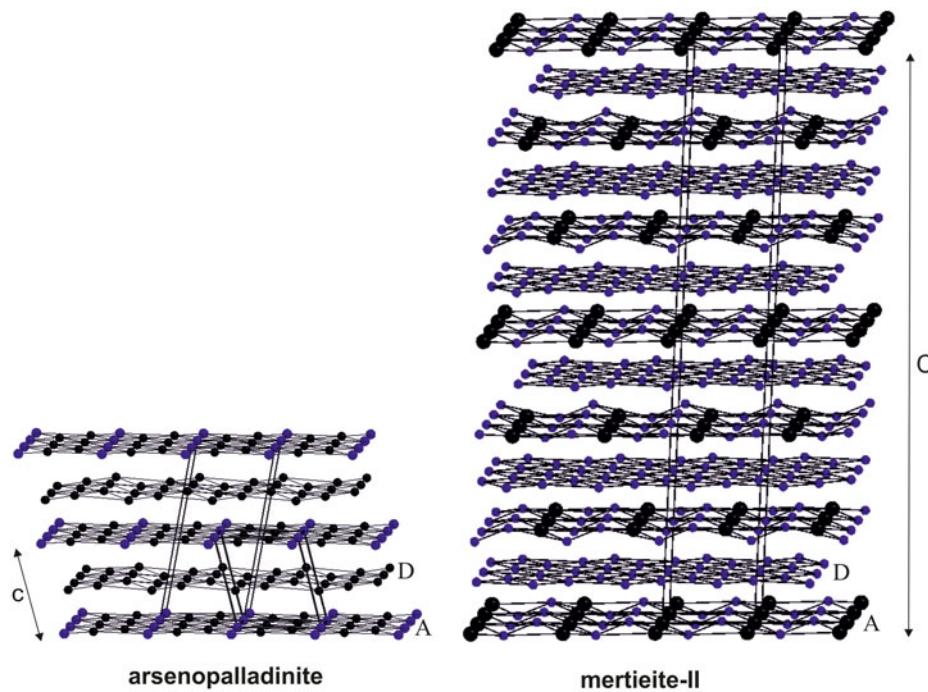
In the range  $[\text{Pd}_8\text{Sb}_3, \text{synthetic compound}]$ – $[\text{mertieite-II}, \text{Pd}_8\text{Sb}_{2.5}\text{As}_{0.5}]$ – $[\text{arsenopalladinite}, \text{Pd}_8\text{As}_{2.5}\text{Sb}_{0.5}]$ , the

Table 6. Occupation of the sites in pnictogen (As/Sb) triangular nets in arsenopalladinite and mertieite-II.

		Mertieite-II		Arsenopalladinite		
Site		Wyckoff symbol	Point symmetry	Site	Wyckoff symbol	Point symmetry
		<i>A</i> net		<i>A</i> net		
T3	As1	6b	$\bar{3}$	Sb1	1a	<i>i</i>
T2	M1 (Sb <sub>0.96</sub> As <sub>0.04</sub> )	12c	3	As3	2i	1
		<i>D</i> net		<i>D</i> net		
T1	Sb1	18e	2	As1	1h	<i>i</i>
				As2	2i	1



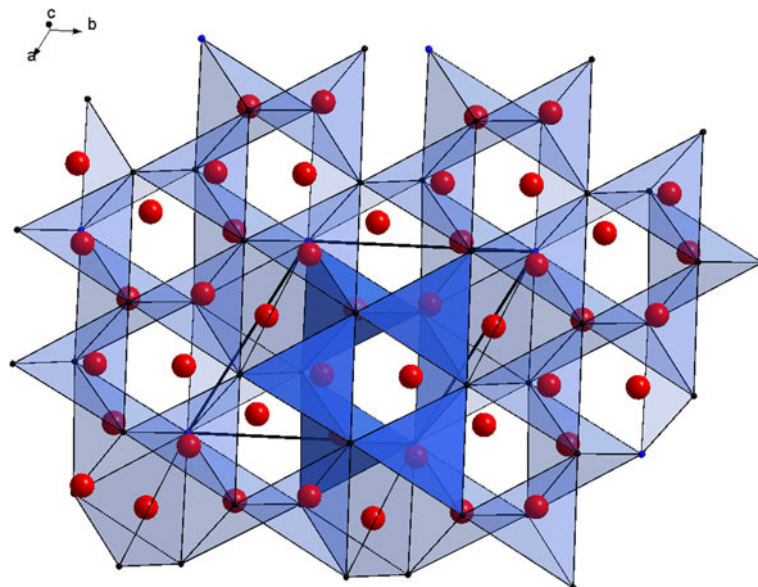
**Fig. 6.** The comparison of the pnicto-gen nets in mertieite-II and arsenopalladinite.



**Fig. 7.** Ordering of As and Sb atoms in the pnicto-gen layers in arsenopalladinite and mertieite-II structures. Palladium layers are omitted. Colour codes as in Fig. 3.

compositional changes favour the occurrence of different structural arrangements. Mertieite-II is isostructural with synthetic  $\text{Pd}_8\text{Sb}_3$  (Karimova *et al.*, 2018, Marsh 1994, Wopersnow and

Schubert, 1976). In that composition range only limited solid solution can exist for  $\text{Pd}_8\text{Sb}_3\text{-Pd}_8\text{Sb}_{2.5}\text{As}_{0.5}$ . The crystal structures of  $\text{Pd}_8\text{Sb}_3$  and  $\text{Pd}_8\text{Sb}_{2.5}\text{As}_{0.5}$  compounds are trigonal with an



**Fig. 8.** Palladium atoms distribution on sites between two adjacent pnictogen layers in arsenopalladinite structure. Five tetragonal cavities are highlighted.

elongated rhombohedral unit-cell. If arsenic content increases up to  $\text{Pd}_8\text{As}_{2.5}\text{Sb}_{0.5}$  composition, then deformation of the structure up to triclinic symmetry is realised.

Arsenopalladinite,  $\text{Pd}_8\text{As}_{2.5}\text{Sb}_{0.5}$ , and mertieite-II,  $\text{Pd}_8\text{Sb}_{2.5}\text{As}_{0.5}$ , are structurally closely related minerals. They can be joined in one mineral group. The crystal structures of mertieite-I,  $\text{Pd}_8(\text{Sb},\text{As})_3$ , and stillwaterite,  $\text{Pd}_8\text{As}_3$ , are not known yet, and their relation to the named minerals is not still clear.

**Acknowledgements.** The authors are grateful to Luca Bindi, an anonymous reviewer, Structural Editor Daniel Atencio and Associate Editor František Laufek for useful comments and editing the manuscript. We thank Kari Kojonen for providing samples. We acknowledge the Resource Centre of X-ray diffraction studies of St. Petersburg State University for collection of the experimental data. This study was supported by the Russian Academy of Sciences, Program of Fundamental Research.

**Supplementary material.** To view supplementary material for this article, please visit <https://doi.org/10.1180/mgm.2020.65>.

## References

- Agilent (2012). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, Oxfordshire, England.
- Bindi L. (2010) Atheneite,  $[\text{Pd}_2][\text{As}_{0.75}\text{Hg}_{0.25}]$ , from Itabira, Minas Gerais, Brazil: crystal structure and revision of the chemical formula. *The Canadian Mineralogist*, **48**, 1149–1155.
- Cabri L.J. (1981) The platinum-group minerals. Pp. 83–150 in: *The Platinum Group Elements: Mineralogy, Geology, Recovery* (L.J. Cabri, editor). Canadian Institute of Mining Metallurgy, S23. CIM, Quebec, Canada
- Cabri L.J. (2002) The platinum-group minerals. In: *The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements* (L.J. Cabri, editor). Canadian Institute of Mining, Metallurgy and Petroleum, Special Volume **54**, 70–71. CIM, Quebec, Canada.
- Cabri L.J. and Laflamme J.H.G. (1979) *Mineralogy of Samples from the Lac Des Iles Area, Ontario*. CANMET Report, pp. 79–27.
- Cabri L.J., Clark A.M. and Chen T.T. (1977) Arsenopalladinite from Itabira, Brazil, and from the Stillwater Complex, Montana. *The Canadian Mineralogist*, **15**, 70–73.
- Clark A.M., Criddle A.J. and Fejer E.E. (1974) Palladium arsenide-antimonides from Itabira, Minas Gerais, Brazil. *Mineralogical Magazine*, **39**, 528–543.
- Claringbull G.F. and Hey M. H. (1957) Arsenopalladinite ( $\text{Pd}_3\text{As}$ ) a new mineral from Itabira, Brazil. *Mineralogical Magazine*, **31**, 237.
- Farrugia L.J. (2012) WinGX and ORTEP for Windows: an update. *Journal of Applied Crystallography*, **45**, 849–854.
- Karimova O.V., Grokhovskaya T.L., Zolotarev A.A. and Gurzhiy V.V. (2016) Crystal structure refinements of ismertieite,  $\text{Pd}_{11}\text{Sb}_2\text{As}_2$ , and tornroosite,  $\text{Pd}_{11}\text{As}_2\text{Te}_2$ . *The Canadian Mineralogist*, **54**, 511–517.
- Karimova O.V., Zolotarev A.A., Evstigneeva T.L. and Johanson B.S. (2018) Mertieite-II,  $\text{Pd}_8\text{Sb}_{2.5}\text{As}_{0.5}$ , crystal-structure refinement and formula revision. *Mineralogical Magazine*, **82**(S1), S247–S257.
- Marsh R.E. (1994) The centrosymmetric-noncentrosymmetric ambiguity: some more examples. *Acta Crystallographica*, **50**, 450–455.
- Matkovic T. and Schubert K. (1978) Kristallstruktur von  $\text{Pd}_5\text{As}$  und  $\text{Pd}_5\text{Ge}$ . *Journal of the Less Common Metals*, **58**, 1–6.
- Pearson W.B. (1972) *The Crystal Chemistry and Physics of Metals and Alloys*. Wiley-Interscience. New York. 806 pp.
- Sheldrick G.M. (2015a) SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallographica, Section A*, **A71**, 3–8.
- Sheldrick G.M. (2015b) Crystal structure refinement with SHELXL. *Acta Crystallographica, Section C*, **C71**, 3–8.
- Wolff P.M. (2005) Reduced bases. Pp. 750–755 in: *International Tables for Crystallography, Volume A* (Th. Hahn, editor). Springer.
- Wopernow W. and Schubert K. (1976) Kristallstruktur von  $\text{Pd}_8\text{Sb}_3$ . *Journal of the Less Common Metals*, **48**, 79–87.
- Wopernow W. and Schubert K. (1977) Kristallstruktur von  $\text{Pd}_{20}\text{Sb}_7$  und  $\text{Pd}_{20}\text{Te}_7$ . *Journal of the Less Common Metals*, **51**, 35–44.