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Article

The crystal structure of Pd_8As_3, a synthetic analogue of stillwaterite

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Abstract

The synthetic analogue of mineral stillwaterite, Pd_8As_3, was synthesised and its crystal structure was solved to $R_1 = 0.0341$ based on single crystal X-ray diffraction data. Pd_8As_3 is trigonal and the space group is $P\bar{3}$. The unit-cell parameters are $a = 7.4261(4)$, $c = 10.3097(9)$ Å and $V = 492.38(7)$ Å^3 with $Z = 3$. The structure builds up by layers of Pd and As atoms. Pd-nets and As-nets are parallel to (110) and stack along the **c** axis direction. The stacking sequence is *ABCDEEDCBA*. The relation between structures of minerals with the common formula Pd_8T_3 (T = As or/and Sb) are discussed. They are formed by nets of pnictogen and palladium atoms. The common feature of the structures is 3^6 topology of pnictogen nets. The differences are stacking sequences and topology of the palladium nets.

Introduction

The mineral stillwaterite, Pd_8As_3, was discovered in 1975 by Cabri *et al.* (1975). A single-crystal precession study established the hexagonal symmetry of the mineral and possible space group $P\bar{3}$ or $P3$. The unit cell parameters were determined by powder X-ray diffraction (XRD) in a Gandolfi camera as $a = 7.399$ and $c = 10.311$ Å, however no more information about the structure solution was published.

The stillwaterite ideal formula is established as Pd_8As_3 (Cabri *et al.*, 1975) and corresponds to the formula of the synthetic phase $Pd_{2.65}As$ reported earlier by Saini *et al.* (1964). The mineral X-ray diffraction pattern for stillwaterite is very similar to those of the synthetic $Pd_{2.65}As$, however there are differences in the weak intensity reflections which are not resolved in the stillwaterite XRD data. A complete crystal structure analysis has not been performed for the mineral, or for the synthetic phase.

It is important to determine the structural characteristics of stillwaterite from an economic perspective. Both chemical and crystallographic characteristics play fundamental roles in the hydro-metallurgical separation processes of these PGM minerals and particularly in the flotation of ores for separation (Shackleton *et al.*, 2007).

The stillwaterite crystal structure is interesting in the context of structural relations in a family of minerals with common formula Pd_8T_3 (T = Sb and/or As): stillwaterite, Pd_8As_3; arsenopalladinite, $Pd_8As_{2.5}Sb_{0.5}$; mertieitete-II, $Pd_8Sb_{2.5}As_{0.5}$; and synthetic, Pd_8Sb_3. The crystal structures of arsenopalladinite, mertieitete-II and Pd_8Sb_3 are known today.

The Pd_8Sb_3 structure was solved by Wopersnow and Schubert (1976), and then refined by Marsh (1994). It is trigonal in

space group $R\bar{3}c$ (Table 1). The stability of the Pd_8Sb_3 structure type extends up to composition of $Pd_8Sb_{2.5}As_{0.5}$, confirmed by the structural study of the mineral mertieite-II, $Pd_8Sb_{2.5}As_{0.5}$ (Karimova *et al.*, 2018). The mineral arsenopalladinite, $Pd_8As_{2.5}Sb_{0.5}$, has another structure type of triclinic in space group $P\bar{1}$ (Table 1) (Karimova *et al.*, 2020).

The Pd_8Sb_3, mertieite-II, $Pd_8Sb_{2.5}As_{0.5}$, and arsenopalladinite, $Pd_8As_{2.5}Sb_{0.5}$, structures have common features. They consist of alternations of layers made by pnictogen (Sb and As) atoms and layers made by palladium atoms stacked along the **c** axis. The pnictogen layers have the same topology in the minerals mertieite-II and arsenopalladinite (Karimova *et al.*, 2020). The Pd_8As_3 structure has close relations to the structures of Pd_8Sb_3, mertieite-II and arsenopalladinite as evidenced by the crystallographic data in Table 1. The aim of this paper is crystal structure analysis of a synthetic analogue of stillwaterite, Pd_8As_3, using single-crystal X-ray diffraction data.

Materials and methods

The synthetic analogue of mineral stillwaterite Pd_8As_3 was prepared using the solid phase reaction method in evacuated silica glass ampoules. Pure elements were used (Pd 99.9% Reakhim, As 99.5% Reakhim). Arsenic was preliminarily purified from oxide in evacuated silica glass ampoules at 450°C for a week. As a result, the more volatile arsenic oxide was transferred to the coldest part of the ampoule and separated easily. Arsenic and palladium, taken in a stoichiometric ratio, were placed in a silica glass ampoule, evacuated to a pressure of <1 Pa, and sealed using a CH_4/O_2 burner. At the first step the ampoule with palladium and arsenic was heated up to temperature 850°C for seven days. It was observed that the reaction proceeds extremely slowly, therefore the sintering Pd–As piece was melted in an ampoule in a CH_4/O_2 flame and quenched in cold water. After that the reacted mixture was removed from the ampoule, weighed, ground in an

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Table 1. Crystallographic parameters for the Pd_8T_3 (T = Sb, As) compounds.

Mineral/ synthetic phase	Symmetry, space group	Unit cell parameters	Z	References
Pd_8Sb_3	Trigonal, $R\bar{3}c$	a = 7.6152, c = 43.032 Å, V = 2161.1 Å^3	12	Wopersnow and Schubert (1976); Marsh (1994)
Mertieite-II, $Pd_8Sb_{2.5}As_{0.5}$	Trigonal, $R\bar{3}c$	a = 7.5172(3), c = 43.037(2) Å, V = 2106.1(2) Å^3	12	Karimova et al. (2018)
Arsenopalladinite, $Pd_8As_{2.5}Sb_{0.5}$	Triclinic, $P\bar{1}$	a = 7.3344(7), b = 7.3870(8), c = 7.5255(7) Å, α = 98.869(8), β = 102.566(8), γ = 119.096(1)°, V = 331.19(7) Å^3	2	Karimova et al. (2020)
Stillwaterite, Pd_8As_3	Trigonal, $P\bar{3}$ or $P3$	a = 7.399, c = 10.311 Å	3	Cabri et al. (1975)
Pd_8As_3	Trigonal, $P\bar{3}$	a = 7.4261(4), c = 10.3097(9) Å, V = 492.38(7) Å^3	3	This paper

Table 2. Electron microprobe analyses of Pd_8As_3.

Grain No.	Anal. No.	As (wt.%)	Pd (wt.%)	Total
1	1	20.15	78.24	98.39
	2	20.64	78.45	99.09
2	3	21.13	76.36	97.49
	4	20.25	78.24	98.48
3	5	20.21	77.91	98.12
	6	20.82	77.43	98.25
4	7	20.64	77.92	98.56
5	8	20.97	77.25	98.21
6	9	20.78	77.54	98.32
7	10	20.64	77.5	98.13
8	11	21.05	78.38	99.42
Mean		20.66	77.75	98.41
Std. deviation		0.32	0.71	
Max.		21.13	78.45	
Min.		20.15	76.36	
Formula*		$Pd_{7.99}As_{3.01}$		

*Calculated with 11 atoms per formula unit.
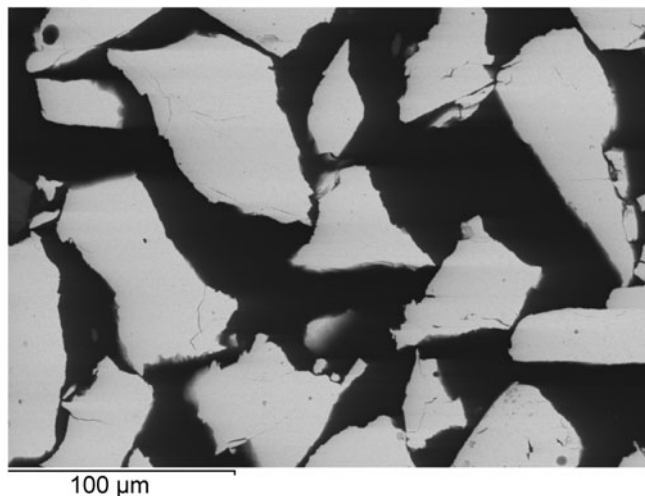
Fig. 1. Back-scattered electron image of Pd_8As_3 grains.

agate mortar under acetone, placed in another silica ampoule, evacuated, and heated at 450°C for 120 days.

The crystals were mounted in an epoxy resin and a polished mount was prepared. The chemical composition of the grains was determined using a TESCAN Vega II XMU spectrometer Energy 450/XT instrument (Table 2). The energy-dispersive X-ray spectroscopy

Table 3. Powder XRD data for Pd_8As_3.

Pd_8As_3 synthetic (This work)			Stillwaterite (Cabri et al., 1975)		Pd_8As_3 synthetic (Cabri et al., 1975)		
I	d_{meas}	hkl	I	d_{meas}	I	d_{meas}	hkl
2	3.217	200			1	3.22	200
5	3.012	112			3	3.013	112
7	2.728	202	3	2.700	3	2.727	202
7	2.523	113	2	2.521	3	2.522	113
9	2.427	210			2	2.434	210
55	2.355	211	8	2.355	10	2.360	211
21	2.200	212	½	2.189	5	2.205	212
56	2.143	300			7	2.144	300
100	2.118	114	10	2.115	8	2.126	114
15	1.984	213	3	1.991	4	1.988	213
9	1.819	221	1	1.818	3	1.826	221
10	1.757	311	1	1.747	4	1.760	311
3	1.634	223			2	1.635	223
6	1.507	224	2	1.511	3	1.508	224
3	1.467	314	½	1.465	2	1.469	314
			½	1.434	½	1.443	017
3	1.420	322			½	1.421	322
2	1.402	216	½	1.403	2	1.401	216
13	1.355	323	5	1.351	5	1.357	323
2	1.300	413			1	1.300	413
4	1.263	108	1	1.264	2	1.263	108
4	1.232	330	½	1.231	2	1.234	330
4	1.219	331			3	1.222	331
14	1.205	421	2	1.201	4	1.208	421
5	1.163	333	2	1.159	3	1.162	333
1	1.152	227			1	1.152	227
2	1.139	128	½	1.138	1	1.138	128
4	1.060	335	½	1.060	1	1.058	335
3	1.047	138	1	1.043	1	1.043	138
			½	1.019	½	1.021	251
			½	1.003	½	1.002	336
3	1.993	160	1	0.9765	½	0.9772	160
3	0.952	605	2	0.9493	3	0.9483	605

Table 4. Crystal data and structure refinement for Pd_8As_3.

Crystal data	
Structural formula	Pd_8As_3
Crystal system, space group	Trigonal, $P\bar{3}$
a (Å)	7.4261(4)
c (Å)	10.3097(9)
V (Å^3)	492.38 (7)
Z	3
D_{calc} (g/cm^3)	10.886
μ (mm^{-1})	36.28
Data collection	
Diffractometer	Xcalibur, Eos
Radiation	$MoK\alpha$ ($\lambda = 0.7107$)
Temperature (K)	293
2θ range for data collection (°)	6 to 57
R_{int}, R_{sigma} (%)	0.031, 0.057
Refinement	
Reflections collected	1512
Independent reflections	833
Observed reflections [$I > 2\sigma(I)$]	699
Data / restraints / parameters	833/0/51
S (Goodness-of-fit on F^2)	0.99
R [$I > 2\sigma(I)$]	$R_1 = 0.0341$, $wR_2 = 0.057$
R (all data)	$R_2 = 0.0471$, $wR_2 = 0.571$
$\Delta\rho$ (max)/(min) ($e^-/Å^{-3}$)	3.79/−1.68

$w = 1/[\backslash s^2(F_o^2) + (0.0102P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$.

Table 6. Selected bonds lengths (Å) for Pd_8As_3.

Pd1–As3 ×3	2.592(1)	Pd2–As3 ×3	2.646(1)
Pd1–As1	2.733(1)	Pd2–As2	2.749(2)
Pd1–Pd3 ×3	2.857(1)	Pd2–Pd4 ×3	2.821(1)
Pd1–Pd4 ×3	2.9137(1)	Pd2–Pd3 ×3	2.825(1)
Pd1–Pd5 ×3	3.078(9)	Pd2–Pd5 ×3	3.0531(9)
Pd3–As1	2.4325(8)	Pd4–As3	2.453(1)
Pd3–As2	2.434(1)	Pd4–As3	2.531(1)
Pd3–As3	2.544(1)	Pd4–Pd5	2.781(1)
Pd3–Pd5	2.779(1)	Pd4–As3	2.790(1)
Pd3–Pd2	2.825(1)	Pd4–Pd6	2.806(1)
Pd3–Pd5	2.829(1)	Pd4–Pd4 ×2	2.819(1)
Pd3–Pd1	2.857(1)	Pd4–Pd6	2.8366(8)
Pd3–Pd5	2.861(1)	Pd4–As3	2.848(1)
Pd3–Pd5	2.913(1)	Pd4–Pd1	2.914(1)
Pd3–Pd3 ×2	2.942(1)		
Pd5–As2	2.488(2)	Pd6–As3 ×3	2.511(1)
Pd5–As3	2.596(1)	Pd6–Pd4 ×3	2.806(1)
Pd5–As3	2.609(1)	Pd6–Pd4 ×3	2.837(8)
Pd5–Pd3	2.829(1)	Pd6–Pd5 ×3	2.907(1)
Pd5–Pd3	2.861(1)		
Pd5–Pd6	2.907(1)	As1–Pd3 ×6	2.4325(8)
Pd5–Pd3	2.913(1)	As1–Pd1	2.733(1)
Pd5–Pd5 ×2	2.934(1)		
Pd5–Pd2	3.053(1)		
Pd5–Pd1	3.078(1)		
As3–Pd4	2.453(1)	As2–Pd3 ×3	2.434(1)
As3–Pd4	2.532(1)	As2–Pd5 ×3	2.488(2)
As3–Pd3	2.544(1)	As2–Pd2	2.749(2)
As3–Pd5	2.609(1)		
As3–Pd2	2.646(1)		
As3–Pd4	2.790(1)		
As3–Pd4	2.848(1)		

analyses were performed with an operating voltage of 20 kV and a beam current of 15 nA. Pure Pd and synthetic InAs were used as standards. The quantitative analysis on eight grains gave the empirical formula $Pd_{7.99}As_{3.01}$ calculated on the basis of 11 atoms per formula unit. Scanning electron microscopy analysis of the experimental product confirmed that it consists only of Pd_8As_3. The Pd_8As_3 forms anhedral grains 20×30 to 50×150 μm (Fig. 1).

Powder X-ray diffraction data of the synthetic sample were collected on a Rigaku D/MAX 2200 diffractometer using CuKα radiation. The data were indexed by the *Jade 2004* program (Materials Data, Inc.) on the basis of a hexagonal unit cell with: $a = 7.408$ and $c = 10.322$ Å (Table 3).

Single-crystal X-ray diffraction data for Pd_8As_3 were collected on the Xcalibur Eos diffractometer at the Center of X-ray diffraction studies at St. Petersburg State University (XRD Center SPbSU). A total of 1512 reflections were collected at 293 K using monochromatic MoKα X-radiation. The data were integrated and corrected by means of the *CrysAlisPro* (Agilent, 2012) program package, which was also used to apply empirical absorption correction using spherical harmonics, implemented in the *SCALE3 ABSPACK* scaling algorithm. The structure was solved by direct methods and refined in anisotropic approximation using *SHELX* programs (Sheldrick 2015a, 2015b) in the frame of the *WinGX*

software package (Farrugia, 2012). Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from the *International Tables for X-ray Crystallography* (Prince, 2004). Refinement gave full occupation for all the sites in the structure. Crystal data, experimental and refinement details are presented in Table 4. The final atomic coordinates and displacement parameters are listed in Table 5 and the selected interatomic distances are in Table 6. Table 7 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.

Identity of synthetic Pd_8As_3 to natural stillwaterite

The Pd and As content of the synthetic material is close to that reported for stillwaterite by Cabri *et al.* (1975) using a formula

Table 5. Atomic coordinates and equivalent isotropic and anisotropic displacement parameters (Å^2) for Pd_8As_3.

Atom	Site*	x	y	z	U_{eqv}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd1	2c	0	0	0.2651(1)	0.0056(3)	0.0061(4)	0.0061(4)	0.0044(7)	0.000	0.000	0.0031(2)
Pd2	2d	⅔	⅓	0.2623(1)	0.0057(3)	0.0068(4)	0.0068(4)	0.0033(7)	0.000	0.000	0.0034(2)
Pd3	6g	0.3348(1)	0.0859(1)	0.09270(8)	0.0050(2)	0.0062(4)	0.0059(4)	0.0025(4)	0.0002(3)	−0.0002(3)	0.0026(3)
Pd4	6g	0.3448(1)	0.2913(1)	0.42723(8)	0.0062(2)	0.0095(4)	0.0074(4)	0.0031(4)	−0.0004(3)	−0.0002(3)	0.0053(4)
Pd5	6g	0.3352(1)	0.4395(1)	0.18112(7)	0.0050(2)	0.0057(4)	0.0060(4)	0.0032(4)	−0.0005(3)	0.0001(3)	0.0029(3)
Pd6	2d	⅓	⅔	0.4102(1)	0.0052(3)	0.0061(4)	0.0061(4)	0.0033(7)	0.000	0.000	0.0031(2)
As1	1a	0	0	0	0.0055(5)	0.0058(8)	0.0058(8)	0.005(1)	0.000	0.000	0.0029(4)
As2	2d	⅓	⅔	0.0043(2)	0.0053(4)	0.0063(6)	0.0063(6)	0.0032(9)	0.000	0.000	0.0031(3)
As3	6g	0.0170(2)	0.3459(2)	0.3287(1)	0.0053(2)	0.0051(5)	0.0066(6)	0.0034(5)	0.0000(4)	0.0002(4)	0.0023(5)

*All sites are fully occupied by Pd and As atoms.

Table 7. Coordination number (CN) together with the average bonds lengths (d_m) around the different atoms in Pd_8As_3.

Central atom	CN(Pd)*	d_m (Å)	CN(As)**	d_m (Å)
Pd1	9	2.950	4	2.627
Pd2	9	2.900	4	2.672
Pd3	8	2.869	3	2.470
Pd4	6	2.829	4	2.656
Pd5	8	2.939	3	2.564
Pd6	9	2.850	3	2.511
As1	7	2.475		
As2	7	2.502		
As3	7	2.632		

*CN(Pd) is the number of nearest Pd neighbours.
**CN(As) is the number of nearest As neighbours.

calculated on 3 atoms of As. Stillwaterite grains from the Stillwater Complex type locality showed a Pd/As ratio 7.84/3.00 to 8.13/3.00 (Cabri *et al.*, 1975). The synthetic material of our study has a Pd/As ratio 7.63/3.00 to 8.20/3.00 (Table 2) and its powder XRD pattern fits very well to the those of stillwaterite and synthetic Pd_8As_3 obtained by Cabri *et al.* (1975) (Table 3).

Crystal structure description

Three palladium atoms positions are located on the 3-fold axis of symmetry (Wyckoff symbols are *2c* and *2d*) and the other three are general with Wyckoff symbol *6g* of the space group (Table 5). Two arsenic atoms occupy sites on the 3-fold axis of symmetry: on the *1a* and *2d* Wyckoff sites. The third arsenic atom is in general position *6g*.

The coordination polyhedra around atoms in the structure are shown in Fig. 2. The interatomic Pd–As distances varies from 2.4325 to 2.8480 Å (Table 6). The overall average Pd–As distance is 2.593 Å. These values are typical for the bonds in the crystal structures of ternary Pd–As–Sb minerals. The minimum Pd–As distance is equal to 2.465 Å in isomertieite, $Pd_{11}Sb_2As_2$, and 2.488 Å in mertieite-II, $Pd_8Sb_{2.5}As_{0.5}$ (Karimova *et al.*, 2016, 2018). It is slightly less at 2.378 Å in the arsenopalladinite, $Pd_8As_{2.5}Sb_{0.5}$ (Karimova *et al.*, 2020). The maximum palladium to arsenic distance is 2.662 Å and 2.537 Å in isomertieite and mertieite-II, respectively, and very long at 2.967 Å in arsenopalladinite (Karimova *et al.*, 2016, 2018, 2020). In the crystal structures of palladium arsenides the greatest variation in the palladium to
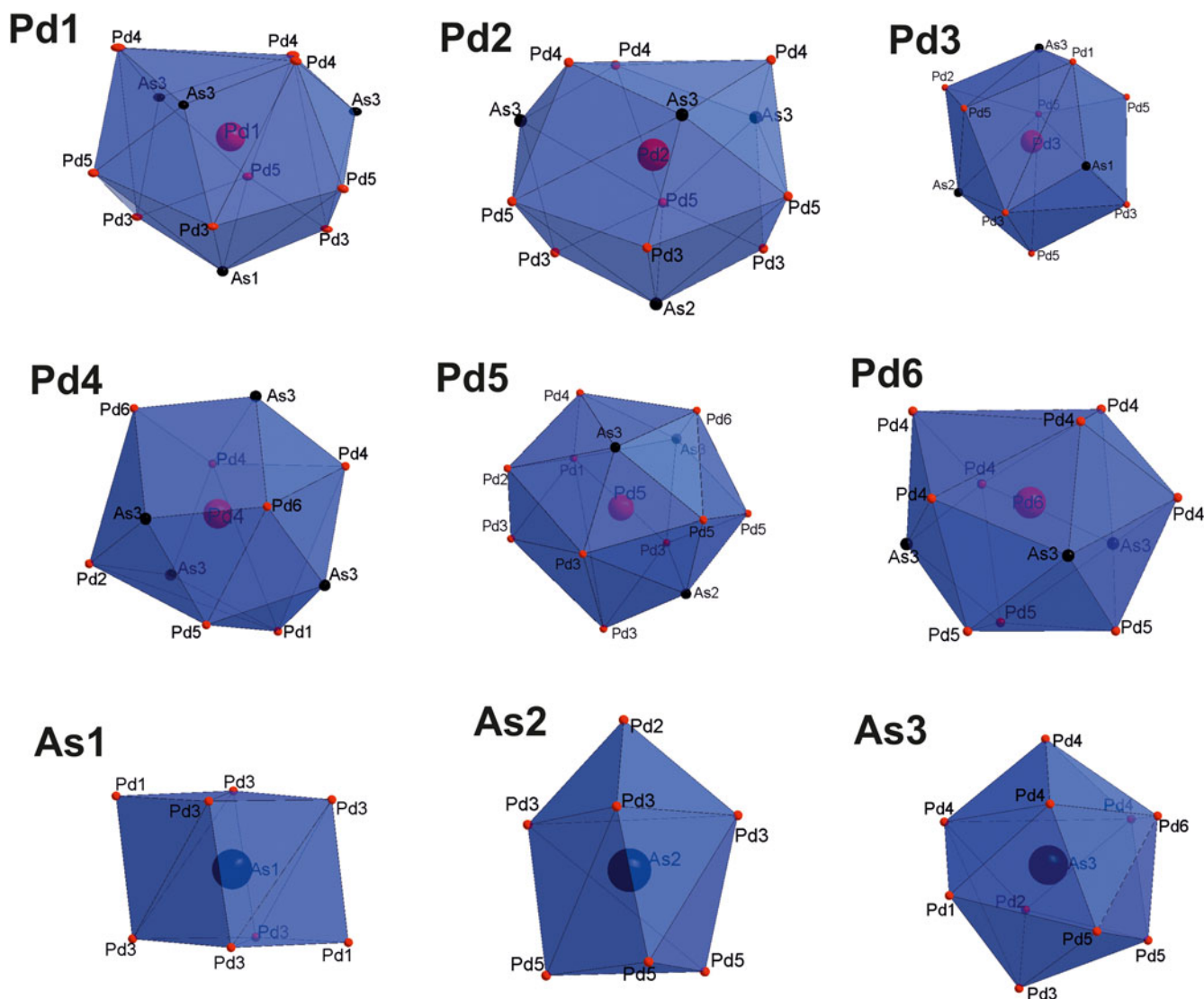
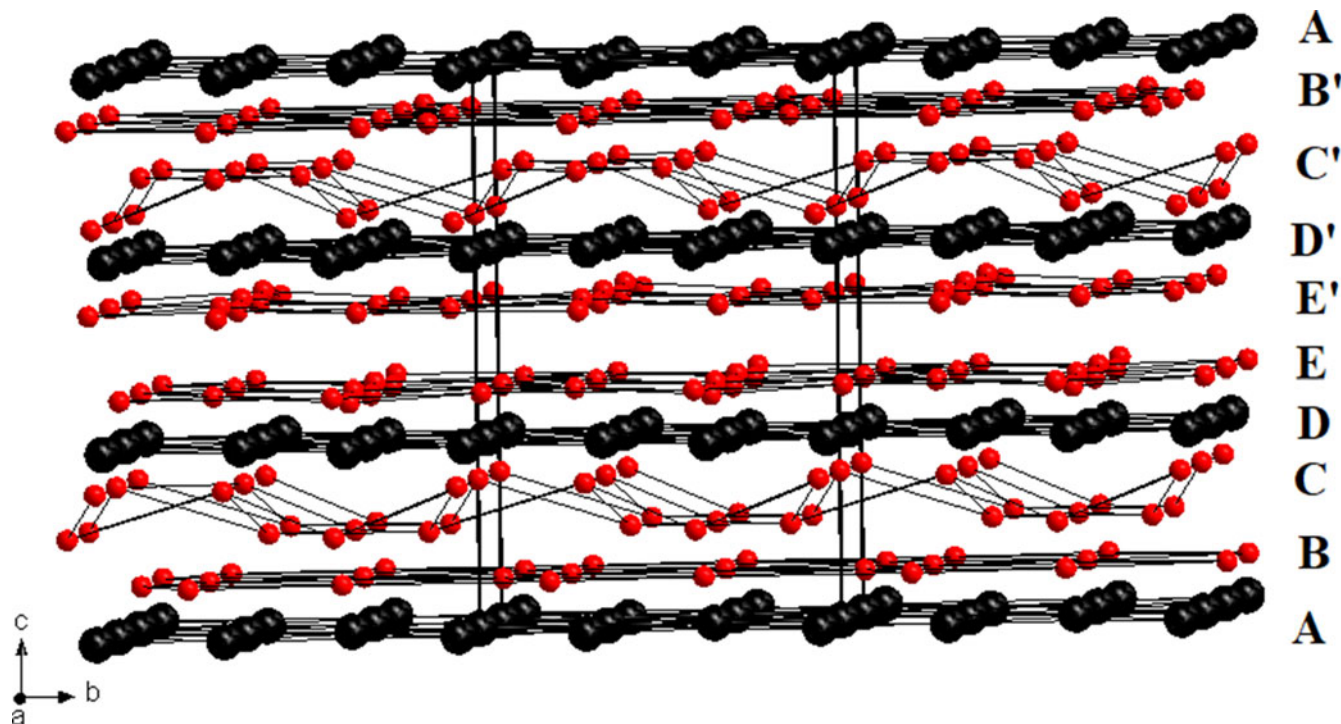**Fig. 2.** Coordination polyhedrons in the Pd_8As_3 structure.

Fig. 3. The crystal structure of Pd$_8$As$_3$, perspective view along *c* axis. Black circles – As atoms, red circles – Pd atoms.

arsenic distances is found in the synthetic phase Pd$_5$As: from 2.361 Å to 3.241 Å, average 2.788 Å (Matkovic and Schubert, 1978). The mineral palladoarsenide, Pd$_2$As, has the average Pd–As bonds length equal to 2.59 Å, the minimum is 2.39 Å and the maximum is 2.70 Å (Baelz and Schubert, 1969; Begizov *et al.*, 1974). In the crystal structure of synthetic PdAs$_2$ each palladium atom is surrounded by 6 arsenic atoms with octahedral coordination and bond lengths equal to 2.495 Å (Breese and Schnering, 1994).

We used the principles of a structure description in terms of atomic nets proposed by Pearson (1972). The Pd$_8$As$_3$ structure consists of palladium and arsenic atoms layers alternated along the **c** axis (Fig. 3). Projection of the structure along the **a** axis is shown in Fig. 4. Topology of the layers is drawn in Fig. 5. The layers of arsenic atoms are 3^6 triangular nets (named '*A*' and '*D*'). The layers of palladium atoms are triangular ('*B*'), pentagon–triangular ('*C*') and the triangle–quadrangle ('*E*') nets (Fig. 5). The stacking sequence is: *ABCDEEDCBA* (Fig. 4). The first layer in the stacking sequence is formed by As1 and As2 atoms sites (*A* net, Fig. 5). It is followed by two palladium layers: highly buckled triangular net *B* (built up by the Pd3 site) and pentagon–triangular net *C* (consists of Pd1, Pd2 and Pd5 sites). The next layer is arsenic triangular net *D* (contains As3 sites). The Pd4 and Pd6 sites form the triangle-quadrangle *E* net.

Discussion

The Pd$_8$*T*$_3$ (*T* = As and/or Sb) family includes minerals mertieite-II, Pd$_8$Sb$_{2.5}$As$_{0.5}$, arsenopalladinite, Pd$_8$As$_{2.5}$Sb$_{0.5}$, stillwaterite, Pd$_8$As$_3$, and synthetic Pd$_8$Sb$_3$. The structural motive is the same in these compounds: nets of pnictogen atoms are the base of the structures. The alternation of the arsenic and antimony nets along the **c** axis in the Pd$_8$*T*$_3$ compounds is shown on Fig. 6.

The common scheme of the pnictogen nets is represented on Fig. 7. The pnictogen nets are triangular with 3^6 topology. They contain three atomic sites possibly hosting arsenic or antimony atoms: *T*$_1$, *T*$_2$ and *T*$_3$.
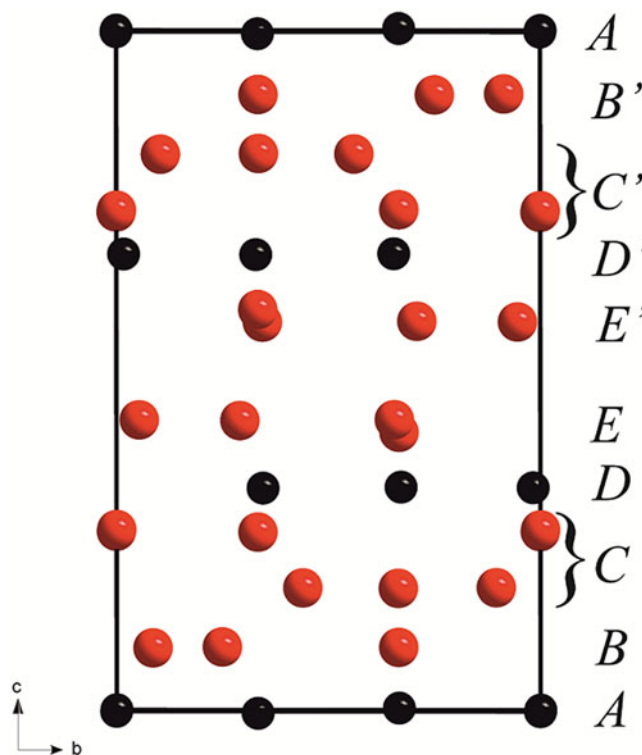

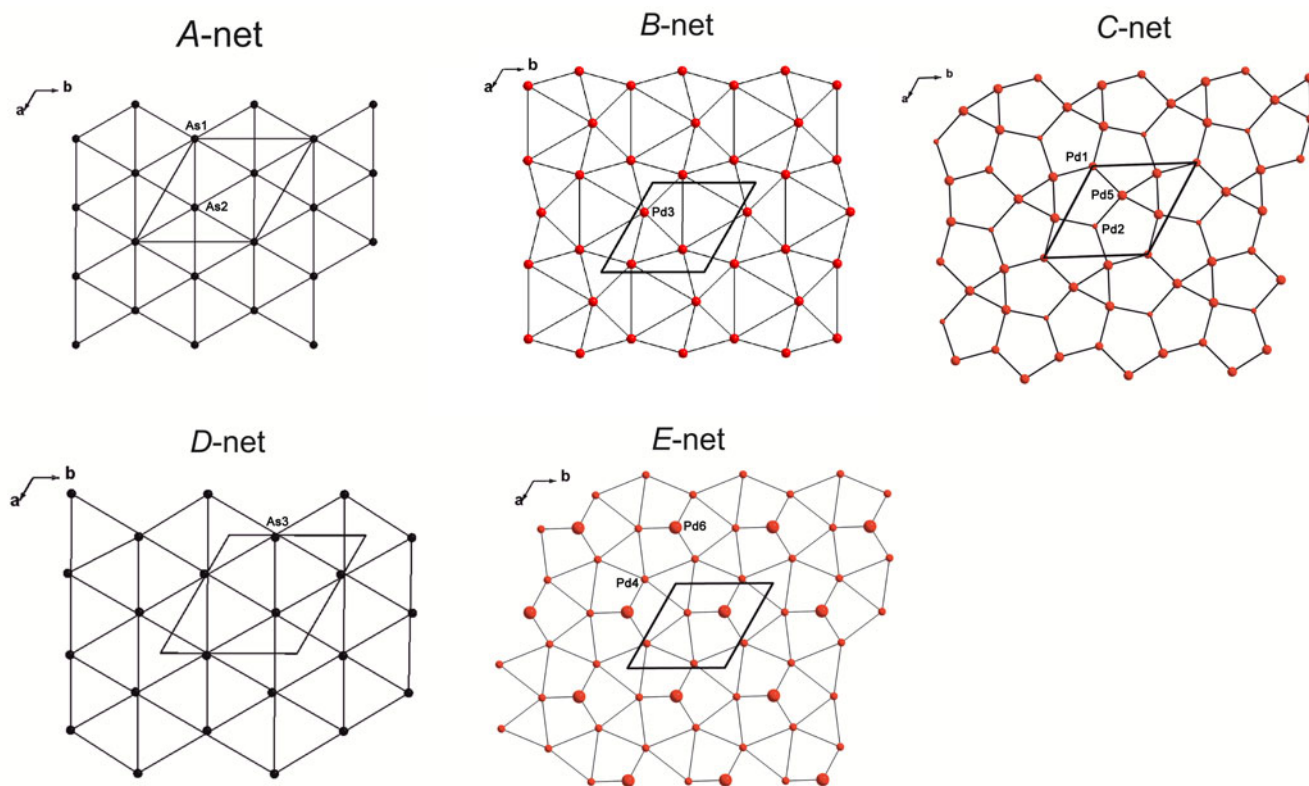**Fig. 4.** The crystal structure of Pd$_8$As$_3$, projection along the *c* axis. Colour code as in Fig. 3.

Fig. 5. Atomic nets in the crystal structure of Pd_8As_3. Colour code as in Fig. 3.

The distribution of pnictogen atoms on the triangle nets sites in the structures of Pd_8T_3 compounds is given in Table 8. Four variants of pnictogen site occupation are represented: all T-sites are occupied by antimony (Pd_8Sb_3); all T-sites are filled by arsenic (stillwaterite); only one T-site is filled by arsenic (mertietite-II); and only one T-site is filled by antimony (arsenopalladinite) (Table 8).

Synthetic Pd_8Sb_3 ($Pd_8Sb_{2.5}Sb_{0.5}$) and mertieite-II, $Pd_8Sb_{2.5}As_{0.5}$ – the antimony end-members of the Pd_8T_3 (T = As, Sb) family – are isostructural. They have the highest symmetry of the structures (Table 1) and the highest symmetry of the pnictogen nets among the named compounds (Table 8). Incorporation of arsenic atoms in the $T3$ site of the Pd_8Sb_3 pnictogen nets does not affect the structure symmetry in the case of mertieite-II, $Pd_8Sb_{2.5}As_{0.5}$.

In contrast, arsenopalladinite, $Pd_8As_{2.5}Sb_{0.5}$, contains pnictogen nets constituted mainly by arsenic atoms, except for one site (Table 8). The symmetry of the structure changes from
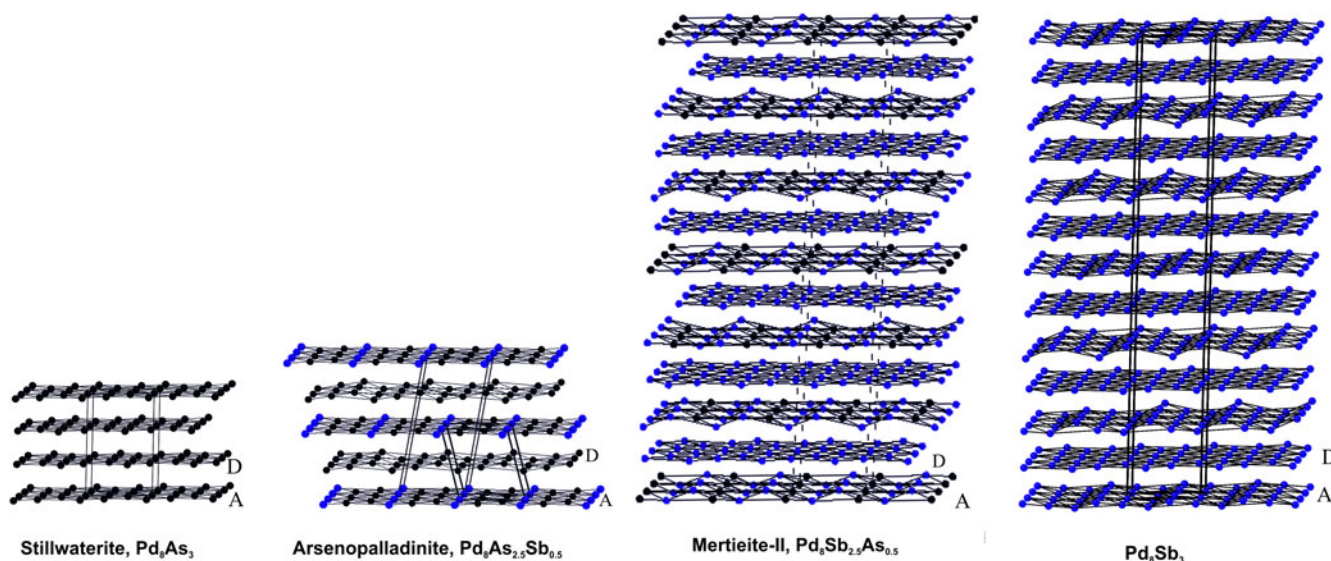

Fig. 6. Pnictogen nets in the structures of the Pd_8T_3 (T = As, Sb) compounds. The blue balls are antimony atoms, the black balls are arsenic atoms. The palladium atoms are omitted.

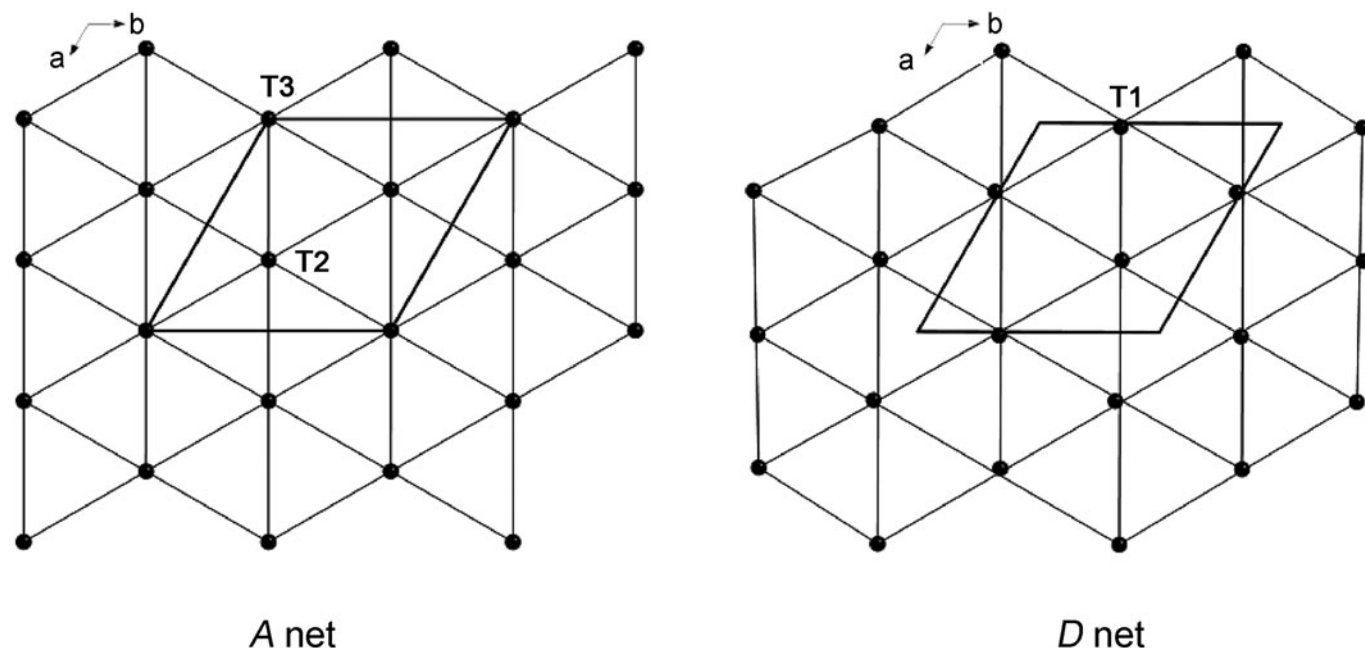**Fig. 7.** The idealised plan of the pnictogen nets in the Pd_8T_3 (T = As, Sb) compounds.

Table 8. Occupation of the sites in pnictogen (As/Sb) triangular nets in Pd_8T_3, (T = As, Sb).

| | A net | | | | | | | D net | | | |
| | T3 site | | | T2 site | | | | T1 site | | | |
Mineral/ synthetic phase	Occ.	Wyck. symb.	Point sym.	Occ.	Wyck. symb.	Point sym.	Plane sym.	Occ.	Wyck. symb.	Point sym.	Plane sym.
Pd_8Sb_3	Sb	6*b*	$\bar{3}$	Sb	12*c*	3	*p*3*m*	Sb	18*e*	2	*p*3
Mertieite-II $Pd_8Sb_{2.5}As_{0.5}$	As	6*b*	3	Sb*	12*c*	3	*p*3*m*	Sb	18*e*	2	*p*3
Arsenopalladinite $Pd_8As_{2.5}Sb_{0.5}$	Sb	1*a*	*i*	As	2*i*	1	*p*2	As**	1*h*	*i*	*p*2
								As	2*i*	1	
Stillwaterite Pd_8As_3	As	1*a*	3	As	2*d*	3	*p*32	As	6*g*	1	*p*3

*The crystal of mertieite-II from Kaareoga River placer is enriched with arsenic and occupation of the T2 site is $Sb_{0.96}As_{0.04}$ (Karimova *et al.*, 2018).
**The T2 site in arsenopalladinite is divided into two sites (Karimova *et al.*, 2020).

trigonal in mertieite-II to triclinic in arsenopalladinite (Karimova *et al.*, 2020).

Stillwaterite, Pd_8As_3 – the arsenic end-member of the Pd_8T_3 (T = As, Sb) family – has the same 3^6 topology of the pnictogen nets: arsenic atoms occupy all atomic sites of the pnictogen nets. The pnictogen nets symmetry of the Pd_8As_3 structure is lower than those of Pd_8Sb_3 (Table 8). The main difference between the structure of stillwaterite, Pd_8As_3, and structures of Pd_8T_3 compounds is the topology of palladium layers. Triangular and pentagon–triangular palladium nets are found in the Pd_8Sb_3, $Pd_8Sb_{2.5}As_{0.5}$ and $Pd_8As_{2.5}Sb_{0.5}$ structures (Karimova *et al.*, 2018, 2020). The Pd_8As_3 structure contains these types of palladium layers too (named the *B* and *C* nets), however it has also triangle–quadrangle (*E*) layers which are not found in other Pd_8T_3 structures.

References

Agilent (2012). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, Oxfordshire, England.

Baelz U. and Schubert K. (1969) Kristallstruktur von $Pd_2As(r)$ und Pd_2Sb. *Journal Less-Common Metals*, **19**, 300–304.

Begizov V.D., Meshchankina B.I. and Dubakina L.S. (1974) Palladoarsenid Pd2As-nature arsenid of palladium from copper-nickel ores Oktyabr'skiy Locality. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, **103**, 104 [in Russian].

Breese N.E. and Schnering N.G. (1994) Bonding trends in pyrites and a reinvestigation of the structures of $PdAs_2$, $PdSb_2$, $PtSb_2$ and $PtBi_2$. *Zeitschrift für anorganische und allgemeine Chemie*. **620**, 393–404.

Cabri L.J., Laflamme J.H.G., Stewart J.M., Rowland J.F. and Chen T.T. (1975) New data on some palladium arsenides and antimonides. *The Canadian Mineralogist*, **13**, 321–335.

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 isomertieite, $Pd_{11}Sb_2As_2$, and tornroosite, $Pd_{11}As_2Te_2$. *The Canadian Mineralogist*, **54**, 511–517.

Karimova O.V., Zolotarev A.A., Evstigneeva T.L. and Johanson B.S. (2018) Mertieite-II, $Pd_8Sb_{2.5}As_{0.5}$, crystal-structure refinement and formula revision. *Mineralogical Magazine*, **82**(S1), S247–S257.

Karimova O.V., Zolotarev A.A., Johanson B.S. and Evstigneeva T.L. (2020) The crystal structure of arsenopalladinite, P $d_8As_{2.5}Sb_{0.5}$, and its relation to mertieite-II, $Pd_8Sb_{2.5}As_{0.5}$. *Mineralogical Magazine*, **84**, 746–752.

Marsh R.E. (1994) The centrosymmetric-noncentrosymmetric ambiguity: some more examples. *Acta Crystallographica*, **50**, 450–455.

Matkovic T. and Schubert K. (1978) Kristallstruktur von Pd_5As und Pd_5Ge. *Journal of the Less-Common Metals*, **58**, 1–6.

Prince E. (2004) (editor). *International Tables for Crystallography. Vol. C, Mathematical, Physical, and Chemical Tables, 3rd ed*. Tables 4.2.6.8 and 6.1.14. Kluwer Academic Publishers, Dordrecht, The Netherlands.

Pearson W.B. (1972) *The Crystal Chemistry and Physics of Metals and Alloys*. Wiley–Interscience. New York. 806 p.

Saini G.S., Calvert L.D., Heyding R.D. and Taylor J.B. (1964) Arsenides of the transition metals. VII. The palladium-arsenic system. *Canadian Journal of Chemistry*, **42**, 620–629.

Shackleton N.J., Malysiak V. and O'Connor C.T. (2007) Surface characteristics and flotation behaviour of platinum and palladium arsenides. *International Journal of Mineral Processing*, **85**, 1–3, 25–40.

Sheldrick G.M. (2015a) SHELXT – Integrated space-group and crystal-structure determination. *Acta Crystallographica*, **A71**, 3–8.

Sheldrick G.M. (2015b) Crystal structure refinement with SHELXL. *Acta Crystallographica*, **C71**, 3–8.

Wopersnow W. and Schubert K. (1976) Kristallstruktur von Pd_8Sb_3. *Journal of the Less-Common Metals*. **48**, 79–87.