







Article

A re-evaluation of stannopalladinite using modern analytical techniques

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Abstract

An investigation of sample 41647 from the Platinum Placer of Ugol'nyi Ruchei, Norilsk Cu–Ni deposit, Russia, stored in the systematic collection of the Fersman Mineralogical Museum, revealed that it contained a mineral that can be identified as the original stannopalladinite described in 1947. As the literature information on the latter is controversial, the mineral was re-investigated using modern analytical techniques. Stannopalladinite occurs as spherical and ovoid-shaped grains up to 0.08 mm, closely intergrown with tetraferroplatinum as part of flattened, prismatic crystals up to 6 mm long. The micro-indentation hardness of stannopalladinite (VHN, 30 g load) is 244 kg/mm² (range 233–266, $n = 4$), corresponding to a Mohs hardness of 4. The calculated density is 9.781 g/cm³. In reflected light, stannopalladinite is pale pink. The bireflectance is noticeable only in oil immersion. In crossed nicols the mineral exhibits strong anisotropy with colour effects changing from reddish purple to greyish blue and polysynthetic twinning of grains. The reflectance curves show distinct anomalous dispersion. The chemical composition (wt.%, electron microprobe data, mean of 11 analyses) is: Cu 8.48, Pd 61.21, Pt 0.89, Sn 25.87, Pb 3.70, total 100.15. The empirical formula calculated on the basis of 4 atoms per formula unit is (Pd_{2.42}Cu_{0.56}Pt_{0.02})_{Σ3.00}(Sn_{0.92}Pb_{0.08})_{Σ1.00}. The ideal chemical formula of stannopalladinite is therefore proposed as (Pd,Cu)₃Sn instead of Pd₃Sn₂ used in the official IMA List of Minerals. The strongest powder X-ray diffraction lines are [d_{obs} , Å (I , %) (hkl)]: 2.292 (42) (231), 2.166 (100) (331), 2.034 (10) (710), 1.916 (15) (141) and 1.851 (15) (630). The powder X-ray data are indexed in the orthorhombic unit cell with $a = 14.634(2)$, $b = 8.5253(6)$, $c = 4.5946(3)$ Å and $V = 573.24(7)$ Å³ ($Z = 8$). Stannopalladinite can be reliably identified among all other minerals belonging to the binary Pd–Sn and ternary Pd–Cu–Sn systems by a combination of chemical, optical and X-ray data.

Keywords: stannopalladinite; optical properties; chemical formula; X-ray data; Ugol'nyi Ruchei; Norilsk deposit; Pd–Sn; Pd–Cu–Sn systems

(Received 18 July 2023; accepted 10 September 2023; Accepted Manuscript published online: 20 September 2023; Associate Editor: Ian Terence Graham)

Introduction

In the course of a scanning electron microscopy study using energy-dispersive spectroscopy of an old collection of platinum-group minerals from the Norilsk ore district, the senior author of the present paper encountered various phases containing Pd and Sn as major elements. However, their unambiguous assignment to a particular mineral species on the basis of chemical composition alone turned out to be quite difficult. The most problematic issue was the correct identification of stannopalladinite, as the available literature data on this mineral turned out to be very contradictory. In order to better understand the

problem and try to solve the above issue, a detailed investigation of the latter was undertaken.

The official International Mineralogical Association (IMA) List of Minerals (Pasero, 2023) includes stannopalladinite as a valid mineral species with ‘grandfathered’ status which applies to minerals discovered before the establishment of the IMA in 1958. Indeed, stannopalladinite dates back to 1947 when this name first appears in the paper of Maslenitskiy *et al.* (1947). However to date, the mineral remains poorly studied. Its official chemical formula is reported as Pd₃Sn₂ with a question mark. Various literature sources contain contradictory information regarding its physical properties, chemical composition and X-ray data. The structure of stannopalladinite is unknown.

The aim of this paper is to provide new data obtained on what we believe is the exact analogue of the original material studied by Maslenitskiy *et al.* (1947). New chemical and X-ray analyses conducted in this work combined with the critical perception of the data published in the literature led us to propose a new chemical

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Cite this article: Kasatkin A.V., Vymazalová A., Nestola F., Gurzhiy V.V., Agakhanov A.A., Škoda R., Belakovskiy D.I. and Generalov M.E. (2023) A re-evaluation of stannopalladinite using modern analytical techniques. *Mineralogical Magazine* 87, 773–782. <https://doi.org/10.1180/mgm.2023.73>

formula and unit-cell parameters for stannopalladinite and unambiguously demonstrate its difference from other minerals of the Pd–Sn and Pd–Cu–Sn systems.

Historical background

Maslenitskiy *et al.* (1947) reported on a mineral with the formula Pd_3Sn_2 called “stannopalladinite” from “the placer and concentrates of the processing plant”. The new mineral was described as very small but abundant inclusions in well-formed cubic skeletal, platy and prismatic elongated crystals of ferroplatinum. Apart from very limited physical (Table 1) and chemical properties (weak reaction with concentrated HNO_3 and fast reaction with *aqua regia*), the authors provided a bulk chemical composition of grains where stannopalladinite was “maximally concentrated”. Because of the substantial copper content, the mineral was also named “cuprian stannopalladinite”.

One year later, Maslenitskiy (1948) added more information on the above findings. In particular, he provided the detailed description and photos of ferroplatinum crystals and stannopalladinite inclusions in them and reported eight more chemical analyses related to this mineral.

Twenty four years later, Berry and Thompson (1962) published under the name “stannopalladinite” the powder X-ray data of a synthetic material with the formula Pd_3Sn_2 and assigned to it a $P6_3/mmc$ space group and hexagonal unit cell with $a = 4.399$ and $c = 5.666$ Å, referring to the paper of Nowotny *et al.* (1946). The latter authors were first to provide the powder X-ray data of synthetic Pd_3Sn_2 , its hexagonal unit cell similar to the one mentioned above and suggested the structure of this compound to be a filled NiAs type.

Genkin (1968) disclosed the type locality of stannopalladinite described by Maslenitskiy *et al.* (1947) as the platinum placer of Ugol'nyi Ruchi ('Coal stream') Mine in the Norilsk Cu–Ni deposit. Obviously, this locality could not be mentioned in 1947 given that in 1935–1956 the Norilsk deposits were managed by Noril'lag (a soviet concentration camp that was part of the infamous GULAG system), mined by prisoners and all the relevant mining information was under secrecy. Apart from the type locality, A.D. Genkin also reported on stannopalladinite from the 203 m level of the Taimyr Mine in the Oktyabrskoe Cu–Ni deposit as small rounded, oval or elongated grains up to 0.3 mm rimmed by “tetragonal ferroplatinum” in chalcopyrite veins. A lot of other important information was added by the author to further characterise this mineral such as optical properties, including a reflectance dataset, hardness and powder X-ray diffraction data (Table 1). It was suggested that the latter are similar to synthetic Pd_3Sn_2 . The direct comparison of the data revealed that several d spacings of the synthetic compound are absent in natural stannopalladinite, however, the author explained it by the chemical features of the mineral. The microspectral analysis showed Cu to be an essential part of the mineral along with Pd and Sn, so after Maslenitskiy *et al.* (1947) the mineral was called “cuprian stannopalladinite”.

Chernyaev and Yushko-Zakharova (1968) reported on stannopalladinite from the Monchegorsk Cu–Ni deposit (Murmansk Oblast) as grains up to 0.1 mm in size intergrown with niggliite (PtSn). Some of their data, however, differed from the stannopalladinite from Norilsk. In particular, the reported hardness was substantially larger and the chemical composition, measured for the first time by the electron microprobe method, showed the absence of Cu and the empirical formula to be closer to Pd_5Sn_3 rather than Pd_3Sn_2 . No X-ray data were provided.

Vyalsov (1973) provided a new reflectance dataset and some other optical data for stannopalladinite “from Norilsk” with no more details on the locality. The chemical formula was given with admixed Pb (Table 1).

L.J. Cabri in his handbooks on PGM minerals (Cabri, 1972, 1981) compiled the data on stannopalladinite given by predecessors and assigned to natural material the hexagonal unit-cell parameters (e.g. $a = 4.399$ and $c = 5.666$ Å) similar to those reported by Berry and Thompson (1962). For powder X-ray data, he referred to the PDF card #4-801 of the synthetic Pd_3Sn_2 .

Genkin *et al.* (1981) noted the difficulties in calculating the formula and characterisation of stannopalladinite and stressed the necessity to conduct a detailed check of all chemical compositions mentioned in the literature along with structural studies in order to establish the real position of copper atoms in the unit cell of the mineral. Nevertheless, the authors reported on stannopalladinite from another locality – the Talnakh deposit in the Norilsk ore district where the mineral forms a central part of zoned grains included in massive chalcopyrite and talnakhite ores. Stannopalladinite is often intergrown with plumbopalladinite, polarite and silver and is rimmed by isoferroplatinum. Its intergrowths with arsenides of Pd and Ni are rarer. Optical and chemical data of this material were given. The authors noted the constant presence of copper (~6 wt.%) as the main feature of the chemical composition of the mineral but, at the same time, stressed the significant variations in the content of other elements (Pd, Pt, Sn, Pb, Bi, Sb and As). Their chemical analyses were calculated in three possible ways: (1) Pd and Cu in one position; (2) Cu and Sn in one position; and (3) Pd, Cu and Sn all in independent positions. The last option gave the most stoichiometric formula close to $(\text{Pd,Pt})_6\text{Cu}_1(\text{Sn,Pb,Bi,Sb,As})_3$, or Pd_6CuSn_3 . The reported d spacings of the debyegram (Table 1) were suggested to be close to the synthetic Pd_3Sn_2 .

Evsstigneeva and Nekrasov (1984) studied in detail natural and synthetic compounds belonging to the ternary Pd–Cu–Sn system. They provided chemical and powder X-ray data for stannopalladinite but, unfortunately, with no information on its provenance. These authors came to the conclusion that stannopalladinite is the natural analogue of the synthetic $\text{Pd}_5\text{Sn}_2\text{Cu}$ for which they suggested an orthorhombic symmetry with $a \approx 7.8$ and $b \approx c \approx 3.9$ Å and $Pmmm$ space group. Optical data were given for the synthetic material.

Cabri (2002) tried to summarise all the previous information on stannopalladinite from various publications. He assigned to stannopalladinite the formula $\text{Pd}_5\text{Sn}_2\text{Cu}$ (with a question mark) and the orthorhombic cell proposed by Evstigneeva and Nekrasov (1984) but clearly noted that the rarity of this phase, the existence of other Pd–(Pt) minerals with Cu and Sn (atokite, paolovite, cabriite and taimyrite), the very small grain size and frequent occurrence as intergrowths with other minerals have caused confusion in the literature. He stated that there is no certainty that the mineral studied by Maslenitskiy *et al.* (1947) is the same as that studied by subsequent authors, including Genkin *et al.* (1981) and Evstigneeva and Nekrasov (1984). The key to this problem is X-ray diffraction, but most publications contain no X-ray data and all conclusions are made solely on the basis of electron probe microanalyses. The author suggested that a formal redefinition of stannopalladinite is needed, including the re-examination of type material, determination of ideal formula/range of compositions and re-investigation of powder X-ray diffraction/symmetry.

Table 1. Literature data on stannopalladinite.

Source	Locality	Formula	Physical properties				System, space group, unit cell (Å)	
			General description	Optical properties	Density	Hardness		Powder X-ray data
Maslenitskiy <i>et al.</i> (1947), Maslenitskiy (1948)	Placer and concentrates of the processing plant	Pd ₃ Sn ₂	Inclusions in cubic skeletal, platy and prismatic elongated crystals of ferroplatinum	Brownish or pinkish colour, darker than ferroplatinum	n.d.	Lower than ferro-platinum	n.d.	n.d.
Genkin (1968)	Platinum Placer of Ugol'nyi Ruchej, Norilsk Cu–Ni deposit, Krasnoyarsk Krai Taimyr Mine, 203 m level, Oktyabrskoe Cu–Ni deposit, Krasnoyarsk Krai	Pd ₃ Sn ₂	Rims around big, up to 5 mm, crystals of ferroplatinum and inclusions in them Rounded, oval or elongated grains up to 0.3 mm, often rimmed by ferroplatinum, in chalcopryrite veins	Pale pink in reflected light. Bireflectance is observed only in oil. Distinct anisotropy, from lilac-red to greyish-blue. Polysynthetic twinning of grains. In some grains two systems of twin individuals are located at an angle of 90° to each other	n.d.	265 (220–228*) kg/mm ²	See Table 4 See Table 4	n.d. n.d.
Chernyaev and Yushko-Zakharova (1968)	Monchegorsk Cu–Ni deposit, Murmansk Oblast	Pd ₅ Sn ₃	Grains to 0.1 mm intergrown with niggliite	Brownish-pink in reflected light. Strong anisotropy from red to bluish.	n.d.	387–452 kg/mm ²	n.d.	n.d.
Cabri (1972)	Norilsk	~Pd ₃ Sn ₂	Same as in Genkin (1968)	Same as in Genkin (1968)	n.d.	Same as in Genkin (1968)	Ref. to Berry and Thompson (1962)	Hex., <i>P6₃/mmc?</i> , <i>a</i> = 4.399, <i>c</i> = 5.666
Vyalsov (1973)	Norilsk	Pd ₃ (Sn,Cu,Pb) ₂	n.d.	Light pink in reflected light. Very weakly bireflectant. Anisotropic.	n.d.	n.d.	n.d.	n.d.
Cabri (1981)	Same as in Genkin (1968)	Ideal formula Pd ₃ Sn ₂ ? General formula (Pd,Cu) ₃ Sn ₂ ?	Same as in Genkin (1968)	Same as in Genkin (1968)	9.79 g/cm ³	Same as in Genkin (1968)	Ref.to PDF card #4–801	Hex., <i>a</i> = 4.390, <i>c</i> = 5.655
Genkin <i>et al.</i> (1981)	Talnakh deposit, Krasnoyarsk Krai	Pd ₆ CuSn ₃	Central parts of zoned grains in chalcopryrite and talnakhite ores	Light pink in reflected light. Very weakly bireflectant in air, colour effects change from light pink to light purple-pink. Anisotropic with bright colour effects in orange-brown and dark blue tones. Polysynthetic twinning of grains.	n.d.	n.d.	Main lines of debyegram: 2.30 (10), 2.16(10), 2.01(3), 1.440(2), 1.222(2)	n.d.
Evstigneeva and Nekrasov (1984)	n.d.	Pd ₅ Sn ₂ Cu	n.d.	For synthetic Pd ₅ Sn ₂ Cu: bright pink in reflected light, distinctly bireflectant, pleochroic from pinkish-brown to golden-yellow and anisotropic	n.d.	n.d.	See Table 4	Orth., <i>Pmmm</i> , <i>a</i> ≈ 7.8, <i>b</i> ≈ 3.9, <i>c</i> ≈ 3.9
Cabri (2002)	Ugol'nyi Ruchej; Majak Mine; Taimyr Mine; Oktyabr Mine; Monchegorsk	Pd ₅ Sn ₂ Cu?	Rounded 'cubic', oval, or elongated grains up to 0.1 mm. Also as small emulsion-type inclusions in Pt–Fe alloy	Pale pink or brown-rose, bireflection observed only in oil, anisotropism distinct to strong, with colour effects from lilac-red to grey-blue	11.31 g/cm ³ (synthetic material)	VHN: 265 (220–228*) and 387–452 kg/cm ³ ; Mohs: 4.5 to 5.	2.30 (30), 2.18 (100), 1.230 (40), 1.098 (50), 1.084 (50)	Orth., <i>Pmmm</i> , <i>a</i> ≈ 7.88, <i>b</i> ≈ <i>c</i> ≈ 3.94, <i>V</i> = 122.33 Å ³

*Probably a typo, correct range is likely to be 220–328.
n.d. = no data available

A summary of the literature data on stannopalladinite, as compiled in Table 1, clearly demonstrates a lack of unified approach to what this species should be considered. It is obvious that some of the data assigned to stannopalladinite probably belong to other phases and, as was correctly suggested by Cabri (2002), more work is required to properly define this mineral.

Samples and experimental methods

Unfortunately, no information is available on the location of the original material of stannopalladinite from Ugol'nyi Ruchei studied by Maslenitskiy *et al.* (1947), Maslenitskiy (1948) and Genkin (1968). The nomenclature designations for the type mineral specimens and the encouragement to authors to deposit such specimens in museums were approved by the Commission on New Minerals and Mineral Names (CNMNC) of the IMA much later (Dunn and Mandarino, 1987).

However, the collections of the Fersman Mineralogical Museum comprise three samples with catalogue numbers 41647, 45863 and 46887 that originate from Ugol'nyi Ruchei and whose general appearance look very similar to the material studied by the above-mentioned predecessors. These samples were registered to the Museum's collection in 1938 and 1949 and were probably mined during panning out in the placer of Ugol'nyi Ruchei in this period of time. They represent cubic, prismatic, flattened elongated crystals up to 10 mm with features of skeletal growths in many of them. A more detailed description of these three samples and their photographs are given by Generalov and Pautov (2005).

The visual comparison of the samples from the Fersman museum with those studied by Maslenitskiy *et al.* (1947) and Maslenitskiy (1948) show their very close resemblance (Fig. 1a). Also, similarly to the original material, considerable parts of crystals from the Fersman museum show strong ferromagnetism. Finally, the chemical analysis of one of the cubic crystals from sample 41647 done by Generalov and Pautov (2005) revealed its inhomogeneous composition with most of the grain matching

Pt-Fe-bearing minerals (tetraferroplatinum, ferrorickelplatinum and isoferroplatinum) with inclusions of Pd-Cu-Sn-Pb-phases, some of which were interpreted as stannopalladinite. This is also in line with the information provided by Maslenitskiy *et al.* (1947) and Maslenitskiy (1948).

All the above information led us to undertake a more detailed investigation of the material from the Fersman museum's collections. As the cube-shaped crystal was already chemically studied by Generalov and Pautov (2005) we decided to investigate one of the flattened, prismatic crystals, 6 mm long, from sample 41647 (Fig. 1b), especially as Maslenitskiy (1948) suggested these to be richer in stannopalladinite than cubic crystals. A small fragment of the crystal was separated, put in the thin section and examined using a variety of analytical techniques.

Micro-indentation hardness was measured with a PMT-3 instrument calibrated with respect to NaCl.

The optical properties in reflected light were studied using POLAR-3 and POLAR-215 polarising light microscopes. Reflectance values have been measured in air using a MSF-R (LOMO, St. Petersburg, Russia) microspectrophotometer with silicon used as a standard. The photometric aperture diameter was 0.3 mm, monochromator exit slit size – 0.1 mm, spectral interval – 6 nm.

The chemical composition was analysed with a Cameca SX-100 electron microprobe (Masaryk University, Brno) using the wavelength dispersive spectroscopy mode mode, 25 kV, 10 nA, 2 µm beam diameter. Analysed elements, analytical X-ray lines, analysing crystals (in parentheses) and standards were as follows: FeK α (LLIF) – FeS₂; NiK α (LLIF) – pararammelsbergite; CuK α (LLIF) – Cu; PdL α (LPET) – Pd; SnL β (PET) – Sn; PtL α (LLIF) – Pt; and PbM α (LPET) – PbSe. Other elements heavier than F were sought for but their contents were below the detection limit. The raw intensities were converted to concentrations using X-PHI matrix-correction software (Merlet, 1994).

In order to get single-crystal X-ray diffraction (SCXRD) data, grains of minerals studied optically and by electron microprobe were extracted from the thin section and analysed using a

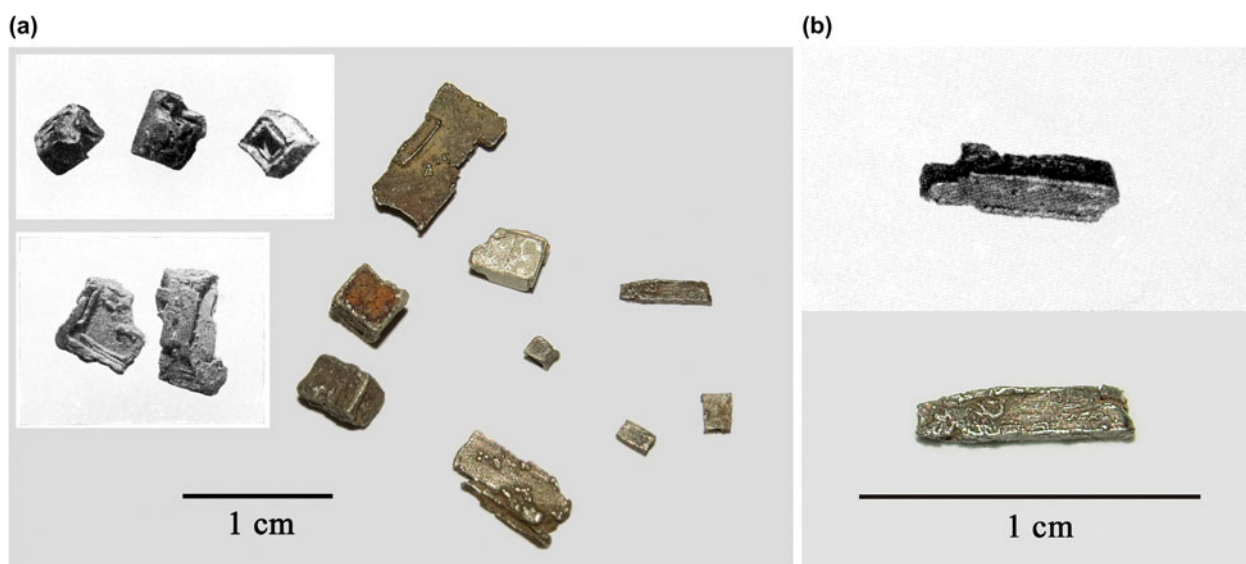


Figure 1. Original material from Ugol'nyi Ruchei studied by Maslenitskiy *et al.* (1947) and Maslenitskiy (1948) in comparison with the material from the Fersman museum's collections: (a) cube-shaped (top left) and platy skeletal (mid left) crystals of Maslenitskiy (1948, their figures 1 and 4) and crystals of different habit from sample 41647; (b) prismatic crystal pictured by Maslenitskiy (1948, their figure 3) (top) and a similar-looking crystal from sample 41647 (bottom), from which a fragment was separated for further research.

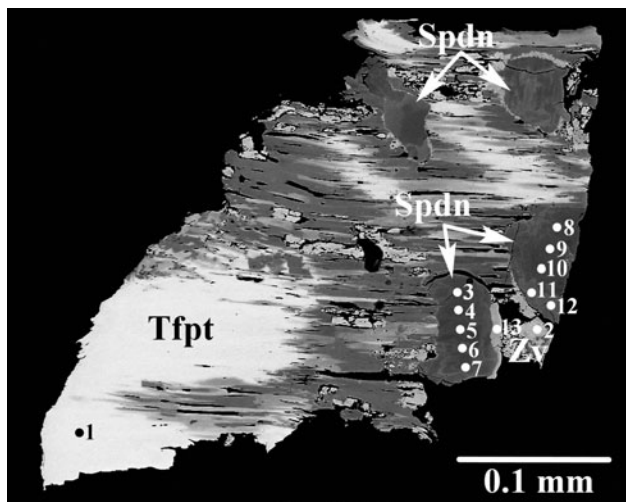


Figure 2. Intimate intergrowth of stannopalladinite (Spdn, various shades of grey) and tetraferroplatinum (Tfpt, white) in association with zvyagintsevite (Zv). Analytical spots have the same numbers as in Table 2. Thin section, back-scattered electrons image.

Rigaku Oxford Diffraction SuperNova diffractometer (University of Padova) equipped with a Pilatus 200K Dectris detector and an X-ray micro-source (MoK α radiation) with accelerating voltage of 50 kV, beam current of 0.8 mA and beam size on the sample ~0.12 mm. The detector-to-sample standard distance was 68 mm. The powder X-ray diffraction (PXRD) data were collected on the same instrument using microdiffraction mode with 0–360° rotation scan and exposure time varying from 15 minutes (tetraferroplatinum) to 12 hours (for stannopalladinite).

In an attempt to improve the quality of the SCXRD data, an additional experiment with the same grain of stannopalladinite was carried out at a low temperature (100 K) using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer (Research

Centre for X-ray Diffraction Studies, St. Petersburg State University) equipped with a HyPix-6000HE detector and an X-ray micro-source (MoK α radiation) with accelerating voltage of 50 kV, and beam current of 1.0 mA. The detector-to-sample distance was 34 mm, and the exposure time per each frame was 60 seconds.

Results and discussion

Optically and chemically, the studied fragment represents an intimate intergrowth of mainly two phases: tetraferroplatinum and a Pd–Cu–Sn-bearing mineral that we determined as stannopalladinite on the basis of the data below (Fig. 2). Tetraferroplatinum is white in reflected light and isotropic. The mineral is strongly magnetic. Its composition corresponds to a nickeloan–cuprian variety (Table 2, an. 1) and its tetragonal unit-cell parameters calculated from the powder X-ray diffraction data are: $a = 2.7003(3)$, $c = 3.6833(6)$ Å and $V = 26.86(6)$ Å³. Very minor Sn-bearing zvyagintsevite (Table 2, an. 2) is also present in the association studied.

The Pd–Cu–Sn mineral forms spherical and ovoid-shaped grains up to 0.08 × 0.05 mm. It is dark grey, opaque and has a metallic lustre. The values of micro-indentation hardness (VHN, 30 g load) are between 233 and 266 kg/mm², and the average of 4 measurements is 244 kg/mm², corresponding to a Mohs hardness of 4.

The mineral has very distinct optical properties. It is pale pink in reflected light (Fig. 3a). The bireflectance is noticeable only in oil immersion. In crossed nicols, the mineral exhibits strong anisotropy with colour effects changing from reddish purple to greyish blue and polysynthetic twinning of grains (Fig. 3b). Its reflectivity is high but lower than that of neighbouring tetraferroplatinum. Measured reflectance values are given in Table 3 and plotted in Fig. 4 in comparison with the literature data for stannopalladinite. Note a very distinct anomalous dispersion of reflectance curves.

Table 2. Chemical composition (wt.%) of minerals from Ugol'nyi Ruchei.

No. an.	Fe	Ni	Cu	Pd	Pt	Sn	Pb	Total	Empirical formulas
1	18.07	5.63	2.04	–	74.10	–	–	99.84	Pt _{0.92} Fe _{0.78} Ni _{0.24} Cu _{0.08}
2	–	–	–	63.08	–	5.79	30.30	99.17	Pd _{3.01} Pb _{0.74} Sn _{0.25}
3	–	–	8.98	61.31	0.78	29.14	0.40	100.61	Pd _{2.38} Cu _{0.58} Pt _{0.02} Sn _{1.01} Pb _{0.01}
4	–	–	8.91	61.68	0.81	28.91	0.41	100.72	Pd _{2.39} Cu _{0.58} Pt _{0.02} Sn _{1.00} Pb _{0.01}
5	–	–	8.93	61.77	0.85	29.02	0.45	101.02	Pd _{2.39} Cu _{0.58} Pt _{0.02} Sn _{1.01} Pb _{0.01}
6	–	–	8.95	61.11	0.70	28.71	0.88	100.35	Pd _{2.38} Cu _{0.58} Pt _{0.01} Sn _{1.00} Pb _{0.02}
7	–	–	8.93	61.44	1.01	29.19	0.93	101.50	Pd _{2.37} Cu _{0.58} Pt _{0.02} Sn _{1.01} Pb _{0.02}
8	–	–	9.89	60.58	1.14	25.81	1.17	98.59	Pd _{2.39} Cu _{0.65} Pt _{0.02} Sn _{0.91} Pb _{0.02}
9	–	–	8.67	61.26	0.71	27.87	1.35	99.86	Pd _{2.41} Cu _{0.57} Pt _{0.02} Sn _{0.98} Pb _{0.03}
10	–	–	8.82	61.51	0.72	28.41	1.61	101.07	Pd _{2.39} Cu _{0.57} Pt _{0.02} Sn _{0.99} Pb _{0.03}
11	–	–	8.12	60.42	0.98	23.29	6.73	99.54	Pd _{2.55} Cu _{0.44} Pt _{0.02} Sn _{0.84} Pb _{0.14}
12	–	–	8.84	60.06	1.17	20.93	7.62	98.62	Pd _{2.45} Cu _{0.60} Pt _{0.03} Sn _{0.76} Pb _{0.16}
13	–	–	4.20	62.21	0.88	13.24	19.15	99.68	Pd _{2.72} Cu _{0.31} Pt _{0.02} Sn _{0.52} Pb _{0.43}
14	–	–	8.48	61.21	0.89	25.87	3.70	100.15	Pd_{2.42}Cu_{0.56}Pt_{0.02}Sn_{0.92}Pb_{0.08}
15	0.81	–	4.94	51.42	15.13	23.50	1.70	97.50	Pd _{2.25} Cu _{0.36} Pt _{0.36} Fe _{0.07} Sn _{0.92} Pb _{0.04}
16	0.41	–	7.06	59.23	–	17.56	16.08	100.34	Pd _{2.47} Cu _{0.49} Fe _{0.03} Sn _{0.66} Pb _{0.34}
17	0.46	–	8.76	57.90	–	16.22	17.72	101.06	Pd _{2.39} Cu _{0.60} Fe _{0.04} Sn _{0.60} Pb _{0.37}
18	1.30	0.40	8.50	42.50	17.50	30.50	–	100.70	Pd _{1.76} Cu _{0.59} Pt _{0.39} Fe _{0.10} Ni _{0.03} Sn _{1.13}
19	1.09	0.28	10.19	40.73	16.82	30.67	–	100.23	Pd _{1.67} Cu _{0.70} Pt _{0.38} Fe _{0.09} Ni _{0.02} Au _{0.01} Sn _{1.13}

1 – tetraferroplatinum; 2 – zvyagintsevite; 3–14 – stannopalladinite (sample 41647, our data).

Analysis 14 (bold) is the mean of analyses 3–13.

Analyses 15, 16 and 17 correspond to analyses 8, 10 and 11, respectively, from Generalov and Pautov (2005).

Analysis 18 is the mean data calculated by us from the values reported in Table 2 by Maslennitskiy et al. (1947).

Analysis 19 is the mean of eight analyses calculated by us from the values reported in by Maslennitskiy (1948) their table 3; total includes 0.45 wt.% of Au.

Empirical formulas are calculated on the basis of atoms sum of 2 (an. 1) and 4 (an. 2–19).

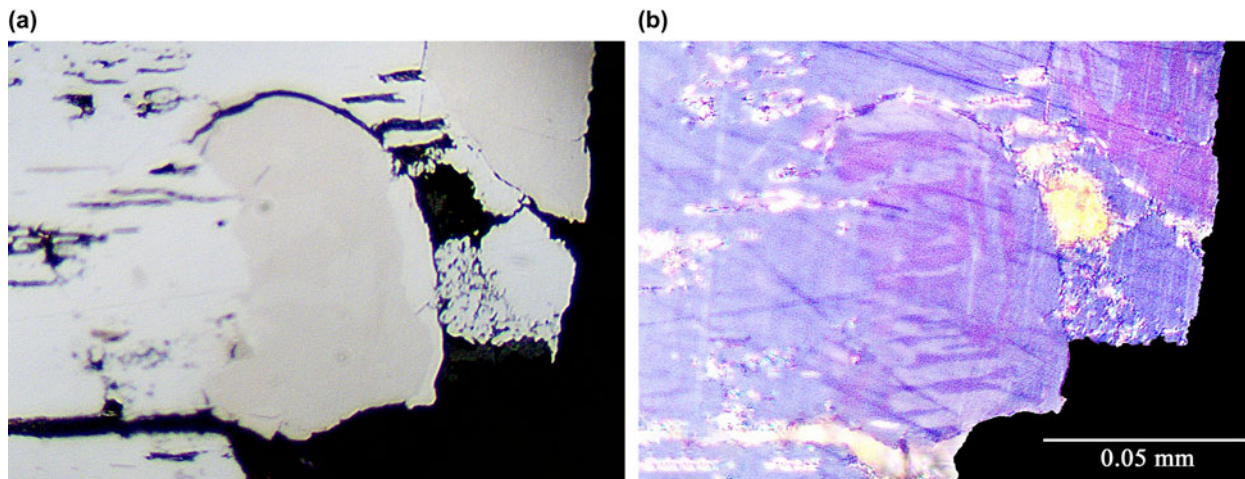


Figure 3. Enlarged fragment of Fig. 2 (right lower part) in reflected light: (a) at one nicol; (b) in crossed nicols.

Table 3. Reflectance values (%) for stannopalladinite.

λ (nm)	R_1	R_2	λ (nm)	R_1	R_2
400	44.2	41.7	560	53.1	51.8
420	45.2	42.9	580	54.0	52.8
440	46.3	44.2	600	55.0	53.7
460	47.1	45.3	620	56.0	54.7
480	48.4	46.7	640	57.0	55.8
500	49.6	48.1	660	57.9	56.8
520	50.8	49.5	680	58.8	57.7
540	52.0	50.6	700	60.0	58.8

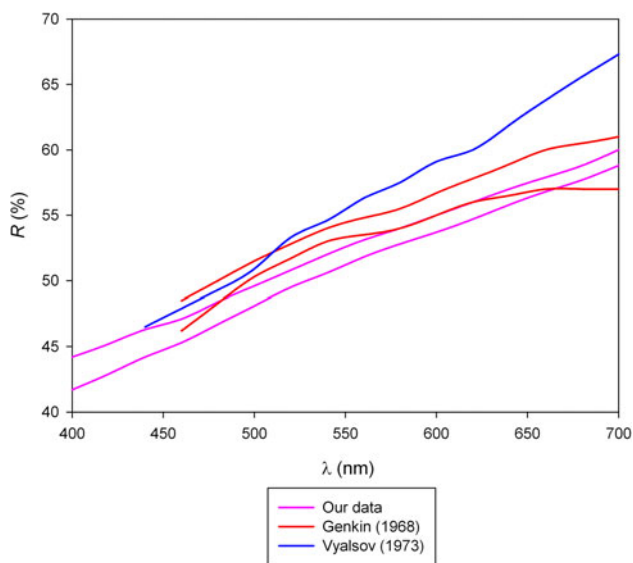


Figure 4. Reflectance curves of stannopalladinite.

As we can see, the optical data of our mineral and its hardness are a very close match to those reported by Maslenitskiy *et al.* (1947) and Genkin (1968) for the original stannopalladinite from Ugol'nyi Ruchej (Table 1).

Chemically, the Pd–Cu–Sn mineral is heterogeneous, as shown in the back-scattered electron image (Fig. 2), and contains various

admixture of Pb and Pt. Dark grey areas are almost Pb-free (Table 2, an. 3–10) whereas in light grey zones the content of Pb (Table 2, an. 11–12) is up to 19.15 wt.% in the most Pb-rich parts (Table 2, an. 13). We do not exclude that Pb admixture is due to an intimate intergrowth of our Pd–Cu–Sn-mineral with zvyagintsevite. Generalov and Pautov (2005) reported on the compositions of apparently the same mineral with 15.13 wt.% Pt (Table 2, an. 15) and up to 17.72 wt.% Pb (Table 2, an. 16 and 17). Such chemical variety, however, does not affect the general stoichiometry which remains always the same for all analyses obtained by us and Generalov and Pautov (2005), i.e. (Pd,Cu,Pt) : (Sn,Pb) \approx 3 : 1. The empirical formula obtained on the sample studied by us as a mean of 11 analyses and calculated on the basis of 4 atoms pfu is $(\text{Pd}_{2.42}\text{Cu}_{0.56}\text{Pt}_{0.02})_{\Sigma 3.00}(\text{Sn}_{0.92}\text{Pb}_{0.08})_{\Sigma 1.00}$.

To compare the chemical composition of our mineral with the original stannopalladinite, we calculated the empirical formulae for the latter using the average values reported by Maslenitskiy *et al.* (1947) and eight chemical analyses given by Maslenitskiy (1948) – see Table 2, an. 18 and 19, respectively. Surprisingly, we found out that, even bearing in mind the imperfectness of the chemical data of that time and probable admixture of other minerals in them, the calculated stoichiometry (Pd,Cu,Pt,Fe,Ni) : Sn is much closer to 3:1 obtained by us rather than 3:2 suggested by Maslenitskiy *et al.* (1947) and following authors.

The combination of factors, such as the similar general appearance of the material and its origin, similar mineral association, physical properties (hardness, unique optical properties etc.) and close chemical composition, led us to the conclusion that the Pd–Cu–Sn-bearing mineral discovered by us in sample 41647 from the Fersman museum collections seems to be the same as the original stannopalladinite described by Maslenitskiy *et al.* (1947), Maslenitskiy (1948) and Genkin (1968).

In order to perform X-ray studies, we extracted from the thin section the most homogenous, almost Pb-free fragment. Unfortunately, it was impossible to obtain reliable single-crystal structure data at ambient temperature as the mineral turned out to be of a completely ‘powdery’ nature (Fig. 5a). The SCXRD data collection of the same stannopalladinite sample at low temperature (100 K) slightly improved the quality of the diffraction patterns, which is seen from the appearance of a few discrete Bragg reflections (Fig. 5b) that were totally absent on the patterns collected at room temperature. However, it was still impossible to

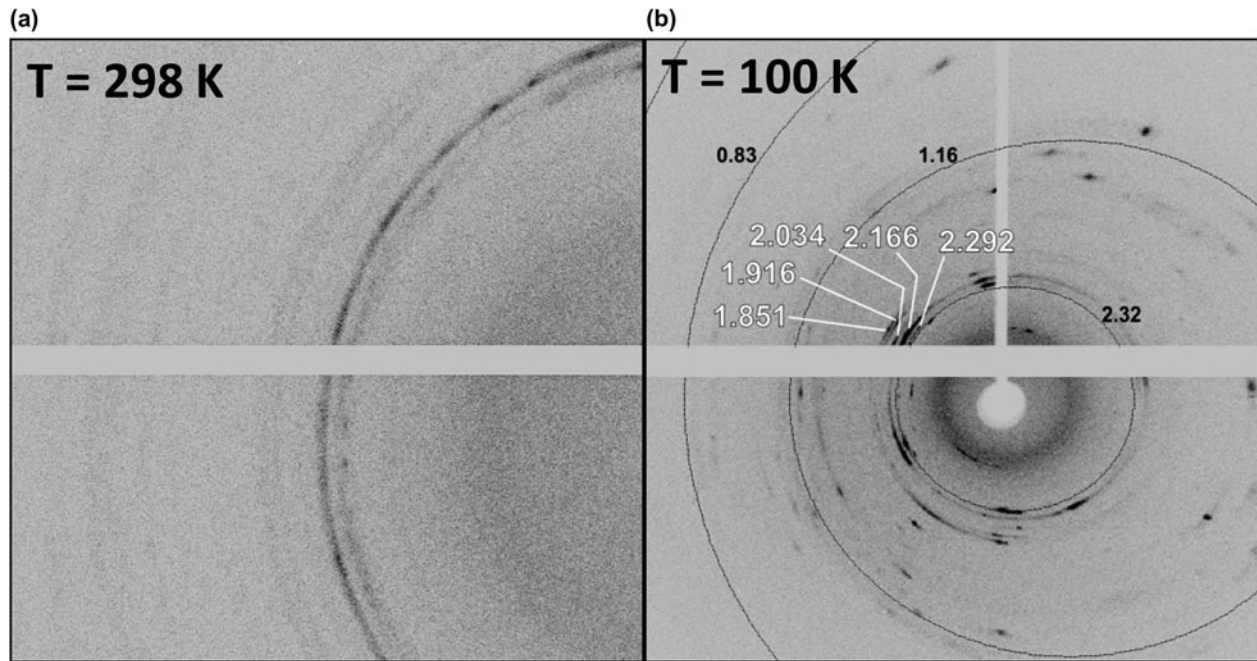


Figure 5. Single-crystal diffraction pattern of the stannopalladinite sample collected at 298K (a) and 100K (b). In Fig. 5b we show the resolution circles (black) and the most intense lines marked (white) in accordance with the PXRD data (see Table 4).

process these data as the main portion of the diffraction results in diffraction arcs (sections of Debye-Scherrer rings), while discrete reflections belong to different domains. So, the final unit cell parameters were determined from the PXRD data collected earlier at room temperature. However, we note that the diffraction arcs

from the SCXRD experiment at low temperature fully correspond to the PXRD data collected at ambient temperature (Fig. 5b, Table 4).

The obtained PXRD data (Table 4) contain all the *d* spacings reported by Genkin (1968) and, to our opinion, are yet another

Table 4. Powder X-ray data for stannopalladinite and synthetic Pd₃Sn₂.

Stannopalladinite												
Sample 41647, our data					Genkin (1968)				Evstigneeva, Nekrasov (1984)		Synthetic Pd ₃ Sn ₂ (PDF card #040801)	
					Ugol'nyi stream		Taimyr Mine		<i>d</i> _{obs}	<i>l</i> _{obs}	<i>d</i> _{obs}	<i>l</i> _{obs}
<i>h</i>	<i>k</i>	<i>l</i>	<i>d</i> _{obs}	<i>l</i> _{obs}	<i>d</i> _{obs}	<i>l</i> _{obs}	<i>d</i> _{obs}	<i>l</i> _{obs}				
4	0	0	3.665	9					3.62	5		
4	1	1	2.710	6			2.84	10			3.160	40
3	2	1	2.630	2					2.58	5	2.830	40
4	2	1	2.375	6								
2	3	1	2.292	42	2.30	80	2.30	100	2.30	30	2.270	100
3	3	1	2.166	100	2.18	100	2.16	100	2.18	100	2.200	100
7	1	0	2.034	10	2.05	10	2.01	30	1.998	10		
1	4	1	1.916	15					1.920	20		
6	3	0	1.851	15								
8	0	1	1.698	3	1.675	10			1.706	10	1.740	20
6	1	2	1.641	4			1.641	10			1.690	10
											1.580	70
9	2	0	1.519	3					1.564	5		
0	2	3	1.442	6	1.440	10	1.440	20	1.434	20	1.420	50
0	6	1	1.358	6			1.349	10	1.365	10		
4	6	0	1.325	7					1.320	20		
3	6	1	1.307	8			1.299	10	1.275	10	1.280	70
											1.270	50
0	4	3	1.244	2					1.230	40		
0	7	0	1.218	9	1.223	20	1.222	20			1.190	70
1	0	4	1.145	7	1.166	20	1.143	10	1.142	20		
3	0	4	1.118	6					1.130	10		
4	1	4	1.087	3			1.078	10	1.084	50	1.100	40

Table 5. Comparative data for the minerals belonging to the Pd–Sn and Pd–Cu–Sn systems.

Mineral	Stannopalladinite	Paolovite	Atokite	Taimyrite	Cabriite
General formula	(Pd,Cu) ₃ Sn	Pd ₂ Sn	Pd ₃ Sn	(Pd,Cu,Pt) ₃ Sn	Pd ₂ CuSn
Empirical formula	Pd _{2.42} Cu _{0.56} Pt _{0.02} Sn _{0.92} Pb _{0.08}	Pd _{1.98} Pt _{0.04} Sn _{1.00} ^a	Pd _{1.94} Pt _{1.21} Sn _{0.85}	Pd _{2.12} Cu _{0.64} Pt _{0.26} Sn _{0.85} Sb _{0.12} Pb _{0.01} ^b	Pd _{1.97} Pt _{0.05} Ag _{0.01} Cu _{0.97} Sn _{0.98} Sb _{0.02} ^c
Crystal system	Orthorhombic	Orthorhombic	Cubic	Orthorhombic	Orthorhombic
Space group			<i>Fm3m</i>		<i>Pmmm</i>
<i>a</i> (Å)	14.634(2)	8.11(1)	3.9887(1)	16.11(2)	7.88(5)
<i>b</i> (Å)	8.5253(6)	5.662(6)		11.27(1)	7.88(5)
<i>c</i> (Å)	4.5946(3)	4.324(2)		8.64(1)	3.94(2)
<i>V</i> (Å ³)	573.24(7)	198.6(3)	63.457(6)	1569(3)	245(2)
Strongest lines of the powder	2.292–42	2.36–40	2.295–100	2.36–50	2.29–100
X-ray diffraction pattern:	2.166–100	2.28–100	1.408–90	2.29–60	2.17–90
<i>d</i> (Å) – <i>l</i> (%)	2.034–10	2.16–70	1.202–100	2.15–100	1.230–80
Optical data:	1.916–15	1.955–50	0.9153–90	1.436–30	1.217–40
Colour in reflected light	1.851–15	1.078–50	0.8145–90	1.217–30	1.182–30
Birefractance	Pale pink	Lilac-rose	Light cream	Light grey with a pink tint	Bright pink with a lilac tinge
Anisotropy	Weak, observed only in immersion	Distinct in air	No	Distinct, from light grey with a rose tint to creamy tint	Weak
Polysynthetic twinning	Strong, from lilac-red to greyish-blue	Strong, in orange-red and dark-blue tones	Slight, due to strain	Colours from dark grey with a blue tint to yellow-grey	Strong, from greyish-brown to golden
Reflectance values at 460, 520, 580, 640 (in nm, <i>R</i> ₁ / <i>R</i> ₂)	Yes	Yes	No	Yes	Yes
Hardness, kg/mm ² mean (range)	47.1/45.3; 50.8/49.5; 54.0/52.8; 57.0/55.8	42.8/41.8; 46.9/44.0; 51.0/48.4; 54.4/54.2 ^d	60.8/57.4; 65.1/59.2; 63.5/60.4; 65.8/62.2 ^e	42.3/39.6; 47.8/44.0; 51.6/47.4; 56.5/51.4	43.4/43.0; 48.4/46.8; 53.2/51.4; 59.4/57.2 ^f
Density (calc.) (g/cm ³)	244 (233–266)	380 (360–400)	357	480±25	272 (258–282)
Source	9.781	n.d.	14.19	n.d.	11.1
	This paper (our data)	Genkin <i>et al.</i> (1974)	Mihálik <i>et al.</i> (1975)	Begizov <i>et al.</i> (1982)	Evstigneeva and Genkin (1983)

^aCalculated by us as an average of 3 analyses from Genkin *et al.* (1974)

^bCalculated by us as an average of 5 analyses from Begizov *et al.* (1982)

^cCalculated by us as an average of 8 analyses from Evstigneeva and Genkin (1983)

^dFor sample 1 from Genkin *et al.* (1974)

^eAt 480, 546, 589 and 656 nm, respectively

^fFor sample 1 from Evstigneeva and Genkin (1983)

proof of the identity of our studied mineral to the original stannopalladinite from Ugol'nyi Ruchei. The comparison with the powder X-ray data of Evstigneeva and Nekrasov (1984) gives an even better match (Table 4) and their chemical formula Pd₅Sn₂Cu has the same ratio (Pd,Cu):Sn = 3:1 as our mineral. Regrettably, these authors provided no information on the locality of their stannopalladinite.

In comparison, the PXRD data of synthetic Pd₃Sn₂ (Table 4) – based on the data of Nowotny *et al.* (1946), as well as data of Schubert *et al.* (1959) who distinguished two modifications (α and β) of Pd₃Sn₂, and data of Sarah *et al.* (1981) for the phase Pd₂₀Sn₁₃ with a Ni₁₃Ga₃Ge₆ type structure – only poorly match with our mineral. The structural correspondence of stannopalladinite to the synthetic analogue of α -Pd₃Sn₂ given by Genkin (1968) and Genkin *et al.* (1981) seem to be improbable.

Using the DicVol indexing method in *HighScore Plus* software (Panalytical), assuming a unit-cell volume $V < 6000 \text{ \AA}^3$, the only solution that used the 100% of the reflections in Table 4 and that was characterized by best Figure of Merit (FOM) provided an orthorhombic cell with the following unit-cell parameters:

$a = 14.634(2)$, $b = 8.5253(6)$, $c = 4.5946(3) \text{ \AA}$ and $V = 573.24(7) \text{ \AA}^3$ ($Z = 8$).

The calculated density of stannopalladinite using the above unit cell data and empirical formula (Table 2, an. 14) is 9.781 g/cm^3 .

Our data clearly show that the hexagonal unit cell with $a \approx 4.4$ and $c \approx 5.7 \text{ \AA}$ attributed to stannopalladinite in some literature sources (Table 1) and databases cannot refer to this mineral.

As the structure of stannopalladinite cannot be refined due to the poor quality of the material studied, we can only speculate if Cu is a species-defining element in stannopalladinite or if it partly substitutes Pd as an admixture. Various synthetic compounds of the Pd–Cu–Sn ternary system were produced by Evstigneeva and Nekrasov (1980, 1984) and later by Kareva *et al.* (2014) but none of these were good enough to refine their structures. Moreover, the authors themselves admitted that the quality of the collected powder X-ray patterns was usually poor and most of the lines were broad and diffuse. We infer, therefore, that the 'revised' chemical formula Pd₅Sn₂Cu as proposed by Evstigneeva and Nekrasov (1984) and used in subsequent

publications (i.e. Spiridonov *et al.*, 2011; Krivolutsкая *et al.*, 2018; Tolstykh *et al.*, 2020 etc.) cannot be applied to stannopalladinite as long as there is no proof of Cu ordering in its structure.

The Cu-free phase from the Monchegorsk deposit described by Chernyaev and Yushko-Zakharova (1968) differs from our data by composition, stoichiometry and hardness and, thus, is unlikely to be stannopalladinite.

In any case, as we are not yet aware of any chemical analyses of Cu-free stannopalladinite and until the position of Cu in the structure of the mineral is resolved, we propose writing the chemical formula of stannopalladinite as $(\text{Pd,Cu})_3\text{Sn}$ instead of the official formula Pd_3Sn_2 used by the IMA and various databases. At the same time, the lack of structural data, unfortunately, precludes the official procedure of the redefinition of this mineral through the CNMNC of the IMA.

Currently, there are five valid mineral species having Pd and Sn or Pd, Cu and Sn as essential elements in their chemical compositions. Considering their ideal formulae, they are assigned to the binary Pd–Sn (atokite and paolovite) or the ternary Pd–Cu–Sn (cabriite, taimyrite and stannopalladinite) systems (Evstigneeva, 1980; Evstigneeva and Nekrasov, 1984). The comparative data for all of these are summarised in Table 5.

The chemically closest phase to stannopalladinite is taimyrite (Begizov *et al.*, 1982) for which the same formula $(\text{Pd,Cu})_3\text{Sn}$ is given. Cabriite (Evstigneeva, Genkin, 1983) is richer in Cu than the other two but still keeps the same stoichiometry $(\text{Pd,Cu})_3\text{Sn} = 3:1$. Atokite, another mineral with the ratio $\text{Pd}:\text{Sn} = 3:1$, was reported as being Cu-free (Mihálik *et al.*, 1975), however, Evstigneeva (1980) noted a possible admixture of Cu in it leading to the same formula $(\text{Pd,Cu})_3\text{Sn}$. We do not exclude that some of these minerals are polymorphs but cannot prove it until their structures are determined. Unfortunately, to date there is no single case of a successfully refined structure of natural nor a synthetic Pd–Cu–Sn compound and proof of Cu ordering in it.

Despite having the same or similar chemical composition, all the above minerals possess different physical properties (optical data including reflectance values, density and hardness) and powder X-ray patterns. We suggest therefore that for the sake of a correct identification of these minerals a combination of analytical methods is necessary, not chemical data alone. As an example, we can refer to the paper of Krivolutsкая *et al.* (2018) where a number of chemical analyses from the Talnakh deposit are reported as “stannopalladinite $\text{Pd}_5\text{Sn}_2\text{Cu}$ ”. The authors noted, however, the excess of Cu in most of the studied grains and added it to Pd, writing the formula as $(\text{Pd,Cu})_5\text{Sn}_2\text{Cu}$. As all their analyses can be recalculated to $(\text{Pd,Cu})_3\text{Sn}$, their assignment to stannopalladinite (and not to taimyrite, for example) cannot be considered unambiguous without additional analytical data.

Acknowledgements. The authors are grateful to Iain McDonald, two anonymous reviewers and Associate Editor Ian Graham for a careful review of the manuscript that improved its quality. Principal Editor Stuart Mills is acknowledged for his valuable comments. Maria D. Milshina is deeply thanked for help with photography. This research was supported by the Grant Agency of the Czech Republic (project No. 22-26485S to A.V.).

Competing interest. The authors declare none.

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