

## REVISED UNIT-CELL DIMENSIONS, SPACE GROUP, AND CHEMICAL FORMULA OF SOME METALLIC MINERALS

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### ABSTRACT

New data are given for algodonite (formula), awaruite (formula, space group), billingsleyite (space group, unit cell), bogdanovite (formula, space group), hexatestibiopanickeleite (formula), keithconnite (formula), mgriite (formula), polarite (formula), roaldite (space group), sobolevskite (space groups, unit cells), stibiopalladinite (space group, unit cell), stützite (formula), urvantsevite (space group, unit cell), wairauite (space group), and weissite (space group, unit cell). The structure-type AuCu, tetraauricupride, is shown to have the Pearson Symbol Code of *tP2* rather than *tP4*, so that  $a(tP4) = \sqrt{2}a(tP2)$ . New unit-cell dimensions are given for four minerals (tetraauricupride, tetraferroplatinum, ferronickelplatinum, and tulameenite) and 19 metals in *tP2* rather than *tP4*.

**Keywords:** algodonite, awaruite, billingsleyite, bogdanovite, ferronickelplatinum, hexatestibiopanickeleite, keithconnite, mgriite, polarite, roaldite, sobolevskite, stibiopalladinite, stützite, tetra-auricupride, tetraferroplatinum, tulameenite, urvantsevite, wairauite, weissite.

### SOMMAIRE

Des données nouvelles sont décrites pour l'algodonite (formule), awaruite (formule, groupe spatial), billingsleyite (groupe spatial, maille élémentaire), bogdanovite (formule, groupe spatial), hexatestibiopanickeleite (formule), keithconnite (formule), mgriite (formule), polarite (formule), roaldite (groupe spatial), sobolevskite (groupes spatiaux, mailles élémentaires), stützite (formule), urvantsevite (groupe spatial, maille élémentaire), wairauite (groupe spatial), et weissite (groupe spatial, maille élémentaire). La structure de type AuCu, tétra-auricupride, aurait le symbole de Pearson de *tP2* plutôt que *tP4*, de sorte que  $a(tP4) = \sqrt{2}a(tP2)$ . De nouvelles mailles élémentaires pour quatre minéraux (tétra-auricupride, tétraferroplatine, ferronickelplatine et tulameenite) et dix-neuf métaux sont exprimés dans le groupe *tP2* plutôt que *tP4*.

(Traduit par la Rédaction)

**Mots-clés:** algodonite, awaruite, billingsleyite, bogdanovite, ferronickelplatine, hexatestibiopanickeleite, keithconnite, mgriite, polarite, roaldite, sobolevskite, stibiopalladinite, stützite, tétra-auricupride, tétraferroplatine, tulameenite, urvantsevite, wairauite, weissite.

### INTRODUCTION

During a review of the Mineral Powder Diffraction

File by Bayliss *et al.* (1986), inconsistencies were found between the crystal structure of a synthetic compound given in the literature or deduced from the structure-type and the chemical formula of some metallic minerals as given by Fleischer (1987). The purpose of this paper is to tabulate corrections for the unit-cell dimensions, space groups, and structural chemical formulae of some metallic minerals.

### METHODS

In many simple metallic minerals, the possible structure-types are limited. In each of the possible structure-types, the majority of the atoms have all or some atomic coordinates in fixed positions. From each possible structure-type or a crystal structure given in the literature, the intensities of the X-ray powder-diffraction reflections were calculated with POWD (Smith & Smith 1987). The calculated intensities were compared to the observed intensities of the X-ray powder-diffraction reflections found in the literature. Some *hkl* indices of the observed X-ray powder-diffraction reflections were set, then a least-squares unit-cell refinement (Bayliss 1989) gave improved unit-cell dimensions. Further *hkl* indices of the observed X-ray powder-diffraction reflections were set, followed by further least-squares unit-cell refinements, until the refinement of the cell dimensions was complete. When the calculated and observed intensities of the powder-diffraction reflections matched completely, then the chemical formula, space group, crystal-structure type, and unit-cell dimensions were considered established.

### RESULTS

The revised unit-cell dimensions, space group, and chemical formula of some metallic minerals are listed in Table 1. Since the chemical elements cannot be subdivided into cations and anions, because the minerals have metallic bonding, the chemical formulae have been listed in alphabetical order, except that only the first element in parentheses has been considered. The PSC in Table 1 represents the Pearson Symbol Code, which was described by Hubbard & Calvert (1981), and has three parts: The first letter represents the crystal system, where *c* is cubic, *h* is hexagonal, *t* is tetragonal, *o* is orthorhom-

TABLE 1. REVISED PEARSON SYMBOL CODE, CHEMICAL FORMULA, SPACE GROUP, AND UNIT-CELL DIMENSIONS

Mineral	PSC	Chemical Formula	Space Group	a (Å)	b (Å)	c (Å)	PDF No.
Algodonite	hP2	As <sub>x</sub> Cu <sub>1-x</sub>	P6 <sub>3</sub> /mmc				9-429
Awaruite	hP4	FeNi <sub>3</sub>	Pm $\bar{3}$ m				38-419
Billingsleyite	cP56	Ag <sub>7</sub> AsS <sub>6</sub>	P2 <sub>1</sub> 3	10.481(4)			21-1334
Bogdanovite	cP4	Au <sub>3</sub> Cu	Pm $\bar{3}$ m	4.0876(15)			34-1302
Hexatetstibiopanickelitelite	hP4	Ni(Te, Sb)	P6 <sub>3</sub> /mmc	3.983(3)		5.339(3)	29-932
Keithconnite	hR27	Pd <sub>20</sub> Te <sub>7</sub>	R $\bar{3}$	11.458(10)		11.296(12)	34-1461
Mgriite	cF8	(Se, Cu, As)	Fd $\bar{3}$ m				35-675
Polarite	oC32	BiPbPd <sub>2</sub>	Ccm2 <sub>1</sub>	7.14(13)	8.656(17)	10.501(16)	23-1298
Roaldite	cP5	Fe <sub>4</sub> N	P4 $\bar{3}$ m				6-627
Sobolevskite	hP4	$\alpha$ -BiPd	P6 <sub>3</sub> /mmc	4.220(17)	5.709(4)		
	mC32	$\beta$ -BiPd	B2 <sub>1</sub>	7.16(2)	10.66(5) $\beta = 90^\circ$	8.74(2)	29-238
Stibiopalladinite	hP42	Pd <sub>5</sub> Sb <sub>2</sub>	P6 <sub>3</sub> cm	7.606(11)		14.21(4)	25-597
Stützite	hP55	Ag <sub>7</sub> Te <sub>4</sub>	P6 <sub>3</sub> /mmc				18-1187
Urvantsevite	tI6	$\beta$ -Bi <sub>2</sub> Pd	I4/mmm	3.3628(16)		12.902(11)	29-232
Wairauite	cP2	CoFe	Pm $\bar{3}$ m	2.857			
Weissite	hP72	Cu <sub>2-x</sub> Te	P3m1	8.342(15)		21.69(9)	10-421
Tetra-aurocupride	tP2	AuCu	P4/mmm	2.800		3.670	25-1220
Tetraferroplatinum	tP2	FePt	P4/mmm	2.7235(10)		3.720(3)	26-1139
Ferronickelplatinum	tP2	(Ni, Fe)Pt	P4/mmm	2.731(3)		3.641(8)	35-702
Tulameenite	tP2	(Cu, Fe)Pt	P4/mmm	2.7477(4)		3.5870(8)	26-528

PSC Pearson Symbol Code  
PDF No. Powder Diffraction File number

bic,  $m$  is monoclinic, and  $a$  is anorthic (triclinic). The second letter represents the Bravais lattice, where  $P$  is primitive,  $I$  is body-centered,  $F$  is all faces centered,  $C$  is one face centered, and  $R$  is rhombohedral. The number represents the number of atomic sites within the unit cell.

#### DISCUSSION

Algodonite is isostructural with allargentum, Ag<sub>1-x</sub>Sb<sub>x</sub>. Since the 2(Cu,As) atoms (Cu:As = 6:1; Naud & Priest 1972) completely occupy the fixed atomic positions  $2c$  at (0.333, 0.667, 0.25) in space group  $P6_3/mmc$ , the correct formula for algodonite

is As<sub>x</sub>Cu<sub>1-x</sub>, although metallurgists prefer As<sub>0.29</sub>Cu<sub>1.71</sub> so that it may be sorted in metallurgical alphabetical formula indices. Such indices will be produced by JCPDS - International Center for Diffraction Data in its new Metals and Alloys data compilation scheduled for production in 1991.

Awaruite is isostructural with isoferroplatinum, FePt<sub>3</sub>. Since all atomic positions are fully occupied with Fe in the fixed atomic position  $1a$  at (0,0,0) and Ni in the fixed atomic positions  $3c$  at (0,0.5,0.5) in space group  $Pm\bar{3}m$ , the correct formula for awaruite is FeNi<sub>3</sub> (Lutts & Gielen 1970). The Ni-Fe ordering is shown by the 100 and 110 reflections, which both have a calculated relative intensity of only 0.4 compared to 100 for the most intense reflection.

Billingsleyite, Ag<sub>7</sub>AsS<sub>6</sub>, described by Frondel & Honea (1968) in the orthorhombic space-group  $C222_1$ , with  $Z = 8$ , has  $F_{25} = 7(0.047, 78)$  according to Smith & Snyder (1979), where 7 is the observed number of reflections (25) divided by the possible number of independent reflections (78) and by delta  $2\theta$  (0.047). Least-squares analysis of billingsleyite in cubic space-group  $P2_13$  (the low-temperature phase of Blachnik & Wickel 1980) gave an  $a$  of 10.481(4) Å with  $Z = 4$ , to give a significantly higher  $F_{25}$  at 17(0.049, 30).

Bogdanovite was described by Spiridonov & Chvileva (1979) as a cubic mineral with a small unit-cell dimension. This suggests that bogdanovite is isostructural with isoferroplatinum, FePt<sub>3</sub>. Least-squares analysis of bogdanovite yielded a unit-cell dimension of 4.0876(15) Å in space group  $Pm\bar{3}m$ , which suggests a formula of (Au, Te, Pb)<sub>3</sub>(Cu, Fe), with  $Z = 1$ . The Au fully occupies the fixed atomic positions  $3c$  at (0,0.5,0.5), and the Cu occupies the fixed atomic position  $1a$  at (0,0,0).

Hexatetstibiopanickelitelite (Platinum Metal Mineral

TABLE 2. X-RAY POWDER-DIFFRACTION DATA OF SOBOLEVSKITE

Sobolevskite		$\alpha$ -BiPd		$\beta$ -BiPd	
$d_{obs}$ Å	$I_{obs}$	$d_{calc}$ Å	$I_{calc}$	$d_{calc}$ Å	$I_{calc}$
		3.65	67		
3.07	100	3.08	28	3.37	13
2.68	20			2.68	100
				2.53	23
2.26	100	2.25	100	2.27	16
2.19	10			2.185	49
2.11	90	2.11	63		
				1.800	8
1.74	40	1.74	26		
1.69	50	1.69	24	1.69	17
1.642	10			1.648	12
1.575	10			1.585	5
1.541	30	1.539	19		
				1.492	6
1.450	10			1.43	1
1.426	20	1.427	4	1.40	8
1.342	40			1.335	4
1.321	20			1.313	1
1.244	40	1.243	14	1.231	4
1.218	20	1.218	5	1.215	3
1.182	50	1.182	10	1.179	6
1.117	40	1.118	12		
1.09	20			1.089	1
1.065	20			1.065	1
0.998	10	0.998	8		

Research Group, 1974) is isostructural with nickeline, NiAs (Hewitt 1948). Since all the atomic positions are fully occupied with ( $\text{Ni}_{0.69}\text{Pd}_{0.31}$ ) in fixed atomic positions  $2a$  at (0,0,0) and ( $\text{Te}_{0.50}\text{Sb}_{0.49}\text{Bi}_{0.01}$ ) in fixed atomic positions  $2c$  at (0.333,0.667,0.25) in space group  $P6_3/mmc$ , the correct formula of hexatestibiopanickeite is  $\text{Ni}(\text{Te,Sb})$  with  $Z = 2$ . Imgreite, NiTe, has been rejected by the International Mineralogical Association (Nickel & Mandarino 1987).

Keithconnite was originally described by Cabri *et al.* (1979) as  $\text{Pd}_{3-x}\text{Te}$ , with  $Z = 7$ . The observed X-ray powder-diffraction data are similar to those calculated from the crystal structure of Wopersnow & Schubert (1977), so that the correct chemical formula is  $\text{Pd}_{20}\text{Te}_7$ , with  $Z = 1$  in space group  $R\bar{3}$ .

Mgriite (Dymkov *et al.* 1982) is isostructural with sillon and diamond. Majid & Hussain (1987) gave ( $\text{Se}_{0.5}\text{Cu}_{0.375}\text{As}_{0.125}$ ) with  $a = 5.530$  Å, ( $\text{Se}_{0.5}\text{Cu}_{0.25}\text{As}_{0.25}$ ) with  $a = 5.515$  Å, and  $\text{Se}_{0.43}\text{Cu}_{0.43}\text{As}_{0.14}$  with  $a = 5.758$  Å for synthetic phases. Since all the atomic positions are fully occupied in fixed atomic positions  $8a$  at (0,0,0) in space group  $Fd\bar{3}m$ , the correct formula of mgriite is ( $\text{Se}_{0.423}\text{Cu}_{0.415}\text{As}_{0.139}\text{Fe}_{0.023}$ ), with  $Z = 8$ .

Polarite, which was studied by Genkin *et al.* (1969), has an empirical formula  $\text{Bi}_{1.01}\text{Pb}_{1.04}\text{Pd}_{1.95}$ . The phase diagram BiPd-PbPd of Mayer *et al.* (1979) shows a distinct phase of stoichiometry  $\text{BiPbPd}_2$ , whose crystal structure shows the Bi and Pb in different atomic sites in space group  $Ccm2_1$ . The published calculated pattern (PDF 33-207) is similar to the observed pattern (PDF 23-1298) of polarite, so that the chemical formula of polarite is  $\text{BiPbPd}_2$ . Polarite described by Tarkian (1987) as Pb-free, but without X-ray powder-diffraction data, probably is sobolevskite, BiPd.

Roaldite,  $\text{Fe}_4\text{N}$ , is isostructural with the synthetic phase  $\text{Fe}_4\text{C}$  (Pinsker & Kaverin 1956). The N fully occupies a fixed atomic position  $1a$  at (0,0,0) and the Fe fully occupies atomic positions  $4e$  at (0.265,0.265,0.265) in space group  $P4\bar{3}m$ , so that the formula of roaldite is  $\text{Fe}_4\text{N}$ , with  $Z = 1$ .

Sobolevskite,  $\alpha$ -BiPd, was originally described by Evstigneeva *et al.* (1975) as isostructural with nickeline, NiAs. A calculated X-ray powder-diffraction pattern in space group  $P6_3/mmc$ , with Pd in fixed atomic positions  $2a$  at (0,0,0) and Bi in fixed atomic positions  $2c$  at (0.333,0.667,0.25) compared to the observed powder-diffraction data, accounts for only 12 reflections. Therefore, there are nine additional reflections. A calculated X-ray powder-diffraction pattern (PDF 33-213) based on the crystal structure of Bhatt & Schubert (1979) in space group  $B2_1$ , with the chemical formula  $\beta$ -BiPd and  $Z = 16$ , accounts for the additional nine reflections. Since the  $\beta$  angle of  $\beta$ -BiPd at  $90.3^\circ$  is close to  $90^\circ$  and the number of reflections is small, the

TABLE 3. UNIT-CELL DIMENSIONS OF METALS IN STRUCTURE TYPE  $tP2$ 

Metal	$a$ (Å)	$c$ (Å)	PDF No.
AgTi	2.9014 (18)	4.066 (4)	6-560
AlPu <sub>3</sub>	3.1736 (18)	4.534 (4)	19-41
AlTi	2.8185 (4)	4.0803 (8)	5-678
Au <sub>2</sub> Pt	2.7771 (13)	3.880 (4)	15-43
BiLi	3.367 (3)	4.256 (5)	27-422
CaPb	3.6159 (13)	4.4885 (19)	32-169
CdHg	3.943 (4)	2.8855 (24)	8-337
cdPd	3.0253 (9)	3.6200 (17)	6-570
CdPt	2.9565 (10)	3.825 (3)	14-7
FePd	2.7255 (20)	3.720 (3)	2-1440
HgNi	2.982 (3)	3.139 (3)	31-853
HgPt	2.9704 (19)	3.813 (4)	6-572
Hg <sub>3</sub> Ti <sub>3</sub> Zn	2.9275 (21)	4.045 (4)	22-1253
InMg	3.2316 (6)	4.3939 (16)	19-583
InPu	3.4013 (5)	4.527 (3)	18-621
IrV	2.7465 (25)	3.647 (11)	29-692
Mn <sub>0.55</sub> RhSb <sub>0.45</sub>	2.9568 (11)	3.471 (4)	32-39
PdZn	2.8984 (7)	3.372 (3)	6-620
PtZn	2.8461 (8)	3.492 (3)	6-604

$\beta$  angle was set at  $90^\circ$  for the least-squares analysis, the results of which are reported in Table 2. Therefore, sobolevskite is considered a mixture of the two BiPd polymorphs.

Stibiopalladinite,  $\text{Pd}_2\text{Sb}_2$ , is isostructural with orcelite,  $\text{Ni}_5\text{As}_2$ . The crystal structure of  $\text{Pd}_2\text{Sb}_2$  in space group  $P6_3cm$  has been described by El-Boragy *et al.* (1970), with  $Z = 6$ .

Stütztite (Stumpfl & Rucklidge 1968) has been attributed a chemical formula of  $\text{Ag}_{5-x}\text{Te}_3$  with  $Z = 7$ ; however, the crystal-structure analysis of Imamov & Pinsker (1966) gives  $\text{Ag}_7\text{Te}_4$  with  $Z = 5$  in space group  $P6/mmm$ .

Urvantsevite,  $\beta$ - $\text{Bi}_2\text{Pd}$ , is the high-temperature polymorph of froodite,  $\alpha$ - $\text{Bi}_2\text{Pd}$  (Brasier & Hume-Rothery 1959). The crystal structure of  $\beta$ - $\text{Bi}_2\text{Pd}$  in space group  $I4/mmm$  has been confirmed by Zhuravlev & Zhdanov (1953).

Wairauite is isostructural with CsCl. Since the Co atom fully occupies the fixed position  $1a$  at (0,0,0), and the Fe atom fully occupies the fixed position  $1b$  at (0.5,0.5,0.5) in space group  $Pm\bar{3}m$ , the chemical formula is  $\text{CoFe}$  (Ellis & Greiner 1941), with  $Z = 1$ . The Co-Fe ordering is shown by the 100 reflection, which has a calculated relative intensity of only 0.02 compared to 100 for the most intense reflection.

Weissite,  $\text{Cu}_{2-x}\text{Te}$ , with  $Z = 24$ , has a crystal structure in space group  $P3m1$  (Baranova *et al.* 1974). Of the 36 atomic sites in the crystal structure, three of the  $3d$  atomic sites are exactly half-filled with Cu. The exact formula of  $\text{Cu}_{43.5}\text{Te}_{24}$  with  $Z = 1$  may be expressed as  $\text{Cu}_{1.8125}\text{Te}$  with  $Z = 24$ , so that  $x = 0.1875$  in  $\text{Cu}_{2-x}\text{Te}$ .

Tetra-aurocupride,  $\text{AuCu}$ , is given as the structure-type  $tP_4$  by Villars & Calvert (1985). The fixed atomic positions are Au in  $1a$  at (0,0,0), Au in  $1c$  at (0.5,0.5,0), and Cu in  $2e$  at (0,0.5,0.5) in space group  $P4/mmm$ . If the atomic positions  $1a$  and  $1c$  have equivalent occupancies, then the structure type  $tP_4$  becomes  $tP_2$ , with the fixed atomic positions of

Au in 1a at (0,0,0) and Cu in 1d at (0.5,0.5,0.5), where  $a(tP4) = \sqrt{2}a(tP2)$ . Similarly, tetraferroplatinum, FePt, belongs to *tP2*, just as potarite, HgPd.

Tulameenite, (Cu,Fe)Pt, does not show the additional reflections to indicate ordering of Cu and Fe for the structure-type *tP4*. A calculated pattern of CuFePt<sub>2</sub> in structure-type *tP4* and in space group *P4/mmm* shows that the strongest reflection not in the (Cu,Fe)Pt structure type *tP2* is the 100 reflection, with an intensity of only 0.1 compared to 100 for the most intense reflection. Similarly, ferrornickelplatinum, (Ni,Fe)Pt, does not show the additional reflections to indicate ordering of Ni and Fe in the structure-type *tP4*. Because the crystal-chemistry properties of the transition elements Fe, Co, Ni and Cu are similar, atomic ordering is unlikely to occur. Additional mineral species names should not be given until ordering has been proven.

A review of metals with the structure-type *tP4* in the Powder Diffraction File showed that a further 19 metals out of 24 could be satisfactorily indexed in the structure-type *tP2*. The new unit cell dimensions of these metals are listed in Table 3.

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