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THE CRYSTAL STRUCTURES OF JAGUÉITE, $Cu_2Pd_3Se_4$, AND CHRISSTANLEYITE, $Ag_2Pd_3Se_4$

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ABSTRACT

The crystal structure of jaguéite, ideally $Cu_2Pd_3Se_4$, monoclinic, *a* 5.672(5), *b* 9.909(9), *c* 6.264(6) Å, β 115.40(2)°, space group $P2_1/c$, has been solved by direct methods and refined to an R_1 index of 5.52% for 956 unique reflections measured with Mo$K\alpha$ X-radiation on a P–4 Bruker diffractometer equipped with a CCD area-detector. The crystal structure of chrisstanleyite, ideally $Ag_2Pd_3Se_4$, monoclinic *a* 5.676(2), *b* 10.342(4), *c* 6.341(2) Å, β 114.996(4)°, space group $P2_1/c$, has been solved by direct methods and refined to an R_1 index of 8.3% for 1203 unique reflections measured with Mo$K\alpha$ X-radiation. There are two unique Pd sites, one Cu (or Ag) and two Se sites in the unit cell. Atom Pd1 forms isolated square arrangements $PdSe_4$, whereas the adjacent arrangements involving Pd2 are paired *via* a common edge. The (Cu,Ag) coordination tetrahedra form (100) layers which, together with the Pd2–Cu(Ag)–Pd1–Cu(Ag)–Pd2 system of metal–metal bonds, help to stabilize the open-work structure composed of $PdSe_4$ squares.

Keywords: jaguéite, chrisstanleyite, crystal structure.

SOMMAIRE

Nous avons résolu la structure cristalline de la jaguéite, de composition idéale $Cu_2Pd_3Se_4$, monoclinique, *a* 5.672(5), *b* 9.909(9), *c* 6.264(6) Å, β 115.40(2)°, groupe spatial $P2_1/c$, par méthodes directes, et nous l'avons affinée jusqu'à un résidu R_1 de 5.52% en utilisant 956 réflexions uniques mesurées avec rayonnement Mo$K\alpha$ sur un diffractomètre Bruker P–4 muni d'un détecteur à aire de type CCD. De même, nous avons résolu la structure cristalline de la chrisstanleyite, de composition idéale $Ag_2Pd_3Se_4$, monoclinique, *a* 5.676(2), *b* 10.342(4), *c* 6.341(2) Å, β 114.996(4)°, groupe spatial $P2_1/c$, par méthodes directes, et nous l'avons affinée jusqu'à un résidu R_1 de 8.3% en utilisant 1203 réflexions uniques mesurées avec rayonnement Mo$K\alpha$. Il y a deux sites Pd uniques, un site Cu (ou Ag) et deux sites Se dans la maille élémentaire. L'atome Pd1 possède un agencement de coordinence carré $PdSe_4$, tandis que l'agencement adjacent de l'atome Pd2 implique une coordinence en paires à arête partagée. Le tétraèdre de coordinence (Cu,Ag) se présente en couches (100) qui, de concert avec le système de liaisons métal–métal Pd2–Cu(Ag)–Pd1–Cu(Ag)–Pd2, aident à stabiliser la trame ouverte composée d'agencements carrés $PdSe_4$.

(Traduit par la Rédaction)

Mots-clés: jaguéite, chrisstanleyite, structure cristalline.

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INTRODUCTION

Jaguéite, $Cu_2Pd_3Se_4$, was described by Paar *et al.* (2004) from the deposit of El Chire, in La Rioja, Argentina. It occurs in a telethermal selenide vein deposit, associated with its silver analogue, chrisstanleyite, as well as clausthalite, naumannite, tiemannite, and several selenides of copper. Chrisstanleyite itself was described by Paar *et al.* (1998) from a selenide association at Hope's Nose, Torquay, Devon, England. Both occurrences represent rare but recurring associations of palladium (and minor platinum) with selenide minerals, enumerated in Paar *et al.* (2004). Before it was named, $Cu_2Pd_3Se_4$ was described by Nickel (2002) from the Pilbara region of Australia. Also, $Cu_2Pd_3Se_4$ occurs as a distinct phase in the ternary system Cu–Pd–Se at 300° and 400°C (S. Karup-Møller & E. Makovicky, in prep.).

Unlike the phases showing substitution of Cu for Pd in several palladium chalcogenides (*e.g.*, Pd_4S and $Pd_{2.2}S$, Karup-Møller & Makovicky 1999), jaguéite and its synthetic analogue are distinguished by a fixed Cu:Pd ratio. Moreover, jaguéite is isostructural with $Ag_2Pd_3Se_4$, chrisstanleyite, although the structural analogy of corresponding Cu and Ag sulfides and selenides is rare. Therefore, an analysis of the structural aspects of both phases is desirable. We present here the results of the single-crystal structural investigation of jaguéite and chrisstanleyite.

EXPERIMENTAL

Both phases come from the same ore material from the El Chire deposit, in which they occur in intimately oriented intergrowths. The jaguéite is slightly silver-bearing (Table 1), whereas chrisstanleyite contains some copper. The respective formulae are $Cu_{1.9}Ag_{0.1}Pd_3Se_4$ and $Cu_{0.4}Ag_{1.6}Pd_3Se_4$.

Jaguéite and chrisstanleyite were liberated as independent, irregular small fragments from the pre-analyzed polished sections. These were used both for the measurement of the unit-cell parameters and for the crystal-structure determination. The chrisstanleyite material is twinned, and its quality is inferior to that of jaguéite, which is reflected in the values of the reliability coefficients (Table 2).

TABLE 1. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF CHRISSTANLEYITE AND JAGUÉITE FROM EL CHIRE

	chrisstanleyite	jaguéite
Formula	$(Ag_{1.59}Cu_{0.41})_{\Sigma 2}Pd_{3.03}Se_{3.97}$	$(Cu_{1.91}Ag_{0.11})_{\Sigma 2.02}Pd_{3.03}Se_{3.95}$
Cu wt%	3.09	15.70
Ag	20.55	1.59
Pd	38.64	42.04
Se	37.54	40.15
Total	99.84	99.48

JEOL Superprobe JXA–8600, Link–*eXL*, operating conditions 25 kV, 30 nA, 20 s counting time. Standards: natural Cu_3Se_2, HgS, Sb_2S_3, metallic Ag and Pd. On-line ZAF–4 correction procedure.

The crystal fragments examined were measured on a Bruker AXS four-circle diffractometer equipped with a CCD 1000K area detector using monochromatized Mo*K*α radiation from a fine-focus sealed X-ray tube. Experimental details are summarized in Table 2. The SMART system of programs was used for crystal-lattice determination and data collection, SAINT+ for the calculation of integrated intensities, XPREP for empirical absorption-correction based on pseudo Ψ-scans (only for jaguéite), and SHELXS (Sheldrick 1997a) and SHEXL (Sheldrick 1997b) for the structure solution and refinement, respectively. The resulting value of R_{INT} is listed in Table 2. The unit-cell parameters are listed in Table 3.

The crystal structure of chrisstanleyite was solved with a twinned crystal. The twin-law transformation matrix was found to be $1\ 0\ 0/0\ \bar{1}\ 0/\bar{1}\ 0\ \bar{1}$, which gives (001) as the twin plane. The intensities for the two components were collected by the twin routine in SAINT+ and corrected for absorption effects by the program TWINABS using up to the 5th order of uneven

TABLE 2. X-RAY DIFFRACTION (SINGLE CRYSTAL): EXPERIMENTAL DETAILS

Diffractometer	Bruker AXS, four-circle goniometer, P4	
Detector	1000 CCD	
X-ray radiation source	fine focus sealed tube, Mo*K*α	
X-ray radiation monochromator	flat graphite	
Temperature	298 K	
Detector-to-sample distance	4 cm	
Mineral	chrisstanleyite	jaguéite
Formula (idealized)	$Ag_2\,Pd_3\,Se_4$	$Cu_2\,Pd_3\,Se_4$
Rotation width	0.3°	0.3°
Total number of frames	1680	1680
Frame size	512 * 512 pixels	512 * 512 pixels
Measurement time per frame	60 seconds	45 seconds
Highest resolution	0.77 Å	0.7 Å
Maximum 2θ	55.25°	60.86°
Measured reflections	2912	3277
Index ranges	$-6 \le h \le 7$, $-13 \le k \le 13$, $-7 \le l \le 8$	$-8 \le h \le 8$, $-14 \le k \le 13$, $-8 \le l \le 8$
Unique reflections	1203	956
Reflections $I > 2\sigma(I)$	1060	650
R_{INT}	7.81%	9.58%
R_σ	2.59%	8.01%
Number of l.s. parameters	43	43
GooF	1.080	1.099
R_1, $F_o > 4\,\sigma(F_o)$	8.30%	5.52%
R_1, all data	8.80%	8.26%
wR_2 (on F_o^2)	24.18%	15.47%
a and b in w	0.2, 0	0.0763, 0
Final difference-Fourier map	–5.77 to +6.46 Å^{-3}	–2.34 to +4.42 Å^{-3}

$R_{INT} = \Sigma\,|F_o^2 - F_o^2(\text{mean})|\,/\,\Sigma\,F_o^2$

$R_\sigma = \Sigma\,\sigma(F_o^2)\,/\,\Sigma\,F_o^2$

$R_1 = \Sigma\,||F_o| - |F_c||\,/\,\Sigma\,|F_o|$

$wR_2 = \{\,(\Sigma\,w[F_o^2 - F_c^2]^2\,/\,\Sigma\,w[F_o^2]^2)\,\}^{1/2}$

$\text{Goof} = \{\,(\Sigma\,w[F_o^2 - F_c^2]\,/\,[n - p])\,\}^{1/2}$

$w = 1\,/\,(\sigma^2[F_o^2] + [a * P]^2 + b * P)$

$P = (\max(F_o^2, 0) + 2\,F_c^2)\,/\,3$

and 8th order of the even spherical harmonics. There were 912, and 915 non-overlapping reflections for the two components, plus 1085 overlapping ones. Of these, 432, 430, and 410, respectively, were considered to be unique. The correction decreased the R_{INT} from 0.1357 to 0.0781. The ratio of the average intensities of the non-overlapping reflections of the two components was 2.65, which gives their approximate volume-proportion of 5:2.

The systematic absences suggested the space group $P2_1/c$ for both phases. The *a* and *c* parameters and the β angle are similar for both phases, but the *b* parameter differs by about 0.4 Å, being longer for the chrisstanleyite (Table 3). The structures were solved by direct methods (SHELXS) and difference-Fourier syntheses. Christanleyite is isostructural with jaguéite. The Pd and Se sites, as well as the Cu position in jaguéite, were refined with anisotropic displacement factors. The Ag site in chrisstanleyite showed a lower number of electrons than for pure Ag, and was consequently refined as a mixed (Ag,Cu) site, resulting in 20 at.% Cu. The occupancies of Ag and Cu were refined with equal isotropic displacement factors, but with free positional parameters. The positional splitting of the site in chrisstanleyite was checked by a difference-Fourier synthesis based on a refinement with only an isotropic Ag atom ascribed to the site. The difference map clearly showed a small but regular maximum at the expected position of the Cu atom. No correlation factors greater than 0.7 were present. An attempt to refine the mixed (Ag,Cu) site with anisotropic displacement factors resulted in correlation factors between the positional and displacement parameters for the two atoms larger than 0.9 and was abandoned.

TABLE 3. UNIT-CELL PARAMETERS OF CHRISSTANLEYITE AND JAGUÉITE

	chrisstanleyite	jaguéite
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
Cell parameters		
a (Å)	5.676(2)	5.672(5)
b (Å)	10.342(4)	9.909(9)
c (Å)	6.341(2)	6.264(6)
β (°)	114.996(4)	115.40(2)
V (Å^3)	337.3(2)	318.0(5)
Z (formula units/unit cell)	2	2
ρ_c (g/cm^3)	8.289	7.959

The fractional coordinates, isotropic and anisotropic displacement parameters of the atoms for jaguéite are listed in Table 4, and in Table 5 for christanleyite, respectively. The selected *Me*–S bond distances are presented in Table 6 and Table 7. The tables of structure factors for jaguéite and chrisstanleyite may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 4. POSITIONAL AND DISPLACEMENT PARAMETERS OF ATOMS IN JAGUÉITE

Atom	*x/a*	*y/b*	*z/c*	sof	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Pd1	0	0	0	1	0.0136(7)	0.0169(7)	0.0184(8)	0.0001(6)	0.0055(6)	-0.0012(6)	0.0168(4)
Pd2	0.2585(2)	0.1270(1)	0.5001(2)	1	0.0169(6)	0.0179(6)	0.0179(6)	0.0005(4)	0.0052(5)	0.0014(5)	0.0184(3)
Se1	0.4685(3)	0.0546(2)	0.2418(3)	1	0.0144(7)	0.0201(7)	0.0197(8)	0.0005(6)	0.0062(6)	0.0018(6)	0.0185(4)
Se2	0.0159(3)	0.1860(2)	0.7362(3)	1	0.0193(8)	0.0171(7)	0.0188(8)	-0.0001(6)	0.0078(6)	-0.0022(6)	0.0185(4)
Cu	0.6183(2)	0.1929(2)	–0.0172(4)	1	0.0200(9)	0.0249(9)	0.037(1)	-0.0039(9)	0.0104(9)	-0.0023(9)	0.0278(5)

TABLE 5. POSITIONAL AND DISPLACEMENT PARAMETERS OF CHRISSTANLEYITE

ATOM	*x/a*	*y/b*	*z/c*	sof	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Pd1	0	0	0	1	0.0085(9)	0.001(1)	0.012(1)	0.0013(6)	0.0052(8)	-0.0013(7)	0.0069(6)
Pd2	0.2649(3)	0.1271(1)	0.5071(2)	1	0.0099(8)	0.002(1)	0.012(1)	0.0003(4)	0.0070(6)	0.0010(5)	0.0071(5)
Se1	0.4645(3)	0.0500(2)	0.2518(3)	1	0.0081(9)	0.005(1)	0.011(1)	0.0017(6)	0.0046(7)	0.0017(7)	0.0080(6)
Se2	0.0445(3)	0.1836(2)	0.7593(3)	1	0.0130(9)	0.002(1)	0.012(1)	0.0002(6)	0.0084(8)	-0.0029(6)	0.0081(6)
Ag	0.6298(4)	0.1964(2)	0.9789(3)	0.796(9)							0.0115(6)
Cu	0.645(3)	0.189(1)	0.041(3)	0.20							0.0115(6)

DESCRIPTION OF THE STRUCTURES

The crystal structures examined contain two distinct Pd sites, one of which is a special 0, 0, 0 position, two selenium sites, and a Cu(Ag) site in which the minor component is not coincident with the major one in either structure.

Jaguéite

In jaguéite (Fig. 1), Pd1 forms a square planar coordination, with the Se1 sites and, in turn, the Se2 sites in a *trans* configuration. The configuration is perfectly planar, but the distances differ slightly (2.489 Å and 2.503 Å for Se1 and Se2, respectively), and the Se1–Pd1–Se2 angle is 95.1° instead of 90°.

Whereas the Pd1Se$_4$ coordination polyhedron is isolated, similar polyhedra of Pd2 are paired *via* a common Se1–Se1 edge. The atom Pd2 is slightly asymmetric in its essentially square planar coordination, the distance to the center of the square being 0.05 Å. The Pd2–Se1 distances are 2.471 Å and 2.490 Å, respectively; the Pd2–Se2 distances are 2.471 Å and 2.485 Å, the average of all values being 2.48(1) Å. Its planarity is less perfect; the Se1–Pd2–Se2 angles are 174.9° and 175.4°, and the other Se–Pd2–Se angles vary from 82.8° to 97.7° (Table 6). The coordination polyhedron of copper is a very elongate tetrahedron, with Cu–Se

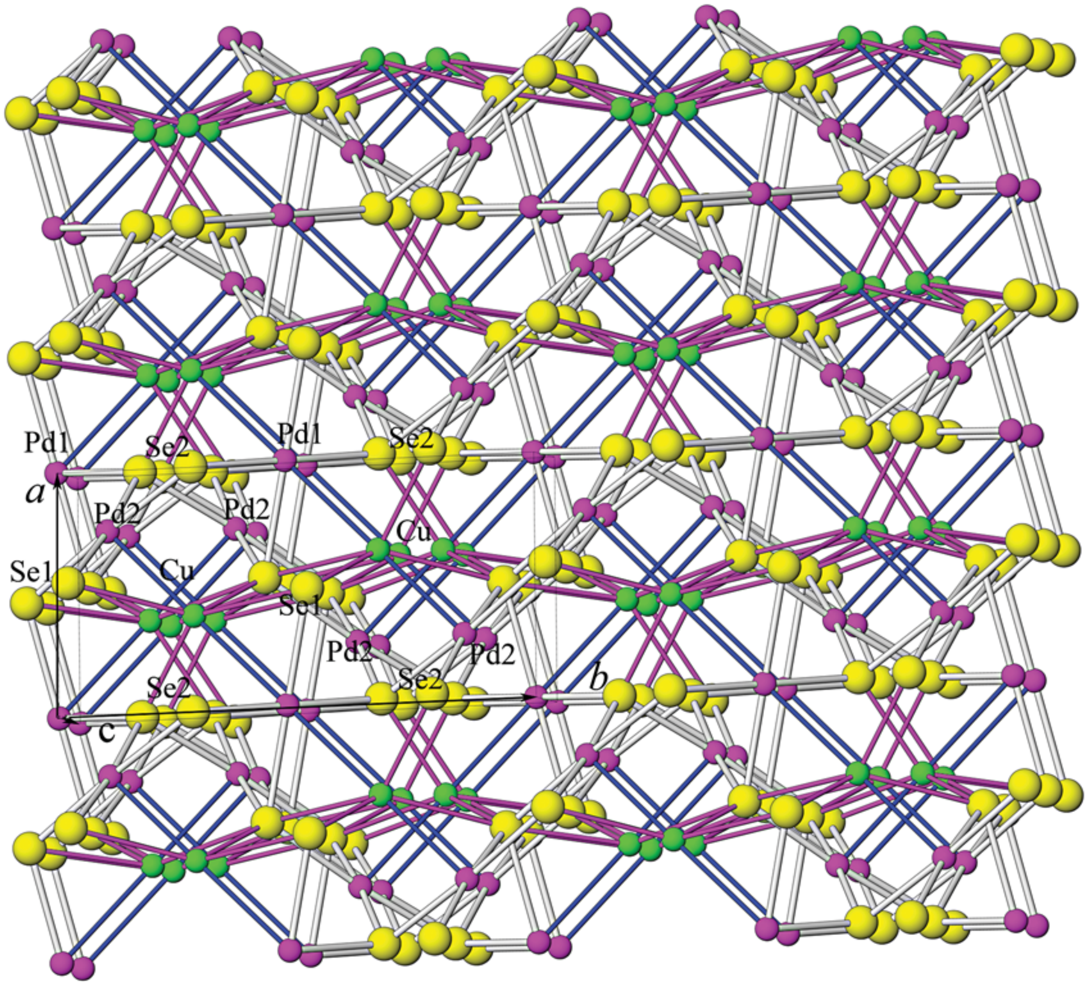

FIG. 1. The crystal structure of jaguéite. Se atoms are yellow, Pd atoms purple, and Cu atoms green. Pd–Se bonds are shown in white, Cu–Se bonds in purple, and cation–cation bonds in blue. Pd1 is situated in the centers of metal-bond strips, Pd2 at their ends. Projection upon (001), with the *b* axis horizontal.

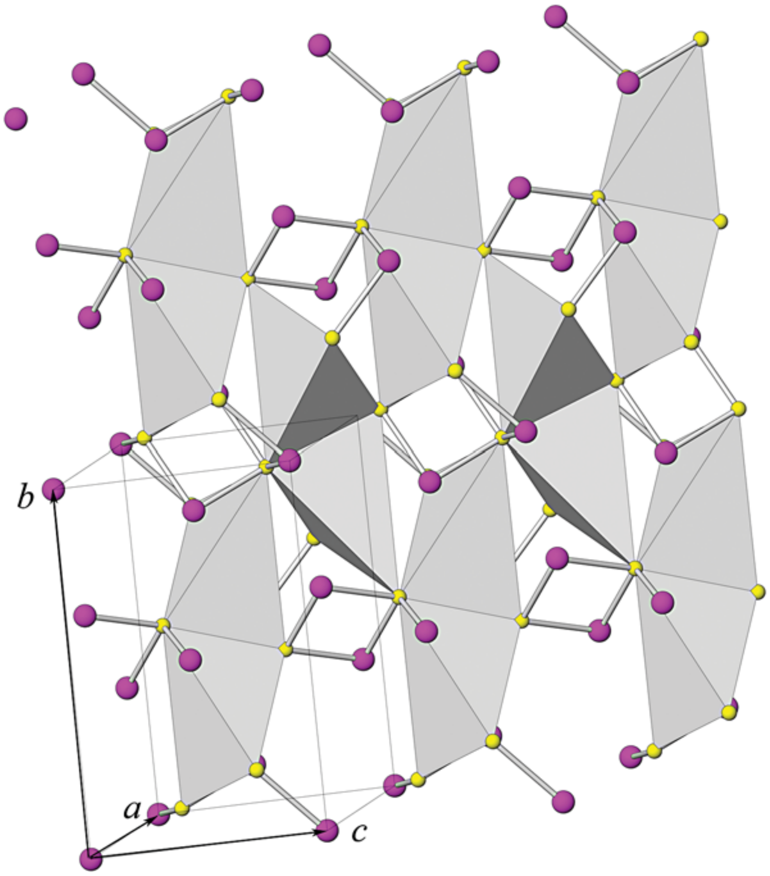

FIG. 2. A (100) layer of paired $CuSe_4$ tetrahedra in the crystal structure of jaguéite. The Se atoms are yellow, and the Pd atoms, purple. The *b* axis is vertical, and the *c* axis, horizontal.

distances 2.444, 2.533, 2.764 and 2.857 Å, and the Se–Cu–Se angles range from 79.1° to 132.8°, instead of being 109.47° for a regular tetrahedron with a centered cation. The volume-based eccentricity (Makovicky & Balić-Žunić 1998), ECC = $1 - [(r_s - \Delta)/ r_s]^3$ (where r_s is the radius of the circumscribed sphere, and Δ is the distance between the center of the sphere and the central atom), is 0.322. The volume-based measure of distortion (Makovicky & Balić-Žunić 1998) is 24%. The next shortest Cu–Se distances are 3.09 Å and longer. In agreement with the shape of the $CuSe_4$ tetrahedron, the Se–Se distances concentrate in two ranges, 3.38–3.56 Å and 4.77–4.98 Å, with one Se2–Se2 distance equal to 4.04 Å (Table 6).

All cations are involved in short metal–metal bonds. Whereas there are no very short Pd1–Pd2 interactions in the structure (Pd1–Pd2 = 3.099 Å), each atom of Pd2 interacts with two copper atoms, at distances equal to 2.748 and 2.906 Å, respectively. The Se and Cu atoms make up a trigonal prism with Pd in one of the faces, without additional capping (Fig. 1). Interactions of the Pd1 atom with two Cu atoms result in the distances of 2.855 Å. Each Cu atom has three close Pd neighbors, one Pd1 and two Pd2 at the above unequal distances.

Chrisstanleyite

The situation in chrisstanleyite is very similar to that just described. Irregularity of the Pd1 coordination square is slightly greater (Table 7), and the distortion of the Pd2 polyhedron increases as well. The largest departure from 180° is observed for the Se1–Pd2–Se2 angle, 172.4° (Table 7), and the range of Pd2–Se distances increases from the interval 2.471–2.490 Å observed for jaguéite to 2.463–2.492 Å in chrisstanleyite.

TABLE 6. SELECTED INTERATOMIC DISTANCES (Å) IN JAGUEITE

Pd1	Se1	Se1	Se2	Se2	Cu	Cu
Se1	**2.489(2)**	180.0(1)	95.1(1)	84.9(1)	61.9(1)	118.2(1)
Se1	4.978(4)	**2.489(2)**	84.9(1)	95.1(1)	118.2(1)	61.9(1)
Se2	3.684(3)	3.368(3)	**2.503(2)**	180.0(1)	73.9(1)	106.1(1)
Se2	3.368(3)	3.684(3)	5.005(4)	**2.503(2)**	106.1(1)	73.9(1)
Cu	2.764(3)	4.588(5)	3.234(4)	4.286(4)	**2.855(3)**	180.0(1)
Cu	4.588(5)	2.764(3)	4.286(4)	3.234(4)	5.710(5)	**2.855(3)**

Pd2	Se1	Se2	Se2	Se1	Cu	Cu
Se1	**2.471(2)**	175.4(1)	97.7(1)	82.8(1)	103.4(1)	61.3(1)
Se2	4.938(4)	**2.471(2)**	86.0(1)	93.8(1)	72.4(1)	117.9(1)
Se2	3.730(3)	3.379(4)	**2.485(3)**	174.9(1)	118.8(1)	69.4(1)
Se1	3.282(4)	3.623(3)	4.970(4)	**2.490(3)**	65.9(1)	115.0(1)
Cu	4.098(4)	3.089(4)	4.505(5)	2.857(3)	**2.748(3)**	72.1(1)
Cu	2.764(3)	4.613(4)	3.089(4)	4.556(5)	3.330(5)	**2.906(3)**

Cu	Se2	Se1	Pd2	Se1	Pd1	Se1	Pd2	Se2
Se2	**2.444(3)**	108.6(1)	98.6(1)	132.8(1)	80.3(1)	84.0(1)	145.8(1)	148.2(1)
Se1	4.042(4)	**2.533(4)**	82.4(1)	79.1(1)	94.1(1)	135.0(1)	105.4(1)	72.9(1)
Pd2	3.941(4)	3.481(3)	**2.748(3)**	128.5(1)	175.7(1)	52.7(1)	89.1(1)	49.7(1)
Se1	4.774(4)	3.377(4)	4.965(4)	**2.764(3)**	52.6(1)	124.1(1)	51.6(1)	79.0(1)
Pd1	3.430(3)	3.949(3)	5.599(4)	2.489(2)	**2.855(3)**	130.9(1)	94.1(1)	131.5(1)
Se1	3.560(3)	4.980(4)	2.490(3)	4.965(5)	5.196(4)	**2.857(3)**	74.3(1)	75.0(1)
Pd2	5.114(3)	4.333(5)	3.969(3)	2.471(2)	4.217(3)	3.481(3)	**2.906(3)**	48.9(1)
Se2	5.324(5)	3.368(3)	2.471(2)	3.730(3)	5.420(5)	3.623(3)	2.485(3)	**3.089(4)**

The values in diagonals (bold) are the central atom – ligand distances; in the upper-right triangle, the bond angles are given, and in the lower left, the ligand-ligand distances.

The most substantial difference lies in the Ag–Se distances, equal to 2.590, 2.746, 2.874, and 2.948 Å. The increase, compared to the corresponding Cu–Se distances in jaguéite, changes from 0.15–0.20 Å for the short distances to 0.09 for the longest distance. The distance from the geometrical center of the coordination tetrahedron to a ligand increases from 2.68 Å in jaguéite to 2.813 Å in chrisstanleyite. The volume of the coordination tetrahedron $AgSe_4$ is 8.74 Å^3, compared to 7.49 Å^3 measured for the $CuSe_4$ tetrahedron in jaguéite, and the volume-based eccentricity decreases to 0.264. The Se–Se distances span 3.33–5.21 Å (Table 7). The volume-based distorsion is 23.5%. The Pd1–Ag distances are 2.885 Å, to be compared with 2.855 Å for copper in jaguéite, and the Pd2–Ag distances are 2.823 and 2.918 Å (analogous to 2.748 and 2.906 Å in jaguéite). The minor Cu position has Cu–Se distances equal to 2.467, 2.474, and then only 3.001 and 3.109 Å, exceeding the fifth Ag–Se distance of 3.014 Å. Clearly, this coordination is dictated by the coordination requirements of silver.

MODULAR DESCRIPTION

The crystal structures of jaguéite and chrisstanleyite consist of two distinct frameworks of polyhedra that interpenetrate and support each other. They share common selenium vertices of the respective coordination-polyhedra.

The first of the frameworks consists of corrugated (100) layers composed of $CuSe_4$ (or $AgSe_4$) tetrahedra (Fig. 2), arranged in dimers of tetrahedra Cu_2Se_6 that share four vertices with adjacent dimers. The two remaining vertices (one for each tetrahedron) are oriented alternatively above and below the layer, which is responsible for the corrugation of the copper-based layer (wave-vector [010]) and leads to the sharing of the Se atoms with Pd polyhedra.

The second framework is palladium-based (Fig. 3). It is an open-work of single and paired coordination squares of Pd1 and Pd2, respectively. It can be described as a zig-zag arrangement of paired Pd2 polyhedra. These are stacked obliquely in slabs (010) and interconnected by "standing" squares of Pd1. Such slabs are then related by *c* glide planes, creating the zig-zag pattern stiffened by the interpenetrating Cu(Ag) skeleton (Fig. 3). Separation of Pd2 pairs along [001] leads to an alternative view of the Pd skeleton as composed of a sequence of one-square-thick (001) layer with identical configurations of inclined Pd1 and Pd2 squares, related by the *c* glide operation.

The metal–metal bonds (Fig. 1) are considered an important stabilizing factor in the two structures studied. A colinear sequence of metal bonds Pd2–Cu(Ag)–Pd1–Cu(Ag)–Pd2 in the direction [210] not only interconnects the metal atoms of one [010] slab of the zig-zag scheme described above, but also involves the Pd2 configurations of both adjacent slabs. Being parallel to the planes of paired Pd2 squares in the central slab of this three-slab combination, the linear sequence helps to stabilize the folding angles of the Pd2 zig-zag scheme.

In terms of anion-based polyhedra (Fig. 4), Se1 forms complicated polyhedra with CN = 6 (3 Cu, 2 Pd2 and 1 Pd1 ligands), whereas Se2 is only in tetrahedral coordination; all polyhedra share only corners, *i.e.*, the cations. In the latter polyhedra, there is only one Cu vertex, and two Pd2 plus one Pd1 vertex. Metal–metal bonds provide a framework for this structure, outlining a chess-board scheme of alternating [001] columns of Se1 polyhedra that alternatively share Pd–Pd and Cu–Cu edges, and of Se2 tetrahedra sharing Pd corners. All metal ligands lie on the (002) planes of the lattice of jaguéite (or chrisstanleyite).

COMPARISON TO OTHER STRUCTURES

The structures described here do not appear to have close relatives among the Pd and Pt sulfides or selenides. Edge-sharing pairs of Pd coordination squares appear in PdSe (Ijaali & Ibers 2001), but in that structure, which is the N = 2 homologue of the structure of PdS (Brese *et al.* 1985), the squares are stacked directly above each other and not diagonally, as in the structures we deal with here.

In the structure of $KCuPdSe_5$ (Chen *et al.* 2003), $PdSe_4$ groups form corrugated layers, but the slabs formed by diagonally stacked coordination squares are only one polyhedron thick. The Cu tetrahedra occur

TABLE 7. SELECTED INTERATOMIC DISTANCES (Å) IN CHRISSTANLEYITE

Pd1	Se1	Se1	Se2	Se2	Ag	Cu		
Se1	**2.492(2)**	180.0(1)	83.2(1)	96.8(1)	115.9(1)	67.1(3)		
Se1	4.984(3)	**2.492(2)**	96.8(1)	83.2(1)	64.1(1)	112.9(3)		
Se2	3.325(2)	3.743(3)	**2.515(2)**	180.0(1)	72.4(1)	101.8(3)		
Se2	3.743(3)	3.325(2)	5.029(3)	**2.515(2)**	107.6(1)	78.2(3)		
Ag	4.561(3)	2.874(3)	3.204(3)	4.361(3)	**2.885(2)**	172.6(3)		
Cu	3.001(15)	4.501(16)	4.211(14)	3.429(22)	5.775(17)	**2.902(17)**		
Pd2	Se1	Se1	Se2	Se2	Cu	Ag		
Se1	**2.463(2)**	80.1(1)	97.3(1)	172.4(1)	101.3(3)	63.9(1)		
Se1	3.173(3)	**2.468(3)**	174.4(1)	95.0(1)	73.6(3)	115.4(1)		
Se2	3.711(3)	4.943(3)	**2.481(3)**	88.0(1)	111.8(3)	67.3(1)		
Se2	4.943(3)	3.657(3)	3.456(3)	**2.492(2)**	71.5(3)	113.8(1)		
Cu	4.084(15)	3.173(14)	4.386(20)	3.109(15)	**2.810(16)**	64.3(3)		
Ag	2.874(3)	4.558(3)	3.014(3)	4.537(2)	3.050(20)	**2.918(2)**		
Ag	Se2	Se1	Pd2	Se1	Pd1	Pd2	Se1	Se2
Se2	**2.590(2)**	106.6(1)	97.2(1)	134.0(1)	82.7(1)	150.1(1)	85.3(1)	147.5(1)
Se1	4.278(3)	**2.746(3)**	82.0(1)	78.0(1)	91.1(1)	103.1(1)	132.5(1)	70.3(1)
Pd2	4.062(3)	3.655(3)	**2.823(3)**	128.5(1)	172.8(1)	90.1(1)	50.6(1)	50.4(1)
Se1	5.030(3)	3.538(3)	5.130(3)	**2.874(3)**	51.3(1)	50.3(1)	126.0(1)	78.1(1)
Pd1	3.623(2)	4.020(2)	5.696(2)	2.492(2)	**2.885(2)**	93.6(1)	136.4(1)	129.0(1)
Pd2	5.323(2)	4.438(3)	4.064(2)	2.463(2)	4.229(2)	**2.918(2)**	77.1(1)	49.4(1)
Se1	3.762(2)	5.212(3)	2.468(3)	5.187(3)	5.416(2)	3.655(3)	**2.948(3)**	75.7(1)
Se2	5.380(3)	3.325(2)	2.492(2)	3.711(3)	5.325(2)	2.481(3)	3.657(3)	**3.014(3)**
Cu	Se1	Se2	Pd2	Pd1	Se1	Se2	Se1	Pd2
Se1	**2.467(19)**	120.0(7)	87.4(5)	96.6(5)	80.0(5)	72.2(4)	134.7(6)	101.8(5)
Se2	4.278(3)	**2.474(14)**	100.3(6)	84.3(5)	133.2(6)	148.8(7)	82.5(5)	138.0(6)
Pd2	3.655(3)	4.062(3)	**2.810(16)**	171.4(7)	123.9(6)	49.5(3)	48.3(3)	84.5(4)
Pd1	4.020(2)	3.623(2)	5.696(2)	**2.902(17)**	49.9(3)	124.6(6)	126.1(6)	87.2(4)
Se1	3.538(3)	5.030(3)	5.130(3)	2.492(2)	**3.001(15)**	74.8(4)	114.3(5)	46.5(2)
Se2	3.325(2)	5.380(3)	2.492(2)	5.325(2)	3.711(3)	**3.109(15)**	71.2(4)	46.1(2)
Se1	5.212(3)	3.762(2)	2.468(3)	5.416(2)	5.187(3)	3.657(3)	**3.173(14)**	69.8(3)
Pd2	4.438(3)	5.323(2)	4.064(2)	4.229(2)	2.463(2)	2.481(3)	3.655(3)	**3.219(15)**

The values in diagonals (bold) are the central atom – ligand distances; in the upper-right triangle, the bond angles are given, and in the lower left, the ligand–ligand distances.

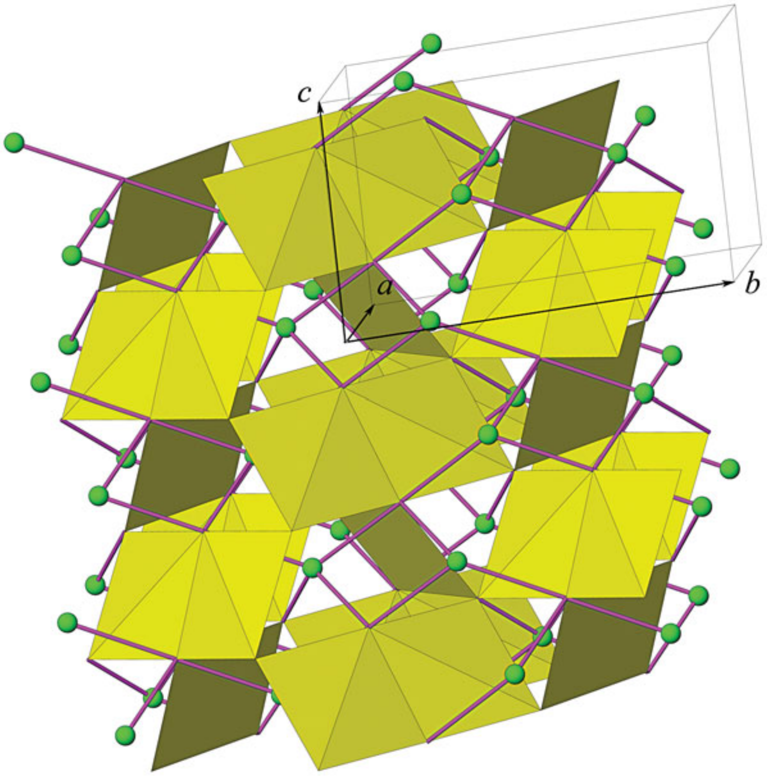

FIG. 3. The openwork of square $PdSe_4$ coordinations. The regular single squares belong to Pd1, and the bent and paired squares, to Pd2. The Cu atoms are shown in green. Projection along [100], with the *b* axis horizontal.

in the crest areas of the corrugated layer but are not interconnected with each other, only with Pd and K polyhedra. A zig-zag scheme of Pd–Cu distances does not represent metal–metal bonds; they are equal to 3.26 Å. We conclude that the jaguéite–chrisstanleyite pair represents a new structure-type which, according to the results of Karup-Møller & Makovicky (1999), apparently lacks a sulfide analog.

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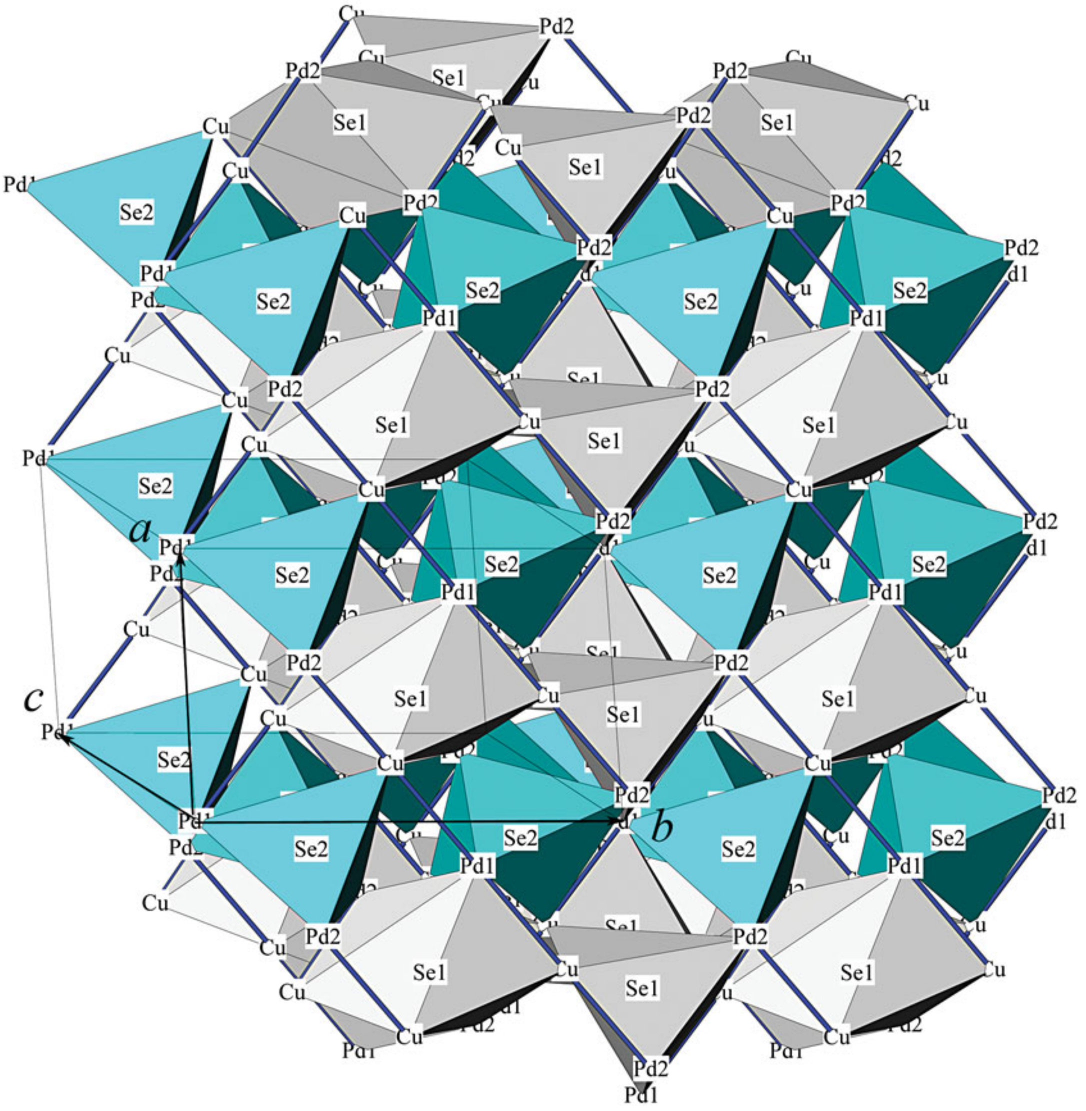

FIG. 4. Anion-based coordination polyhedra in the crystal structure of jaguéite. Cation–cation bonds are dark blue. Oblique projection approximately parallel to [001]; the *b* axis is horizontal, and the *a* axis, vertical.

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