

Crystal structure and twinning of Sb_2AsS_2 , the synthetic analogue of p \ddot{a} akk \ddot{o} nenite

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ABSTRACT

The crystal structure of synthetic p \ddot{a} akk \ddot{o} nenite, $\text{Sb}_{2.07}\text{As}_{0.93}\text{S}_{2.00}$, was determined. This study revealed that, in spite of the strong orthorhombic pseudosymmetry shown by Weissenberg photographs, the structure is monoclinic (space group $C2/m$), with $a = 10.75(2)$, $b = 3.959(3)$, $c = 12.49(2)$ \AA , $\beta = 115.25(8)^\circ$, $V = 481(1)$ \AA^3 , and $Z = 4$. The crystal structure was solved by direct methods using intensity data collected from a twinned crystal. The refinement led to an R index of 4.58%. The observed pseudosymmetry was shown to arise from $\{001\}$ twinning. The structure can be described as a sequence of sheets stacked perpendicular to the a axis and mutually displaced by $1/2b$. Each sheet consists of $\text{Sb}_4\text{S}_4\text{As}_2$ ribbon-like units similar to the Sb_4S_6 chains of stibnite but linked together by As-As bonds. The structural relationships with stibnite are discussed to explain the formation mechanism of p \ddot{a} akk \ddot{o} nenite and the presence of twinning. X-ray powder data for synthetic p \ddot{a} akk \ddot{o} nenite are also reported.

INTRODUCTION

P \ddot{a} akk \ddot{o} nenite, ideally Sb_2AsS_2 , first described by Borodayev et al. (1982), is a rare mineral discovered in the antimony deposit of Kalliosalo, Sein \ddot{a} joki region, Finland, in association with native antimony, arsenopyrite, and nickelous l \ddot{o} llingite. It is one of the three ternary phases of the As-Sb-S system, the other two being getchellite, AsSbS_3 (Weissberg, 1965; Guillermo and Wuensch, 1973), and wakabayashilite, $(\text{As,Sb})_{11}\text{S}_{18}$ (Kato et al., 1972).

A synthetic compound (called X-phase) with chemical composition close to that of p \ddot{a} akk \ddot{o} nenite was obtained during experimental investigations of the systems As-Sb-S (Craig et al., 1974; Bernardini et al., 1992) and Cu-Sb-As-S (Luce et al., 1977). During an experimental study on the thermal behavior and the kinetics of formation of Sb_2AsS_2 (Bernardini et al., 1994), crystals suitable for the structural study were obtained. This paper reports the crystal structure determination performed on a twinned crystal of Sb_2AsS_2 .

EXPERIMENTAL METHODS

The material studied was synthesized in evacuated silica vials in dry conditions at 480 $^\circ\text{C}$ starting from pre-synthesized stibnite (Sb_2S_3) and a stibarsen-like intermetallic compound (Sb_2As_3). The product occurred as radiating aggregates of small platy elongated crystals. These were very brittle and split upon the slightest mechanical manipulation into apparently single, acicular crystals (Fig. 1) susceptible to plastical deformation. A

very thin crystal (approximately $6 \times 12 \times 200$ μm) was selected for the structural study. An Enraf Nonius CAD4 single-crystal diffractometer was used to determine the unit-cell dimensions and to collect the intensity data (experimental details in Table 1). Data were corrected for Lorentz-polarization effects and for absorption following the semiempirical method proposed by North et al. (1968). The X-ray powder pattern was recorded by means of a Philips PW 1130/90 diffractometer (Fe-filtered $\text{CoK}\alpha$ radiation, scan speed 0.25 $^\circ/\text{min}$).

Several crystals were analyzed by means of a JEOL JXA-8600 electron microprobe. Analytical conditions were 10 kV accelerating voltage and 5 nA beam current (Faraday cup); the standards employed were the pure element for As, and stibnite for Sb and S. The chemical composition is reported in Table 2; on the basis of five atoms, the formula is $\text{Sb}_{2.07}\text{As}_{0.93}\text{S}_{2.00}$.

POWDER PATTERN AND UNIT-CELL DETERMINATION

A preliminary X-ray investigation by means of Weissenberg photographs pointed toward an orthorhombic symmetry, with $Fmm2$, $F222$, and $Fmmm$ as possible space groups. Lattice parameters, as measured on the photographs, were $a = 10.75$, $b = 3.96$, and $c = 22.55$ \AA . However, more accurate values refined from 25 high- θ reflections measured with the CAD4 diffractometer gave a β angle value of 89.75(5) $^\circ$. Other crystals tested gave similar results. Therefore, a monoclinic cell (C lattice) with the following parameters was chosen: $a = 10.75(2)$, $b =$

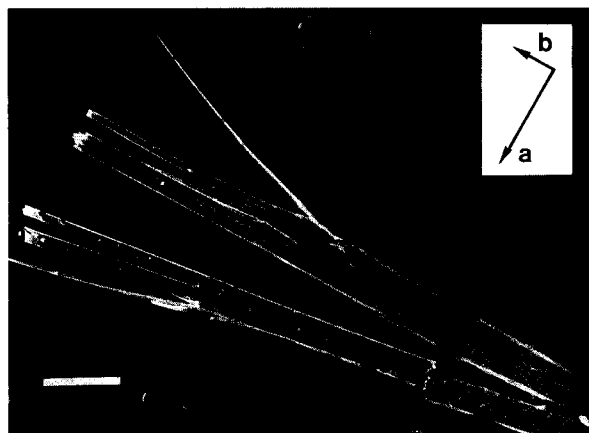


Fig. 1. Electron micrograph of needle-like crystals. Scale bar equals 100 μm .

3.959(3), $c = 12.49(2)$ Å, $\beta = 115.25(8)^\circ$, $V = 481(1)$ Å³, and $Z = 4$. On the basis of this unit cell, the X-ray powder pattern was indexed. Table 3 compares the X-ray powder pattern of the synthetic compound with that of the natural päykkönenite obtained by Borodayev et al. (1982) by means of film methods. On first inspection of the data, these spectra may appear somewhat different: several reflections are apparently absent in the natural material. Most of these omissions are due to the different technique used in this study: $201/\bar{2}03$, $112/\bar{1}13$, and $114/\bar{1}15$ doublets, and $311/\bar{3}14/005$ triplet are not resolved on film. Furthermore, the $\bar{2}01$ and $\bar{4}02$ intensities are enhanced probably because of a preferred orientation of cleavage fragments on the diffractometer mount in contrast to the random orientation of the film method. As discussed below, this fact agrees closely with the structural arrangement, which consists of sheets parallel to $(\bar{2}01)$. A comparison with the intensity calculated on the basis of the structural model (4 and 60 for $\bar{2}01$ and $\bar{4}02$, respectively) supports this assumption. The reflection with $d = 3.13$ Å in the powder pattern of the natural material is presumably due to the presence of native antimony, which is closely associated with päykkönenite in the Kalliosalo deposit. Therefore, we find that there is good agreement between the two sets of d values, which allows us to consider the synthetic material as the analogue of päykkönenite.

TABLE 1. Experimental details of the intensity data collection

Apparatus	Enraf Nonius CAD4
Radiation	MoK α (0.71069 Å)
Crystal size	6 × 12 × 200 μm
θ range	1–28°
Scan mode	ω
Scan width	3.0°
Scan speed	1.8°/min
ψ scan	134; $\bar{1}34$ ($\chi = \pm 83.2$)
Min. trans.	89.7%
Max. trans.	99.7%

TABLE 2. Compositional data for synthetic päykkönenite

Element	wt%*	Atoms
Sb	64.32 (63.96–65.59)	2.07
As	17.85 (16.71–18.42)	0.93
S	16.31 (15.76–16.70)	2.00
Total	98.48 (97.55–99.13)	5.00

* Average of ten microprobe analyses and, in parentheses, range.

The geometrical relationships between both pseudo-orthorhombic and monoclinic unit cells and that proposed by Borodayev et al. (1982) [$a = 5.372(7)$, $b = 3.975(5)$, $c = 11.41(1)$ Å, $\beta = 89.7(2)^\circ$, and $V = 243.6$ Å³] are sketched in Figure 2.

It should be noted that the observed reflections cannot be indexed on the basis of the unit cell proposed by Borodayev et al. (1982). In fact, the transformation matrix ($1/200/010/1/201$) would produce fractional indices for all the reflections with $h = 2n + 1$. Such reflections are present in the powder pattern of natural päykkönenite [e.g., $d = 3.67(10)$ and $d = 2.87(100)$], and so the cell proposed by Borodayev et al. (1982) cannot be a true unit repeat.

TABLE 3. X-ray powder diffraction data for synthetic and natural päykkönenite

hkl	Synthetic compound			Päykkönenite*	
	d_{calc} (Å)	d_{meas} (Å)	$ l_o$	d_{meas} (Å)	$ l_o$
002	5.6385	5.63	5		
201	5.3664	5.36	10		
200	4.8776	4.87	5		
201	3.9202	3.92	55	3.90	40
203	3.8551	3.85	70		
110	3.6643	3.66	15	3.67	10
$\bar{1}11$	3.6575				
$\bar{1}12$	3.3194				
				3.13	40
112	2.8736	2.874	70	2.87	100
$\bar{1}13$	2.8573	2.858	40		
004	2.8193	2.817	<5		
402	2.6832	2.683	100	2.68	60
311	2.6385	2.635	5	2.27	30
312	2.6309				
403	2.6005				
311	2.2992	2.299	15	2.08	20
314	2.2744	2.275	20		
005	2.2554	2.255	60		
114	2.0823	2.083	5		
$\bar{1}15$	2.0711	2.072	15	1.985	20
020	1.9769	1.979	10	1.883	5
513	1.8776	1.881	<5		
313	1.8331	1.833	10		
221	1.7652	1.763	<5		
223	1.7591	1.758	<5		
510	1.7496	1.750	15	1.750	30
403	1.7409	1.742	<5		
515	1.7313	1.732	<5		
601	1.7134	1.712	10	1.672	5
407	1.7124				
605	1.6969	1.696	5	1.595	10
422	1.5916	1.592	10		
206	1.5502	1.550	5		
208	1.5359	1.536	<5		

* Data for päykkönenite from Kalliosalo deposit, Finland, obtained by photographic methods with unfiltered Fe radiation (Borodayev et al., 1982).

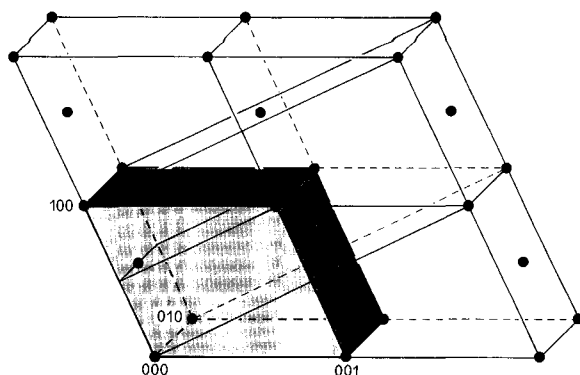


Fig. 2. Lattice of synthetic pääkkönenite. The different unit cells referred to in the text are drawn as $100/010/001 = C$ -type monoclinic cell, $\frac{1}{2}00/010/\frac{1}{2}01 =$ monoclinic cell (Borodayev et al., 1982), and $100/010/102 = F$ -type pseudo-orthorhombic cell. The monoclinic cell proposed by Borodayev et al. (1982) is not a true unit-cell repeat.

STRUCTURE SOLUTION

In spite of the apparent orthorhombic symmetry shown by the Weissenberg photographs, the first attempt to solve the structure by direct methods in the $Fmm2$, $F222$, and $Fmmm$ space groups met with failure. In the $C2/m$ space group, a reliable solution was found by means of the routine EES, an automatic multisolution direct method of SHELX (Sheldrick, 1976). Two Sb and one As atom were located on an F_0 -Fourier map. Four additional peaks, attributed to S atoms, were located on successive F_0 maps. The initial cycles of structure refinement, performed in the $C2/m$ space group, led to an R index of about 25% with unreliable displacement parameters for most of the structural sites. Successive least-squares cycles were performed in the Cm space group, and the site occupancy was refined without any chemical constraint: the R index lowered to about 10%, but the structure still showed a nearly centrosymmetric topology. Some unusual mixed occupancies (mainly Sb-S) suggested the presence of twinning in the crystal. Indeed, the peculiar geometry of the unit cell (with the c parameter almost equal to the ac shortest diagonal) makes $\{001\}$ twinning very probable. In such a case all the reflections of one twin unit would overlap almost exactly those of the other: the Miller indices of pairs of overlapped reflections are hkl for the first member and $h' = -h$, $k' = k$, $l' = (h + l)$ for the second member of the twin. For low values of the θ angle, the pairs of diffraction spots appear completely overlapped, the split increasing with the increasing of the h index. Because of the low diffraction quality of these crystals, this split is masked by the broadness of the diffraction profiles. Finally, a structure refinement was performed using a locally modified version of the program ORFLS (Busing et al., 1962), which works on the twinned crystal structure and allows the fraction of the first member in the whole twinned crystal to be refined. The scattering

TABLE 5. Fractional coordinates and U_{eq} for synthetic pääkkönenite

	x/a	y/b	z/c	U_{eq}
Sb1	-0.0452(3)	0	0.1755(2)	0.025(1)
Sb2	0.3119(3)	$\frac{1}{2}$	0.3979(4)	0.036(1)
As	-0.1058(5)	$\frac{1}{2}$	0.0156(3)	0.018(1)
S1	0.2114(11)	0	0.2376(7)	0.017(3)
S2	0.0937(11)	$\frac{1}{2}$	0.4084(12)	0.032(4)

curves for neutral Sb, As, and S atoms were taken from *International Tables for X-ray Crystallography*, volume IV (Ibers and Hamilton, 1974). By means of some isotropic full-matrix least-squares cycles, the refinement quickly converged to $R = 13\%$. The introduction of the anisotropic displacement parameters and the site-occupancy refinement led to final R values (unit-weighting scheme) of 4.58% for 426 observed reflections ($I > 3\sigma_I$) and 8.62% for all data. The refined percentages for the two components of the twin were 45 and 55%, respectively. The site-occupancy refinement led to the crystal-chemical formula $Sb_2(As_{0.84}Sb_{0.16})S_2$, which is in agreement with that derived from the chemical analyses. Observed and calculated structure factors are listed in Table 4.¹ Atomic coordinates (Table 5) and anisotropic displacement parameters (Table 6) are also given.

DESCRIPTION OF THE STRUCTURE

The structure of synthetic Sb_2AsS_2 consists of a sequence of sheets parallel to $(\bar{2}01)$ and stacked perpendicular to the a axis and mutually displaced by $\frac{1}{2}b$ (Fig. 3). Each sheet can be described as a linkage of $Sb_4S_4As_2$ ribbon-like units (parallel to the b axis) very similar to the Sb_4S_6 ribbons found in the structure of stibnite (Bayliss and Nowacki, 1972) but linked together by As-As bonds to form a homogeneous sheet (Fig. 4). Similar ribbon units, $(Sb,Pb)_4S_6$, composed of face-sharing, back-to-back square pyramids, were also found in the structure of robinsonite, $Pb_4Sb_6S_{13}$ (Skowron and Brown, 1990). In pääkkönenite, as in stibnite, there are two independent Sb atoms, which differ in their configuration. One of these, Sb2, is fivefold-coordinated and approximately located on the basal plane of a square pyramid at 2.692(7) Å from two S1 atoms and 2.951(12) Å from two S2 atoms; another S2 atom occupies the vertex of the pyramid at 2.405(12) Å. The other Sb atom, Sb1, is located at the vertex of a trigonal pyramid and is bonded to one S atom (S1) at 2.526(11) Å and two As atoms at 2.687(3) Å, which occupy the corners of the basal plane. Therefore, the As plays a role analogous to that of the S_{II} atom in the structure of stibnite (Bayliss and Nowacki, 1972); on the other hand, whereas in stibnite S_{II} is only twofold-

¹ A copy of Table 4 may be ordered as Document AM-95-593 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

TABLE 6. Anisotropic displacement parameters for synthetic pääkkönenite

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb1	0.033(2)	0.015(1)	0.030(1)	0	0.017(1)	0
Sb2	0.027(2)	0.027(2)	0.058(2)	0	0.022(1)	0
As	0.025(2)	0.015(2)	0.011(2)	0	0.005(1)	0
S1	0.030(5)	0.020(4)	0.005(2)	0	0.010(3)	0
S2	0.031(6)	0.020(4)	0.057(6)	0	0.029(6)	0

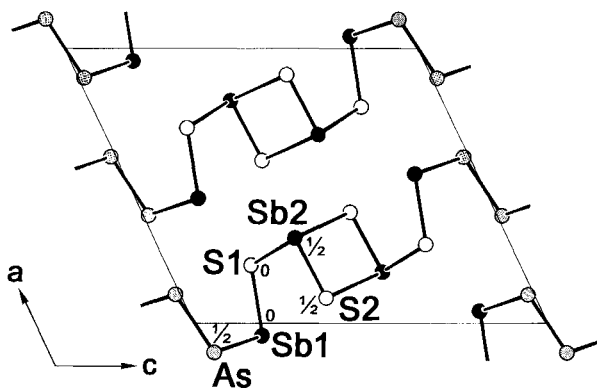
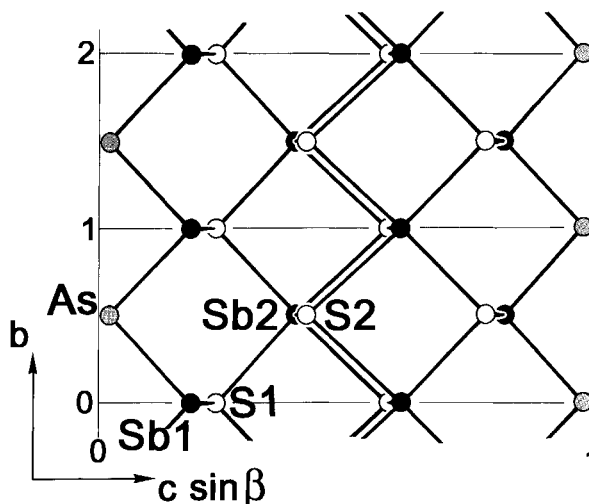
Note: the form of the anisotropic displacement factor is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

coordinated, in the structure of the synthetic pääkkönenite As itself occupies the vertex of another trigonal pyramid (Fig. 3). The As-As bond provides the two-dimensional connection within the sheet. As has a different role in the structure of getchellite, AsSbS_3 , where this element substitutes for Sb at the vertex of trigonal pyramidal (Sb,As) S_3 groups (Guillermo and Wuensch, 1973).

Bond distances and angles for pääkkönenite are listed in Table 7. The shortest interatomic contacts between atoms belonging to different sheets are 3.483(5) (Sb1-As), 3.557(5) (As-As), 3.574(9) (Sb2-S2), and 3.619(9) Å (Sb1-S1), which are greater than those found between ribbons in stibnite (Bayliss and Nowacki, 1972). Such a weak linkage between sheets in the structure of pääkkönenite accounts well for a $\{201\}$ cleavage (Fig. 1), as inferred by the enhanced intensity of $\bar{2}01$ and $\bar{4}02$ reflections in the powder pattern (Table 3).

VALENCE BALANCE

According to Brown (1992), the model of the bond valence "runs into inconsistencies if bonds occur between two cations or between two anions"; such a case occurs in pääkkönenite between pairs of As atoms. However, as Brown (1992) suggests, the bond-valence treatment is still possible if the pair of bonded atoms is treated as a single node, but the difficulty remains as to how the valence is distributed between the two atoms. With this in mind, bond strengths were calculated for all bond lengths <3.8

**Fig. 3.** Structure of synthetic pääkkönenite projected down the b axis.**Fig. 4.** Structure of synthetic pääkkönenite; [100] projection.

Å using the equation $s = \exp[(r_0 - r)/0.37]$, with $r_0 = 2.474$ Å for Sb-S bonds (Brown and Altermatt, 1985). Sb-As bond strengths were calculated using the r_0 value from Brese and O'Keeffe (1991), but the resulting sum for Sb1 was too low; to obtain a sum equal to 3.0 vu, a value $r_0 = 2.634$ Å was calculated. Results (Table 8) indicate a negative formal charge of about 3.7 for the As-As group, fairly close to the value of corresponding S-S pairs in stibnite.

CONCLUSIONS

The close similarity between the structure of synthetic Sb_2As_2 and that of Sb_2S_3 accounts well for the results obtained by Bernardini et al. (1994). In fact, according to these authors, the Sb_2As_2 phase is easily obtained starting from Sb_2S_3 and Sb_2As_3 , which react readily by means of a diffusional mechanism, probably in the solid state.

TABLE 7. Interatomic distances (Å) and angles (°) for synthetic pääkkönenite

Sb1-pyramid		Sb2-pyramid	
Sb1-S1	2.527(11)	Sb2-S2	2.405(12)
-As	2.687(3)	-S1	2.692(7)
-As ^a	2.687(3)	-S1 ^c	2.692(7)
S1-Sb1-As	96.6(2)	-S2 ^d	2.951(12)
-As ^a	96.6(2)	-S2 ^e	2.951(12)
As-Sb1-As ^a	94.9(1)	S2-Sb2-S1	87.1(3)
		-S1 ^c	87.1(3)
		-S2 ^d	87.6(3)
		-S2 ^e	87.6(3)
As-As ^b	2.466(6)	S1-Sb2-S1 ^c	94.7(2)
-Sb1	2.687(3)	-S2 ^d	172.5(9)
-Sb1 ^c	2.687(3)	-S2 ^e	90.3(2)
As ^b -As-Sb1	99.8(1)	S1 ^c -Sb2-S2 ^d	90.3(2)
-Sb1 ^c	99.8(1)	-S2 ^e	172.5(9)
Sb1-As-Sb1 ^c	94.9(1)	S2 ^d -Sb2-S2 ^e	84.3(2)

Note: a = x, -1 + y, z; b = -x, y, -z; c = x, 1 + y, z; d = 1/2 - x, 1/2 + y, 1 - z; e = 1/2 - x, -1/2 + y, 1 - z.

TABLE 8. Valence balance for synthetic pääkkönenite

	Sb1	Sb2	Σ
S1	{ 0.868 0.045($\times 2$) }	0.555($\times 2$)	2.068
S2	0.107($\times 2$)	{ 1.206 0.051($\times 2$) 0.275($\times 2$) }	2.072
$\frac{1}{2}(\text{As-As})$	{ 0.101 0.866($\times 2$) }		1.833
Σ	3.005	2.968	

It is worth emphasizing another point concerning the formation of the Sb_2AsS_2 phase. All crystals tested during this study showed a strong orthorhombic pseudosymmetry. This means that all crystals were twinned, with each twin-related component contributing about 50%. Why does such twinning occur? The twinning may be explained by examining the structures of pääkkönenite and stibnite in terms of the stacking arrangement of modular slabs into which both of these structures are ideally sliced (Fig. 5). Each slab contains a row of identical and equally oriented $\text{Sb}_4\text{S}_4\text{X}_2$ ribbon-like units ($\text{X} = \text{S}$ in stibnite and $\text{X} = \text{As}$ in pääkkönenite). Within the slab, atoms are related by $2_1/m$ symmetry, and distances and angles are very similar in both structures, except for contacts between adjacent ribbons, which are 3.17 Å distant in stibnite and 3.56 Å in pääkkönenite. In the latter mineral, all the slabs, which are parallel to $(\bar{1}01)$, show ribbons oriented in the same way, and the stacking sequence is obtained by translation (vector $\frac{1}{2}[110]$). In this way the As atoms belonging to ribbons of adjacent slabs approach each other, thus allowing linkage into sheets. In stibnite, on the contrary, the relationship of one slab to the next along the a axis is by an n -glide reflection. As a consequence, one half of the ribbons are mirror-related to the

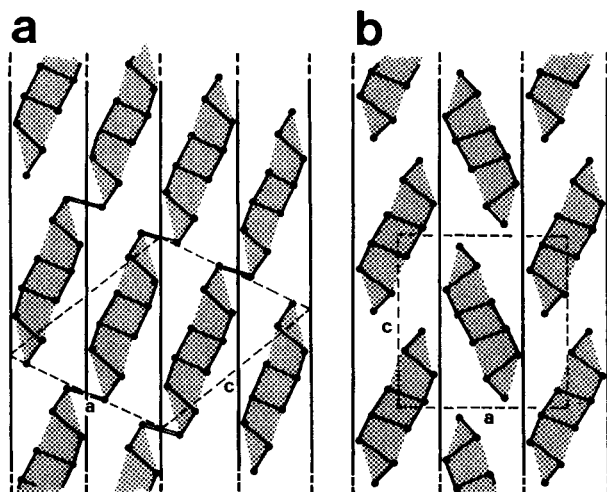


Fig. 5. Stacking sequences in the structure of pääkkönenite (a) and stibnite (b).

other half. When the phase transforms to Sb_2AsS_2 , because of the diffusion of As, the orthorhombic symmetry is lost. If, during this process, the ribbon units migrate without loss of their original orientation, then twinned domains with the proportions close to 0.5 and 0.5 should form in pääkkönenite. This also accounts for the presence of widely developed fine-polysynthetic twinning in this mineral (Borodayev et al., 1982).

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REFERENCES CITED

- Bayliss, P., and Nowacki, W. (1972) Refinement of the crystal structure of stibnite, Sb_2S_3 . *Zeitschrift für Kristallographie*, 135, 308–315.
- Bernardini, G.P., Corsini, F., Mazzetti, G., and Parrini, P. (1992) The As-Sb-S system: A synthetic study at 400 ° and 250 °C and a postulated phase diagram at 25 °C. *Neues Jahrbuch für Mineralogie Monatshefte*, 6, 265–275.
- Bernardini, G.P., Borrini, D., Corsini, F., Danti, C., Guarini del Taja, G., and Mazzetti, G. (1994) The thermal behaviour and the mechanism of formation of the synthetic analogue of pääkkönenite, Sb_2AsS_2 . *Terra Nova* (Abs. Supplement 1), 6, 5.
- Borodayev, Ju.S., Mozgova, N.N., Ozerova, N.A., Bortnikov, N.S., Ojvanen, P., and Ileutujnen, V. (1982) Pääkkönenite, Sb_2AsS_2 , a new mineral from Seinäjoki ore region in Finland. *International Geology Review*, 24, 1234–1240.
- Brese, N.E., and O'Keeffe, M. (1991) Bond-valence parameters for solids. *Acta Crystallographica*, B47, 192–197.
- Brown, I.D. (1992) Chemical and steric constraints in inorganic solids. *Acta Crystallographica*, B48, 553–572.
- Brown, I.D., and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database. *Acta Crystallographica*, B41, 244–247.
- Busing, W.R., Martin, K.O., and Levy, H.A. (1962) ORFLS. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee.
- Craig, J.R., Skinner, B., Francis, C.A., Luce, F.D., and Makovicky, M. (1974) Phase relations in the As-Sb-S system. *Eos*, 55, 483.
- Guillermo, T.R., and Wuensch, B.J. (1973) The crystal structure of getchellite, AsSbS_3 . *Acta Crystallographica*, B29, 2536–2541.
- Ibers, J.A., and Hamilton, W.C., Eds. (1974) *International tables for X-ray crystallography*, vol. IV, 366 p. Kynoch, Birmingham, U.K.
- Kato, A., Sakurai, K.I., and Ohsumi, K. (1972) Introduction to Japanese minerals (abs.). *American Mineralogist*, 57, 1311–1312.
- Luce, F.D., Tuttle, C.L., and Skinner, B.J. (1977) Studies of sulfosalts of copper: V. Phases and phase relations in the system Cu-Sb-As-S between 350 ° and 500 °C. *Economic Geology*, 72, 271–289.
- North, A.C.T., Phillips, D.C., and Mathews, F.S. (1968) A semiempirical method of absorption correction. *Acta Crystallographica*, A24, 351–359.
- Sheldrick, G.M. (1976) *SHELX-Program for crystal structure determination*. University of Cambridge, Cambridge, U.K.
- Skowron, A., and Brown, I.D. (1990) Refinement of the structure of robinsonite, $\text{Pb}_4\text{Sb}_6\text{S}_{13}$. *Acta Crystallographica*, C46, 527–531.
- Weissberg, B.G. (1965) Getchellite, AsSbS_3 , a new mineral from Humboldt County, Nevada. *American Mineralogist*, 50, 1817–1826.