

POLYTIPIsm IN STIBIVANITE

STEFANO MERLINO AND PAOLO ORLANDI

Dipartimento di Scienze della Terra dell'Università di Pisa, Via S. Maria 53, 56100 Pisa, Italy

NATALE PERCHIAZZI

Museo di Storia Naturale e del Territorio dell'Università di Pisa, Via Roma 103, 56011 Calci, Pisa, Italy

RICCARDO BASSO

Dipartimento di Scienze della Terra dell'Università di Genova, Corso Europa 26, 16132 Genova, Italy

ANDREA PALENZONA

Istituto di Chimica-Fisica dell'Università di Genova, Corso Europa 26, 16132 Genova, Italy

ABSTRACT

Stibivanite-2O, a new orthorhombic polytype of Sb_2VO_5 , has been found at Buca della Vena mine. It occurs as emerald-green acicular and fibrous crystals in a vein of recrystallized dolomite. The space group of the mineral is *Pmnc*, with a 17.916(3), b 4.790(1), c 5.509(1) Å. The strongest lines (visual estimation) in the powder pattern [d in Å, intensity in parentheses] are: 3.097(s), 2.986(ms), 9.00(m), 4.62(m), 1.871(ms), 1.747(mw). The OD character of the structure of monoclinic stibivanite has been established. On the basis of OD theory, a structural model for the orthorhombic modification is proposed. The model has been confirmed through a least-squares refinement, carried out with 530 observed reflections, to a final R of 0.032. The structure of stibivanite-2O, as well as that of the monoclinic polytype, is characterized by the presence of complex ribbons very weakly linked in a and b directions. In the complex ribbons, chains of corner-sharing SbO_3 pyramids are attached to both sides of edge-sharing VO_5 pyramids.

Keywords: stibivanite, polytypism, OD theory, Apuan Alps, Italy.

SOMMAIRE

Nous avons découvert la stibivanite-2O, nouveau polytype orthorhombique de Sb_2VO_5 , dans la mine Buca della Vena, dans les Alpes apouennes, en Italie. Elle forme des essais de cristaux circulaires et fibreux vert émeraude dans une diaclase de dolomite recristallisée. Le groupe spatial est *Pmnc*, et les paramètres réticulaires sont: a 17.916(3), b 4.790(1), c 5.509(1) Å. Les six raies les plus intenses du cliché de poudre [d en Å (intensité estimée visuellement)] sont: 3.097(s), 2.986(ms), 9.00(m), 4.62(m), 1.871(ms) et 1.747(mw). Le caractère OD de la structure monoclinique de la stibivanite est établi. En utilisant la théorie dite OD, nous proposons un modèle structural pour la modification orthorhombique. Ce modèle a été confirmé par affinement par moindres carrés de 530 réflexions observées, jusqu'à un facteur R final de 0.032. La structure de la stibivanite-2O, aussi bien que celle du polytype monoclinique, contient des rubans complexes qui sont très faiblement liés dans les directions a et b . Dans ces rubans, des

chaînes de pyramides SbO_3 à sommets partagés sont agrafées de chaque côté des pyramides VO_5 à arêtes partagées.

(Traduit par la Rédaction)

Mots-clés: stibivanite, polytypisme, théorie OD, Alpes apouennes, Italie.

INTRODUCTION

Stibivanite, Sb_2VO_5 , was first described by Kaiman *et al.* (1980) from the Lake George antimony deposit, New Brunswick. They described the mineral as being monoclinic, with space group *C2/c* and a 17.989(6), b 4.792(1), c 5.500(2) Å, β 95.15(3)°. Subsequently, Merlino & Orlandi (1983) found a second occurrence at Buca della Vena mine, in the Apuan Alps, Italy. Stibivanite is the natural counterpart of the compound synthesized by Darriet *et al.* (1976). The structure of the synthetic compound was determined by Darriet *et al.* (1976) and, independently, by Szymański (1980).

The aim of this paper is to present the results of chemical, physical, crystallographic and structural studies carried out on material recently found at Buca della Vena mine and apparently slightly different from the crystals of original stibivanite. These studies clearly point to a new orthorhombic polytype of stibivanite, denoted as stibivanite-2O on the basis of its structural relationships with the monoclinic polytype, stibivanite-2M.

OCCURRENCE

The Buca della Vena iron mine is located north of Stazzema, in the Apuan Alps, Italy. Iron ore (magnetite, hematite and minor pyrite) occurs within a microcrystalline mass of barite. According to Carmignani *et al.* (1976), the mineralization is due to metasomatism by medium-temperature hydrothermal fluids at the contact between phyllite and dolomite; on the other hand Benvenuti *et al.* (1986) pro-

posed a diagenetic origin for the deposit, which was subsequently metamorphosed during the Tertiary Apenninic orogeny. The Buca della Vena mine is the type locality for apuanite and versiliaite (Mellini *et al.* 1979); several rare and interesting minerals, including derbylite and stibivanite, also are present, as reported by Orlandi & Checchi (1986).

New samples from that locality were made available through the kindness of C. Del Tredici and M. Baldi, both mineral collectors. In those samples, stibivanite occurs within a vein of recrystallized dolomite, associated with anatase, apuanite, barite, beryl, derbylite, dolomite, hematite, magnetite, pyrite, tourmaline and versiliaite. Whereas most crystals of stibivanite have a platy habit, some crystals show a more "cylindrical" habit: ten emerald-green crystals, up to 2 mm in length and about 0.1 mm in diameter, lying on a large rhombohedron of dolomite, were found in a unique sample. The sample, together with the crystals studied in the present work, is now preserved (catalog number 4880) in the Museo di Storia Naturale of the University of Pisa.

CRYSTALLOGRAPHIC, PHYSICAL AND CHEMICAL DATA

A crystal from the unique sample was selected and examined by single-crystal X-ray methods. Rotation and Weissenberg photographs indicate that it is

orthorhombic, with approximate unit-cell parameters a 18, b 4.8, c 5.5 Å and possible space-groups $Pm\bar{c}n$ or $P2_1cn$. More precise cell-parameters, a 17.916(3), b 4.790(1), c 5.509(1) Å, were obtained by least-squares fitting of 29 reflections with $2\theta > 36^\circ$ selected among the reflections collected for the structure solution with an Iral Structures four-circle automatic diffractometer.

The close crystallographic relationships with the original stibivanite suggested to us an orthorhombic modification of Sb_2VO_5 , which thus deserved a full characterization.

Chemical data

An energy-dispersion analysis was carried out with a Philips 515 scanning electron microscope on a small crystal fragment previously examined by means of Weissenberg photographs. The analysis indicated that, as expected, vanadium and antimony are the only elements having $Z > 10$ that are present. Data reduction with the SUPERQUAN correction program, without standards, gave Sb_2O_3 79–80% and VO_2 20–21%, in agreement with the chemical formula Sb_2VO_5 . The calculated density is 5.26 g/cm³.

Physical properties

The translucent crystals of the orthorhombic modification have an adamantine luster and a white

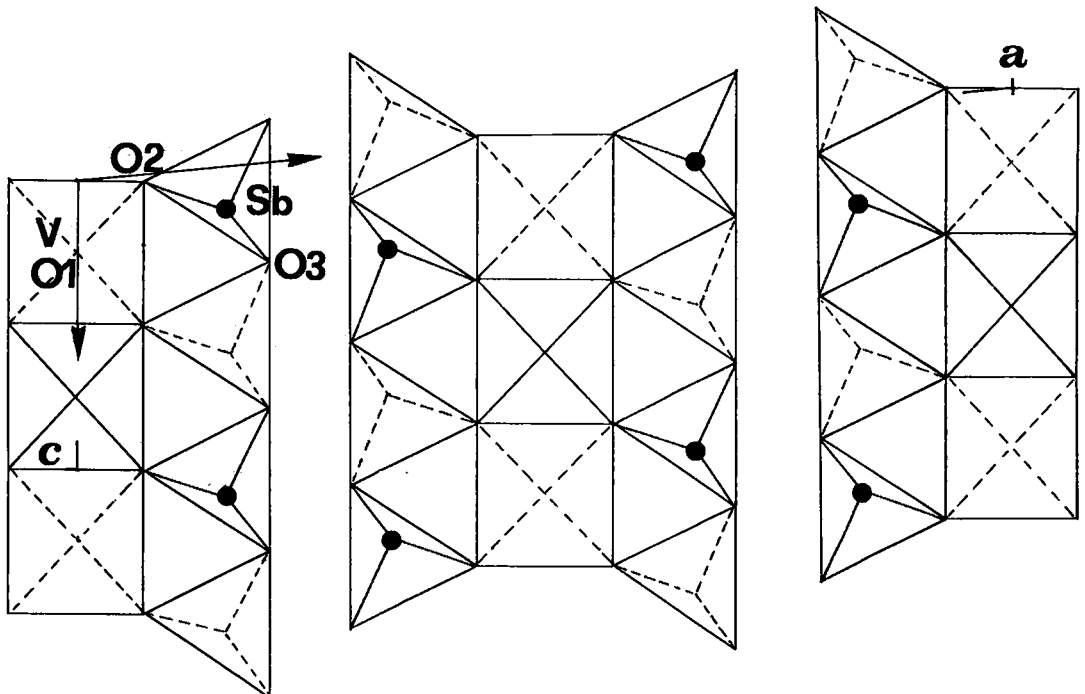


FIG. 1. The structure of monoclinic stibivanite as seen along [010]. Filled circles indicate the positions of Sb atoms in SbO_3 groups that point up. V and O1 are in the special position along the two-fold axis at $0, \frac{1}{4}, z$.

streak. The Mohs hardness is near 4. Parting parallel to c is very easy, and the crystals are easily split into fine, flexible fibers.

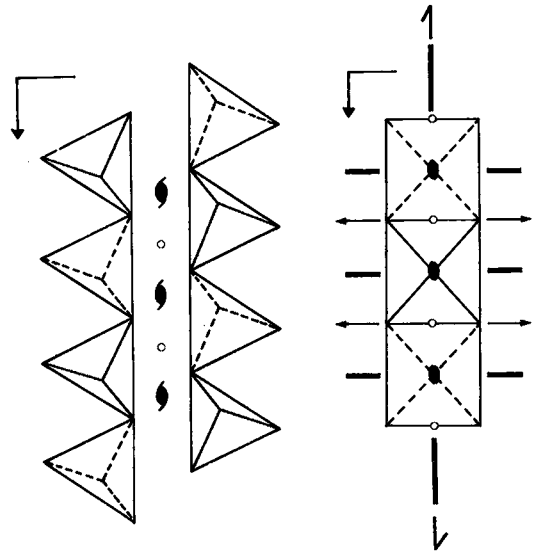
Optical data

Optically, the crystals are biaxial positive, pseudo-uniaxial, with $2V_{\text{obs}}$ very small. The indices of refraction are very high, $\bar{n} > 1.87$, and the optical orientation is: $X = a$, $Y = b$, $Z = c$. Pleochroism is fairly strong, with X and Y emerald-green and Z olive-green.

STIBIVANITE POLYTYPES AS MDO STRUCTURES

A reliable structure for the orthorhombic modification and a full understanding of its relationship with that of the monoclinic phase may be obtained on the basis of the OD theory (Dornberger-Schiff 1964, 1966). The structure of the monoclinic phase (Darriet *et al.* 1976, Szymański 1980) is represented in Figure 1; it may be conveniently described as consisting of two different kinds of layers, represented in Figure 2. One type is built up by chains of corner-sharing SbO_3 trigonal pyramids L_{2n} , and the other by chains of edge-sharing VO_5 tetragonal pyramids L_{2n+1} . The L_{2n} layers and the L_{2n+1} layers, henceforth denoted as SbO_3 and VO_5 layers, respectively, with reference to the kind of polyhedra that characterize them, have the same b and c translation periods, but present different symmetry, $P(1)2_1/c1$ and $P(2/m)2/c2_1/m$, respectively, where the parentheses in the symbols indicate, as usual in the OD theory, the direction of missing periodicity. We should remark that OD layers commonly do not correspond to crystal-chemically significant layers; the artificial nature of the OD layers in the present family is clearly indicated by the fact that O2 atoms at the border between adjoining SbO_3 and VO_5 layers belong half to both layers.

The fact that the symmetry of the VO_5 layer is higher than that of the SbO_3 layer points to the possibility of polytypic relationships. In the monoclinic form, SbO_3 layers L_{2n} and L_{2n+2} are related through the two-fold axes parallel to b and the inversion centers, which convert the VO_5 layer L_{2n+1} , lying between them, into itself. Thus the pair $(L_{2n}; L_{2n+1})$ is converted by these operations into the pair $(L_{2n+2}; L_{2n+1})$. However, because of the symmetry displayed by the VO_5 layers, a different arrangement also is possible. In this arrangement (Fig. 3), which we assume to correspond to the orthorhombic modification of stibivanite, the layers L_{2n} and L_{2n+2} are related through the mirror plane parallel to (100) and the screw axis parallel to c , which convert L_{2n+1} into itself. As in the preceding arrangement, the pair $(L_{2n}; L_{2n+1})$ is converted by these operations into the pair $(L_{2n+2}; L_{2n+1})$. Thus not only the layers but also the pairs of adjacent layers



$P(1)2_1/c1$

$P(2/m)2/c2_1/m$

FIG. 2. The two different kinds of layers in stibivanite, as seen along $[010]$, with c down and a , the direction of missing periodicity, across. For each layer, the kind and position of the symmetry elements are represented, and the corresponding layer-group symbol is indicated.

are the same in both cases; the structures have to be looked upon as belonging to one and the same family of OD structures, consisting of two different kinds of layers.

A closely similar case was described by Dornberger-Schiff & Klevtsova (1967); we followed their account closely and used nearly the same words in the preceding discussion.

An infinite number of ordered polytypes as well as of disordered structures is possible, corresponding to the various possible sequences of operators (two-fold axes and inversion centers or mirror plane and screw axis) that may be active in VO_5 layers. The symmetry relations common to all the polytypes of this family are embodied in the OD groupoid family symbol:

$P(1)2_1/c1$

$P(2/m)2/c2_1/m$
[$\frac{1}{4}$, $-0.0733 \dots$]

where the first line contains the layer-group symbols of the two constituting layers, and the second indicates the positional relations between adjacent layers (Grell & Dornberger-Schiff 1982). Among the infinite

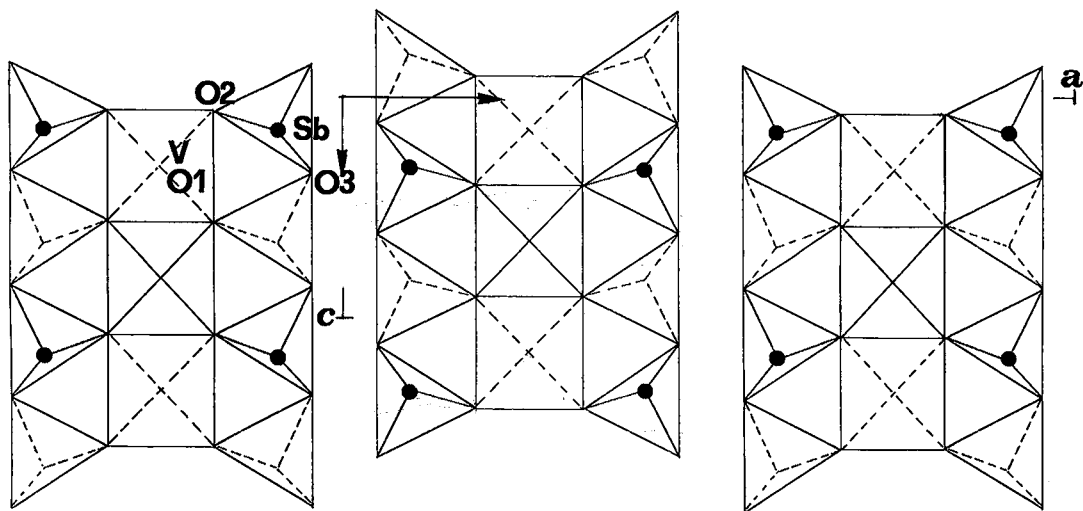


FIG. 3. Crystal structure of orthorhombic stibivanite as projected along [010]. Filled circles indicate the positions of Sb atoms in SbO_3 groups that point up. V and O1 atoms are nearly superimposed in projection.

possible ordered polytypes, OD theory pays special attention to those polytypes with maximum degree of order, the so-called MDO structures, namely those polytypes that contain the smallest possible number of different kinds of layer triples (Dornberger-Schiff 1982, Dornberger-Schiff & Grell 1982). In the present case, as there is only one way to attach VO_5 layers L_{2n+1} to SbO_3 layers L_{2n} , and two distinct ways to attach SbO_3 layers L_{2n} to VO_5 layers L_{2n+1} , one (L_{2n-1} ; L_{2n} ; L_{2n+1}) triple and two different (L_{2n} ; L_{2n+1} ; L_{2n+2}) triples are possible. Evidently the smallest number of different triples necessary to build a periodic polytype is two, from which it follows that only two MDO polytypes are possible in this family.

The two structures we have already described, the monoclinic one, which is obtained where two-fold axes parallel to b and inversion centers are active in the VO_5 layers, and the orthorhombic one, which occurs if the mirror plane parallel to (100) and screw axis parallel to c are active in the VO_5 layers, correspond to the two possible "MDO polytypes" in the family.

It seems useful to derive the space-group symmetry of both MDO structures. In the first MDO structure (Fig. 1) the asymmetric unit at x, y, z (I) is converted by a 2_1 operator in the SbO_3 layer into the asymmetric unit at $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$. (II); this last unit is converted by a 2 operator in the VO_5 layer into the asymmetric unit at $\frac{1}{2}+x, \frac{1}{2}+y, z$. (III). (I) and (III) are related by a $a/2 + b/2$ translation; moreover, the 2 operator in the VO_5 layer is a total symmetry-element, valid for the whole structure, and the c glide normal to b is a symmetry operator for both kinds of layer. Therefore, $C2/c$ is the space-group symmetry for the structure.

In the second MDO structure (Fig. 3) the asymmetric unit at x, y, z (I) is converted by a 2_1 operator in the SbO_3 layer into the asymmetric unit at $-x, \frac{1}{2}+y, \frac{1}{2}-z$. (II); this last unit is converted by a m operator in the VO_5 layer into the asymmetric unit at $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$. (III). Units (I) and (III) are related by a n glide normal to c at $z = \frac{1}{4}$; moreover, the mirror plane normal to a in the VO_5 layer is a total symmetry-element, valid for the whole structure, and the c glide normal to b is a symmetry operator for both kinds of layer. Therefore $Pm\bar{c}n$ is the space-group symmetry for the structure. As $Pm\bar{c}n$ is one of the two possible space-groups of the orthorhombic modification of stibivanite from Buca della Vena mine, the preceding result strongly supports the proposed structure.

STRUCTURE DETERMINATION AND DESCRIPTION

The model for the orthorhombic modification was tested by means of a structural study. The intensity data were collected from a crystal 0.750 mm long and 0.083×0.083 mm² in cross section, by means of an Ital Structures single-crystal four-circle diffractometer, using $\omega-2\theta$ scan, scan width 1.00°.

The crystal was previously examined with Weissenberg photographs: only sharp reflections corresponding to the orthorhombic phase were observed. A total of 530 unique reflections among the measured ones (2θ max = 60°) were considered observed, having $I > 3\sigma(I)$, and were used in the least-squares calculations after reduction for Lorentz and polarization factors.

The starting coordinates were obtained, through appropriate transformations, from those reported by

TABLE 1. FINAL ATOMIC POSITIONAL AND THERMAL PARAMETERS

Atom	x	y	z	B _{eq}
Sb	-0.08889 (3)	0.46995 (10)	0.17640 (9)	0.86
V	-1/4	0.12246 (41)	0.32504 (38)	0.91
O1	-1/4	-0.21343 (187)	0.34081 (182)	1.89
O2	-0.17787 (26)	0.24051 (112)	0.07425 (102)	0.83
O3	-0.04311 (30)	0.16118 (122)	0.36597 (97)	1.13

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
Sb	113 (3)	107 (3)	107 (3)	-7 (2)	-3 (2)	8 (2)
V	107 (8)	151 (9)	86 (8)	4 (7)	0	0
O1	309 (47)	165 (42)	245 (47)	51 (39)	0	0
O2	75 (21)	142 (23)	98 (24)	-8 (19)	14 (21)	-19 (23)
O3	131 (26)	209 (27)	91 (27)	19 (20)	35 (23)	19 (22)

The anisotropic temperature factors ($\times 10^4$) are in the form:

$$\exp\{-2\pi^2(U_{11}h^2a^*2+U_{22}k^2b^*2+U_{33}l^2c^*2+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*)\}$$

The equivalent temperature factors, B_{eq}, in Å², were calculated according to Hamilton (1959). Standard deviations in parentheses.

Szymański (1980) for the synthetic monoclinic modification and were refined in the space group *Pmncn*, by means of the SHELX76 least-squares program (Sheldrick 1976). Isotropic refinement converged to an *R* of 0.045. An empirical correction for the absorption factor was then carried out using the DIFABS program of Walker & Stuart (1983). After the absorption correction, the reliability index *R* dropped to 0.037. Final refinement cycles with anisotropic thermal parameters for all the atoms converged to an *R* of 0.032 (weighted *R* = 0.042, $w = 1/(\sigma^2(F_o) + 0.00081|F_o|^2)$).

The final refined positional and thermal parameters, with their standard deviations, are given in Table 1. A list of observed and calculated structure-factors is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

The structural study fully confirms the proposed model, represented in Figure 3, seen along [010]. Therefore, on the basis of the considerations developed in the preceding chapter and following the indications of the "Procedures involving the IMA Commission on New Minerals and Mineral Names and guidelines on mineral nomenclature" (Nickel & Mandarino 1987), we propose the name stibivanite-2*O* for the orthorhombic modification, which contains two layers of either type in the unit cell. The monoclinic modification should be renamed stibivanite-2*M*, as it contains two layers of either type in the monoclinic unit-cell.

Both stibivanite-2*M* and stibivanite-2*O* are characterized by the presence of complex ribbons very weakly linked in the *a* and *b* directions, which explains the acicular shape and the easy cleavage of the crystals. In the complex ribbons, chains of corner-sharing SbO₃ pyramids are attached to both sides of chains of edge-sharing VO₅ pyramids; the

TABLE 2. BOND LENGTHS AND ANGLES IN Sb AND V POLYHEDRA

Sb - O3	1.988 (8)	O2 - Sb - O3 ⁱ	85.1 (2)
Sb - O3	1.998 (8)	O3 - Sb - O3 ⁱ	92.7 (2)
Sb - O2	2.018 (8)	O2 - Sb - O3	93.9 (2)
V - O1	1.611 (9)	O1 - V - O2 ⁱⁱ	108.9 (3) (x2)
V - O2 ⁱⁱⁱ	1.975 (5) (x2)	O1 - V - O2 ⁱⁱⁱ	108.9 (3) (x2)
V - O2 ⁱⁱⁱ	1.998 (5) (x2)	O2 - V - O2 ^{iv}	87.9 (2) (x2)
		O2 ⁱⁱⁱ - V - O2 ^v	81.8 (2)
		O2 - V - O2 ^v	80.7 (2)
		O2 - V - O2 ^v	144.2 (2) (x2)

The distances and angles are given in Angstroms and degrees respectively. The standard deviations are given in parentheses.

former chains are related through inversion centers in stibivanite-2*M* (Fig. 1) and through a mirror plane (100) in stibivanite-2*O* (Fig. 3).

Bond lengths and bond angles in SbO₃ and VO₅ pyramids are reported in Table 2, whereas a detailed comparison of corresponding distances and bond-valence sums between stibivanite-2*O* and stibivanite-2*M* is given in Table 3, kindly provided by J.T. Szymański (pers. comm., 1988). Note that in Table 2, as in the following text, the atoms of the different units are related to the symmetry-equivalent atoms of the fundamental unit as follows:

<i>i</i> atoms at	<i>x</i> , 1/2- <i>y</i> , -1/2+ <i>z</i>
<i>ii</i> atoms at	- <i>x</i> , 1/2+ <i>y</i> , 1/2- <i>z</i>
<i>iii</i> atoms at	<i>x</i> , 1/2- <i>y</i> , 1/2+ <i>z</i>
<i>iv</i> atoms at	-1/2- <i>x</i> , <i>y</i> , + <i>z</i>
<i>v</i> atoms at	-1/2- <i>x</i> , 1/2- <i>y</i> , 1/2+ <i>z</i>

Antimony is strongly linked to three oxygen atoms: O3 at 1.988 Å, O3ⁱ 1.998 Å and O2 at 2.016 Å (1.963 Å, 2.009, 2.014 Å in Stibivanite-2*M*), with two more distant atoms of oxygen, O3ⁱⁱ and O2ⁱⁱⁱ, at 2.547 Å and 2.892 Å, respectively (2.561 Å, 2.900 Å in stibivanite-2*M*). Vanadium in square pyramidal coordination has the apical oxygen atom at 1.611 Å (1.583 Å in stibivanite-2*M*), with four basal oxy-

TABLE 3. BOND-VALENCE ANALYSIS OF MONOCLINIC AND ORTHORHOMBIC STIBIVANITE (M-O dist. to 3.8 Å)

MONOCLINIC STIBIVANITE-2M			ORTHORHOMBIC STIBIVANITE-2O		
Coordination of Sb ^{III} , $R_1 = 1.910$ Å, $N = 4.5$					
Bonds:					
	d	s		d	s
O1	3.370	.0777	O1	3.384	.0762
O1	3.667	.0531	O1	3.621	.0562
O2	2.014	.7877	O2	2.016	.7842
O2	2.900	.1527	O2	2.892	.1546
O3	1.963	.8841	O3	1.988	.8352
O3	2.009	.7946	O3	1.998	.8165
O3	2.561	.2672	O3	2.547	.2739
O3	3.572	.0598	O3	3.567	.0601
	SUM =	3.075		SUM =	3.057
Coordination of V ^{IV} , $R_1 = 1.770$ Å, $N = 5.2$					
Bonds:					
	d	s		d	s
O1	1.583	1.7871	O1	1.611	1.6314
O1	3.209	.0453	O1	3.182	.0474
O1	3.388	.0342	O1	3.310	.0386
O1	3.388	.0342	O1	3.451	.0311
O2	1.970	.5731	O2	1.975	.5656
O2	1.970	.5731	O2	1.975	.5656
O2	1.990	.5438	O2	1.996	.5353
O2	1.990	.5438	O2	1.996	.5353
O3	3.707	.0214	O3	3.718	.0211
O3	3.707	.0214	O3	3.718	.0211
	SUM =	4.177		SUM =	3.993
O1	d	s	d	s	
Sb	3.370	.0777	Sb	3.384	.0762
Sb	3.370	.0777	Sb	3.384	.0762
Sb	3.667	.0531	Sb	3.621	.0562
Sb	3.667	.0531	Sb	3.621	.0562
V	1.583	1.7871	V	1.611	1.6314
V	3.209	.0453	V	3.182	.0474
V	3.388	.0342	V	3.310	.0386
V	3.388	.0342	V	3.451	.0311
	SUM =	2.162		SUM =	2.014
O2	d	s	d	s	
Sb	2.014	.7877	Sb	2.016	.7842
Sb	2.900	.1527	Sb	2.892	.1546
V	1.970	.5731	V	1.975	.5656
V	1.990	.5438	V	1.996	.5353
	SUM =	2.057		SUM =	2.040
O3	d	s	d	s	
Sb	1.963	.8841	Sb	1.988	.8352
Sb	2.009	.7946	Sb	1.988	.8165
Sb	2.560	.2677	Sb	2.547	.2739
Sb	3.572	.0598	Sb	3.567	.0601
V	3.707	.0214	V	3.718	.0211
	SUM =	2.030		SUM =	1.973

Bond-valence sums calculated according to Brown & Wu (1976).

gen atoms, two at 1.975 Å and two at 1.996 Å (1.970 and 1.990 Å in stibivanite-2M).

The difference in the V-O1 bond length is responsible for the large discrepancies in bond-valence sums for ^{IV}V and O1 atoms in the two compounds (Table 3). Other significant differences between corresponding distances in stibivanite-2M and stibivanite-2O are shown in Table 3, mainly for distances involving the atom O1. Those differences are understandable if we consider that whereas the SbO₃ layer presents in both compounds its ideal symmetry $P(1)2_1/c1$ (Fig. 2), the actual symmetry of the VO₅ layer is lower than the ideal one $P(2/m)2/c2_1/m$ (Fig. 2) and different in stibivanite-2M, $P(1)2_1/c1$, and in stibivanite-2O, $P(m)c2_1$.

X-RAY POWDER PATTERN

Because of the small size of the crystals and the extreme paucity of the material, the powder pattern of stibivanite-2O was collected with a Gandolfi camera of 114.6 mm diameter, using FeK α radiation. The pattern, reported in Table 4 together with that of stibivanite-2M, was obtained from the same crystal previously used in the structure analysis and was indexed taking into account the intensity data collected for the structure analysis.

Stibivanite-2M and stibivanite-2O are easily and unambiguously distinguished with single-crystal X-ray methods. Although their powder patterns are very similar, some differences can be pointed out. As indicated in Table 4, the strong reflections 311 and 600 overlap in the pattern of the monoclinic phase ($d = 2.996$ Å), whereas they appear as a doublet, with $d = 3.097$ and $d = 2.986$ Å, respectively, in stibivanite-2O. Other minor but significant differences may be observed in positions or intensities of some reflections.

Another Gandolfi pattern had been previously obtained from a crystal not tested with Weissenberg photographs and subsequently lost. That pattern closely matched with the one given in Table 4 but presented one additional reflection with $d = 3.133$ Å, not referable to stibivanite-2O and corresponding to the strong reflection $\bar{3}11$ of stibivanite-2M. This finding points to the possible existence, in that crystal, of domains of stibivanite-2M coexisting with stibivanite-2O, and indicates that electron diffraction and HRTEM studies should be useful to disclose possible stacking disorder and more complex polytypes.

ACKNOWLEDGEMENTS

We are indebted to the referees S. Đurovič and E. Makovicky, and the associate editor J.T. Szymański, for the accuracy in reviewing the manuscript and for the useful suggestions and indications. We thank the collectors M. Baldi and C. Del Tredici, who very kindly gave us the unique sample of orthorhombic stibivanite from Buca della Vena mine, and Dr. M. Pasero for his generous help in data collection and structure refinement. The financial support of Ministero della Pubblica Istruzione (M.P.I. 60% to S. Merlini) also is acknowledged; all the calculations were executed at C.N.U.C.E. (C.N.R.), Pisa.

REFERENCES

- BENVENUTI, M., LATTANZI, P., TANELLI, G. & CORTECCI, G. (1986): The Ba-Fe-pyrite deposit of Buca della Vena, Apuan Alps, Italy. *Rend. Soc. Ital. Mineral. Petrol.* **41**(2), 347-358.

TABLE 4. X-RAY POWDER PATTERN OF STIBIVANITE-2M COMPARED WITH THAT OF STIBIVANITE-2H

stibivanite-2M			stibivanite-2O			
I	hkl	d _{meas}	d _{meas}	d _{calc}	hkl	I
2	200	9.01	9.00	8.958	200	m
6	110	4.848	4.82	4.828	110	m
1/2	400	4.436	4.49	4.479	400	w
1/2	310	3.730				
1/2	111	3.579	3.630	3.615	011	w
7	111	3.502	3.558	3.543	111	vw
7	311	3.173				
10	311, 600	2.996	3.097	3.092	311	s
1/2	510	2.975	2.986	2.986	600	ms
1/2	002	2.738				
1/2	202	2.682				
1	511	2.618				
1/2	202	2.558				
1/2	511	2.474	2.508	2.501	302	w
1/2	402	2.436				
2	020	2.394	2.394	2.395	020	w
2	220	2.314	2.307	2.314; 2.302	220; 611	w
1/2	221	2.151				
4	502, 420	2.114	2.113	2.112	420	vw
1/2	512	2.059				
3	711	2.031	2.091	2.089	711	w
1	421	1.942	1.975	1.972	421	vw
4	520	1.870	1.871	1.868	620	m
1/2	802	1.818				
4	10.00, 222, 511	1.787				
1/2	222	1.781				
			1.747	1.743	911	mw
			1.732	1.730	322	w
3	113	1.714				
3	911	1.701				
1/2	113	1.687				
1	802	1.661				
1	422	1.639				
			1.616	1.613	902	w
1	521, 513	1.594				
1/2	10.02	1.587				
1	330	1.545				
1/2	131	1.525	1.531	1.528	131	vw
3	331, 12.00, 513	1.494	1.492	1.493	12.00	w

Relative intensities are indicated as follows: s strong, ms medium-strong, m medium, mw medium-weak, w weak, vw very weak.

BROWN, I.D. & WU, K.K. (1976): Empirical parameters for calculating cation-oxygen bond valences. *Acta Crystallogr.* **B32**, 1957-1959.

CARMIGNANI, L., DESSAU, G. & DUCHI, G. (1976): I giacimenti a barite ed ossidi di ferro delle Alpi Apuane, studio minerogenetico e strutturale. Nuove osservazioni sui giacimenti polimetallici. *Boll. Soc. Geol. Ital.* **95**, 1009-1061.

DARRIET, B., BOVIN, J.O. & GALY, J. (1976): Un nouveau composé de l'antimoine III: VOSb₂O₄. Influence stéréochimique de la paire non liée E, relations structurales, mécanismes de la réaction chimique. *J. Solid State Chem.* **19**, 205-212.

DORNBERGER-SCHIFF, K. (1964): Grundzüge einer Theorie der OD Strukturen aus Schichten. *Abh. Dtsch. Akad. Wiss. Berlin, Kl. Chem. Geol. Biol.* **3**.

_____ (1966): *Lehrgang über OD Strukturen*. Akademie-Verlag, Berlin.

_____ (1982): Geometrical properties of MDO polytypes and procedures for their derivation. I. General concept and applications to polytype families consisting of OD layers all of the same kind. *Acta Crystallogr.* **A38**, 483-491.

_____ & GRELL, H. (1982): Geometrical properties of MDO polytypes and procedures for their derivation. II. OD families containing OD layers of M > 1 kinds and their MDO polytypes. *Acta Crystallogr.* **A38**, 491-498.

_____ & KLEVTSOVA, R.F. (1967): On the relation between the monoclinic and the orthorhombic form of yttrium hydroxychloride, [YCl(OH)₂]_n. *Acta Crystallogr.* **22**, 435-436.

GRELL, H. & DORNBERGER-SCHIFF, K. (1982): Symbols of OD groupoid families referring to OD structures (polytypes) consisting of more than one kind of layer. *Acta Crystallogr.* **A38**, 49-54.

HAMILTON, W.C. (1959): On the isotropic temperature factor equivalent to a given anisotropic temperature factor. *Acta Crystallogr.* **12**, 609-610.

KAIMAN, S., HARRIS, D.C. & DUTRIZAC, J.E. (1980): Stibivanite, a new mineral from the Lake George antimony deposit, New Brunswick. *Can. Mineral.* **18**, 329-332.

MELLINI, M., MERLINO, S. & ORLANDI, P. (1979): Versiliaite and apuanite, two new minerals from the Apuan Alps, Italy. *Am. Mineral.* **64**, 1230-1234.

- MERLINO, S. & ORLANDI, P. (1983): A second occurrence of stibivanite: Buca della Vena mine (Apuan Alps), Italy. *Can. Mineral.* **21**, 159-160.
- NICKEL, E.H. & MANDARINO, J. A. (1987): Procedures involving the IMA Commission on New Minerals and Minerals Names, and guidelines on mineral nomenclature. *Can. Mineral.* **25**, 353-377.
- ORLANDI, P. & CHECCHI, F. (1986): The Buca della Vena mine, Tuscany, Italy. *Mineral. Rec.* **17**, 261-268.
- SHELDRIK, G.M. (1976): *SHELX76. Program for Crystal Structure determination.* Univ. of Cambridge, Cambridge, England.
- SZYMANSKI, J.T. (1980): A redetermination of the structure of Sb_2VO_5 , stibivanite, a new mineral. *Can. Mineral.* **18**, 333-337.
- WALKER, N. & STUART, D. (1983): An empirical method for correcting diffractometer data for absorption effects. *Acta Crystallogr.* **A39**, 158-166.

Received November 28, 1988, revised manuscript accepted May 24, 1989.