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INVESTIGATION OF THE CRYSTAL STRUCTURE OF THE ANTIMONY AND BISMUTH HIGH PRESSURE PHASES

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On the basis of the similarity of the behavior of IV-VI compounds and of elements of group V at high and normal pressures it is suggested that the SbIII and BiIII high-pressure states crystallize in a monoclinally distorted SnS structure. At p equal to 130–160 kbar, the SbIII unit-cell parameters are $a = 5.56$ Å, $b = 4.04$ Å, $c = 4.22$ Å, $\beta = 86°$, $Z = 4$, and $V = 93.8$ Å^3. At p = 35.5 kbar the parameters of the BiIII monoclinic cell are $a = 6.65$ Å, $b = 4.20$ Å, $c = 4.65$ Å, $Z = 4$, $\beta = 85°20'$, and $V = 117.8$ Å^3. Two symmetrical independent Sb_1 and Sb_2 atoms are in the m planes of the C_{2h}^2–$P2_1/m$ space group. The SbIII (BiIII) structure is assumed to be lamellar. The layers consist of two covalently-bound slightly corrugated planes. The interatomic distances correspond to a coordination number equal to seven.

AT high pressure and at room temperature, two reversible first-order polymorphic transitions were observed in Sb[1-3]: whereas the first transition to the primative cubic structure occurs as 73–85 kbar with a very small jump in volume, the second transition, SbII → SbIII at $p \approx 88$ kbar, is accompanied by a volume jump $\Delta V/V_0 = 3.4\%$[4], and by a rather sharp decrease of the electric conductivity[5].

The present paper is devoted to a detailed investigation of the crystal structure of SbIII: the assumption that the atoms of this phase have a hexagonal close packed arrangement[1] turned out to be valid only in first approximation.

1. CHOICE OF THE MODEL OF THE SbIII STRUCTURE

We examined approximately 20 x-ray patterns of SbIII, obtained at pressures 100–160 kbar, of which six were taken with filtered molybdenum radiation. In choosing the model of the SbIII structure, we attempted to use the analogy principle, taking into account the similarity between the physical properties and the structure of the group V elements with compounds of the IV-VI type. It is known that under normal conditions the IV-VI compounds crystallize in one of three structure types: As type (GeTe and the GeTe-SnTe alloys, containing less than 65 mol.% SnTe), NaCl type (PbS, PbSe, PbTe, SnTe, and the GeTe-SnTe alloys, containing more than 65 mol.% SnTe), and SnS type (GeS, GeSe, SnS, and SnSe). Polymorphic transitions from one structure type to the other can be traced under high-pressure conditions. With increasing pressure, the following sequence is observed: As type → NaCl type → SnS type[6].

The first transition (As type → NaCl type) in IV-VI compounds is equivalent to the transition of the type As → primitive cube in group V elements, as observed in Sb[1-3] and in black phosphorus[7]. Continuing analogously, we can expect the transition in Sb from the primitive-cube structure to the next modification to correspond to a polymorphic transformation in IV-VI compounds from the NaCl type into the SnS type, and consequently the structure of SbIII is similar to the rhombic structure of the SnS type. The sequence of transitions in Bi exhibit some deviations from this scheme, and these will be discussed later.

2. CHOICE OF UNIT CELL OF SbIII

In comparing the x-ray patterns of SnS (p = 1 bar) and SbIII (p = 130–160 kbar), the schemes of which are shown in Fig. 1, we can note that there is a definite connection between the two diffraction patterns. This connection can be easily traced in the region of forward reflection angles, namely, each SnS reflection corresponds in the SbIII picture to one or sometimes two lines with close values of the Bragg angle ϑ. For example, each of the SnS reflections, namely (011), (400), and (410) corresponds to one SbIII line, and the very weak reflection (211) corresponds to a doublet of two strongest lines. The splitting is masked in many other cases by the superposition of several reflections. Together with the geometrical "similarity" of the diffraction patterns, the relative intensities of the "similar" reflections on the x-ray patterns of SnS and SbIII differ noticeably, namely, strong lines correspond to weak ones and vice versa.

If it is assumed that the doublets on the x-ray pattern of SbIII appear as a result of monoclinic distortion of the structure, then, by assigning to the lines 2, 3, 4, and 5 (Fig. 1b) the indices (200), (111), (111), and (210) we obtain the parameters and volume of the monoclinic cell of SbIII, which, as expected, are directly connected with the parameters of the rhombic cell of SnS: $a_{mon} = 5.56$ Å $\approx (1/2)a_{rh}$; $b_{mon} = 4.04$ Å $\approx b_{rh}$; $c_{mon} = 4.22$ Å $\approx c_{rh}$; $\beta = 86°$; $Z = 4$, $V_{mon} = 93.8$ Å$^3 \approx (1/2)V_{rh}$. In the case of SnS we have $a = 11.18$ Å, $b = 3.98$ Å, $c = 4.33$ Å and $Z = 4$. The parameters of the SbIII cell, calculated for different pressures in the interval 130–160 kbar, differ from each other on the average by 0.04 Å.

On the basis of the monoclinic cell obtained in this manner, we indexed all the reflections on the x-ray patterns of the SbIII phase. A comparison of the cal-

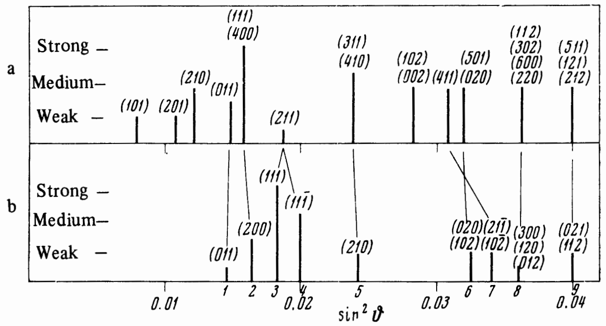

FIG. 1. X-ray patterns of SnS(a) and SbIII(b).

Table I. Interplanar distances and structure factors of the high-pressure phase SbIII at p ≈ 140 kbar. Space group C_{2h}^2 (a = 5.56 Å, b = 4.04 Å, c = 4.22 Å, β = 86°, Z = 4).

hkl	d/n, Å		pF², %		hkl	d/n, Å		pF², %	
	Calculated	Measured	Calculated	Measured		Calculated	Measured	Calculated	Measured
100	5.55	—	4	—	112	1.79	1.78	0.2	20
001	4.18	—	0.2	—	121	1.74	1.72	2	40
101	3.46	—	1	—	301	1.74		15	
110	3.27	—	0.5	—	$11\bar{2}$	1.73		15	
$10\bar{1}$	3.23	—	3	—	202	1.73		22	
011	2.91	2.97	41	3	$12\bar{1}$	1.71		4	
200	2.77	2.77	35	17	310	1.68	—	17	—
111	2.63	2.63	100	100	$30\bar{1}$	1.65	—	1	—
$11\bar{1}$	2.52	2.52	43	41	220	1.63	1.61	45	16
201	2.39	2.41	0.1	8	$20\bar{2}$	1.62		0.4	
210	2.29	2.29	18	14	311	1.60		45	
$20\bar{1}$	2.24	—	13	—	212	1.59	—	4	—
002	2.09	—	6	—	221	1.54	1.53	0.1	20
211	2.06	—	0.7	—	$31\bar{1}$	1.53		1.5	
020	2.02	1.98	47	16	$22\bar{1}$	1.50		17	
102	2.00		30		$21\bar{2}$	1.50	—	0.4	—
$21\bar{1}$	1.96	1.94	50	15	022	1.45	—	9	—
$10\bar{2}$	1.91		36		302	1.44	—	4	—
120	1.90	1.87	5	<7	122	1.42	—	42	—
012	1.86		0.4		003	1.39	1.38	2	57
300	1.85		11		$12\bar{2}$	1.39		50	
021	1.82	1.82	0.2	<7	400	1.39		2	
					103	1.37		0	

Note. The discrepancies in the table between $_pF^2_{calc}$ and $_pF^2_{meas}$ are due to the following causes: 1) for the reflection (011)—apparently to the distortion of the intensities under quasihydrostatic conditions; a similar relation for this reflection was noted also in many IV-VI compounds in the NaCl type → SnS type transition [16]; 2) for the reflections (020) and (102), (21$\bar{1}$) and (10$\bar{2}$), (220) and (311)—to a partial superposition of reflections that are quite far from each other, in which connection the measured intensity is in fact equal not to the sum of the intensities but to the intensity of one reflection; 3) for the reflection (201)—to a superposition of the rather strong line of boron, which was used in the structure of the high pressure chamber.

Table II. Coordinates of atoms and distance between atoms in the structure of SbIII

x_1	z_1	x_2	z_2	R, %	Distances between atoms, Å				
					I—VI	I—II, I—III	I—IV, I—V	I—IX, I—X	I—XI
—0.25	0.06	0.34	0.40	16	2.61	2.87	3.06	2.86	3.67
—0.25	0.08	0.33	0.39	15	2.60	2.89	3.02	2.96	3.56
—0.25	0.08	0.34	0.40	14	2.57	2.93	3.0	2.86	3.63
—0.26	0.08	0.34	0.41	12	2.54	2.95	2.96	2.83	3.70
—0.26	0.08	0.34	0.40	10	2.52	2.92	2.99	2.86	3.68
—0.23	0.12	0.30	0.48	55	2.93	3.28	2.64	3.06	3.41

culated and measured values of the interplanar distances for one of the x-ray patterns is given in Table I. Linear extrapolation of Bridgman's data[4] on the compressibility of Sb up to 100 kbar to the pressure 130 kbar yields for the unit-cell volume ratio $V_p/V_0 = 0.766$. Recognizing that one atom in SbI (As type) occupies a volume $V_0 = 30.195$ Å³/atom, we obtain for the SbIII cell, which contains four atoms, the value $V_p = 92.5$ Å³, which agrees within the limits of experimental error with the x-ray-diffraction data for a monoclinic cell.

3. CHOICE OF SPACE GROUP AND DETERMINATION OF THE PATTERN OF ARRANGEMENT OF THE ATOMS IN THE SbIII STRUCTURE

To construct the pattern of the arrangement of the atoms in the monoclinic cell of SbIII, let us examine the structure of SnS, in which the tin and sulfur atoms are in the symmetry planes m, occupying in the space group D_{2h}^{16}—Pnma the position 4 (c): $x, \frac{1}{4}, z$; $\frac{1}{2} - x, \frac{3}{4}, \frac{1}{2} + z$; $\bar{x}, \frac{3}{4}, \bar{z}$; $\frac{1}{2} + x, \frac{1}{4}, \frac{1}{2} - z$. The coordinates

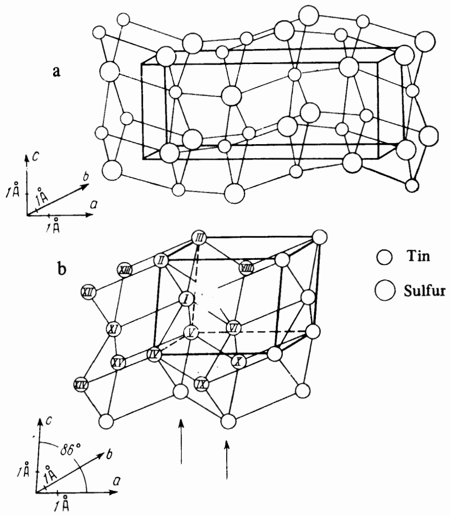

FIG. 2. Structures of the SnS type (a) and of the SbIII type (b); the arrows indicate the atomic planes belonging to one layer.

Table III. Angles between the links for R ≈ 15%

Angle	Degrees	Angle	Degrees
IV—I—V	89	VII—I—II (VII—I—III)	51.5
II—I—III	83.7	VII—I—IV (VII—I—V)	82.3
III—I—V (II—I—IV)	91	VII—I—VI	65.4
VI—I—IV (VI—I—V)	80		

of the atoms are $x_{Sn} = 0.885$, $z_{Sn} = 0.115$, $x_S = 0.150$, and $z_S = 0.478$[8].

Following the analogy, we assume that the antimony atoms are in the symmetry planes m. Since the sought monoclinic structure has a primitive unit cell (see Fig. 1), we can consider only two possible space groups, C_{2h}^1—P2/m and C_{2h}^2—P2₁/m. Both groups make it possible to place four atoms in two symmetrically independent double positions on the m planes, but only in the second group (C_{2h}^2—P2₁/m) is it possible to obtain an arrangement of atoms similar to the arrangement in SnS, owing to the identical mutual placement of the planes and symmetry centers in the groups C_{2h}^2 and D_{2h}^6. To this end it is necessary to place the two symmetrically independent atoms Sb_1 and Sb_2 in the position 2(e): $x, \frac{1}{4}, z; \bar{x}, \frac{3}{4}, \bar{z}$ with coordinates $x_1 \approx 2x_{Sn}$, $z_1 \approx z_{Sn}$, $x_2 \approx 2x_S$, and $z_2 \approx z_S$. The doubling of the coordinate x is obtained from the relation between the cell parameters of SbIII and SnS.

The proposed model of the SbIII structure was verified and refined with the aid of an analysis of the observed intensities I(hkl), which were estimated by visual comparison of the lines on the x-ray diffraction pattern of SbIII with the corresponding density markers. The degree of deviation of the chosen model of SbIII from the experimental results was estimated by means of the reliability factor

$$R=\Big\{\sum_{hkl}|F^2_{\text{meas}}(hkl)-F^2_{\text{calc}}(hkl)|\Big\}\Big/\sum_{hkl}F^2_{\text{meas}}(hkl),$$

where $F^2_{\text{calc}}(hkl)$ is the structure factor calculated for different positions of the atoms Sb_1 and Sb_2 in the space group C_{2h}^2[9], $F^2_{\text{meas}}(hkl)$ is the structure factor obtained from the observed intensities, and hkl are the reflection indices. In the calculation of R we took only seven reflections, for which there were practically no superpositions.

Table II shows several variants of the arrangement of the atoms in the proposed structure of SbIII, for which R ≤ 16%. It also gives the results of a calculation (R = 55%) performed for the case when the coordinates of the antimony atoms coincide exactly with the coordinates of the atoms in SnS.

Taking into account the very small amount of data used for the calculation, and also the possibility of distortion of the observed intensities I(hkl) under conditions of quasihydrostatic pressure, we cannot be definitely assured that the true position of the atoms in the structure of SbIII corresponds to the minimal R. Therefore, in compiling Table II, we took into account also the fact that the distance between the atoms Sb–Sb cannot be much smaller than 2.6 Å (2.62 Å[10] is the diameter of the Sb atom in compounds with double bonding).

Figure 2 shows the proposed structure of SbIII (R = 15%, Table II—distance between atoms, Table III—angles between bonds, Table IV—relative coordinates of the atoms), in which, as shown by an analysis of the interatomic distances, each atom has seven nearest neighbors at distances 2.90 (two), 3.0 (two), 2.96 (two) and 2.61 (one) Å. These data indicate that the structure is layered, and in each of its unit cells there is one layer consisting of two covalently-bonded slightly corrugated planes. Naturally the distances between atoms belonging to neighboring layers (3.60 (one), 4.20 (two), and 5.50 (two) Å) greatly exceed the interatomic distances in one layer (2.6–3.0) Å). If the atoms in the

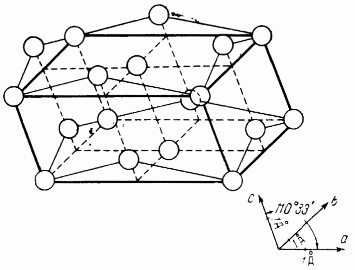

FIG. 3. Structure of BiII.

Table IV. Coordinates of atoms

Number of atom	Relative coordinates	Number of atom	Relative coordinates	Number of atom	Relative coordinates
I	$x_2, {}^1/_4, z_2$	VI	$1+x_1, {}^1/_4, z_1$	XI	$x_1, {}^1/_4, z_1$
II	$\bar{x}_1, {}^3/_4, 1-z_1$	VII	$1-x_2, {}^3/_4, 1-z_2$	XII	$\bar{x}_2, {}^3/_4, 1-z_2$
III	$\bar{x}_1, \overline{{}^1/_4}, 1-z_1$	VIII	$1-x_2, \overline{{}^1/_4}, 1-z_2$	XIII	$\bar{x}_2, \overline{{}^1/_4}, 1-z_2$
IV	$\bar{x}_1, {}^3/_4, \bar{z}_1$	IX	$1-x_2, {}^3/_4, \bar{z}_2$	XIV	$\bar{x}_2, {}^3/_4, \bar{z}_2$
V	$\bar{x}_1, \overline{{}^1/_4}, \bar{z}_1$	X	$1-x_2, \overline{{}^1/_4}, z_2$	XV	$\bar{x}_2, \overline{{}^1/_4}, \bar{z}_2$

structures of SbIII and SnS were to occupy exactly identical positions, then, as follows from Table II, the distances between the atoms in the corrugated plane of SbIII would be 2.64 Å (two) and 3.28 Å (two), and the distances between atoms belonging to neighboring planes would be 2.93 Å (one) and 3.06 (one)1). In this case the structure of the investigated antimony phase would consist of individual chains located parallel at distances 4.22, 2.93, and 3.06 Å from each other. Such a structure cannot be regarded as layered, and should therefore differ appreciably in its physical properties from the rhombic structure of SnS, in which the individual chains are firmly bonded with each other by covalent interactions, forming layers; the interatomic distances in SnS in the corrugated plane are 2.68 Å (two) and 3.37 Å (two), and the distances between neighboring planes are 2.62 A (one) and 3.47 A (one).

Thus, the displacements of the atoms in SbIII from the initial position of SnS, observed with the aid of the analysis of the intensities ($R \approx 15\%$, Table II) can be physically explained and give reasons for hoping that the structure of SbIII shown in Fig. 2 is the correct one. It can be easily seen (Fig. 2) that in this structure the atoms are arranged in a strongly distorted two-layer hexagonal packing scheme (the corrugated plane is a distorted densest layer).

4. POLYMORPHISM OF Bi UNDER PRESSURE

On the basis of a comparison of the diffraction patterns of SbIII and BiIII, it was proposed[11] that both modifications have identical crystal structures; this agrees also with our observations. We obtained x-ray patterns of BiIII, on which one can see quite clearly only the forward reflections (200), (111), (11$\bar{1}$), and (201); they give for the monoclinic cell the parameters a = 6.05 Å, b = 4.20 Å; c = 4.65 Å, β = 85°20′, Z = 4, and V = 117.8 Å^3. Since one atom at p = 1 bar in BiI (type As) occupies a volume V_0 = 35.382 A^3/atom, we get V_p/V_0 = 0.832, which corresponds in accordance with Bridgman's data[4] to p = 35.5 kbar.

Thus, antimony and bismuth, which crystallize under ordinary conditions in a structure of the As type, have at high pressures apparently at least one phase each (SbIII and BiIII) with identical crystal structure.

It is known also that polymorphic transformations from SbI into SbIII and from BiI into BiIII proceed via intermediate modifications SbII and BiII, with different crystal structures: SbII—primitive cubic, and BiII—monoclinic[12] with the following unit cell parameters: a = 6.674 Å, b = 6.117 Å, c = 3.304 Å, β = 110°33′, four atoms of bismuth occupy in the space group C_{2h}^3 the position 4(i): x, 0, z; $\bar{x}$, 0, $\bar{z}$; $\frac{1}{2}$ + x, $\frac{1}{2}$, z; $\frac{1}{2}$ − x, $\frac{1}{2}$, $\bar{z}$; the coordinates of the atoms2) are x = $\frac{1}{4}$ and z = $\frac{1}{8}$.

To establish the connection between the structure of BiII and the primitive-cubic structure, it is necessary to represent the latter as the result of a superposition of two identical "tetragonal" structures shifted relative to each other by a/2. The unit cell of each contains two atoms in the positions 000, and $\frac{1}{2}\frac{1}{2}0$, and is connected with the primitive-cubic cell by the relations $a_{\text{terr}} = 2a_{\text{cub}}$ and $c_{\text{terr}} = a_{\text{cub}}$. If we further displace the tetragonal structures relative to one another along c by $\frac{1}{4}$, and then make each of them, by means of suitable deformations, monoclinic with parameters a = 6.674 Å, b = 6.117 Å, c = 3.304 Å, and β = 110°33′, then we obtain the structure of BiII, which is shown in Fig. 3. Each atom of this phase has neighbors at distances 3.144 Å (one), 3.168 Å (two), 3.304 Å (two), 3.387 Å (one), 3.708 Å (one), 3.936 Å (two), 4.51 Å (four), and 4.804 Å (one). Unlike SbIII, there are no interatomic distances corresponding to covalent interaction.

The polymorphic transitions SbII → SbIII and BiII → BiIII are accompanied by an increase of the electric resistance[5,13]. Qualitatively the same R(p) relation is observed also for IV-VI compounds in phase transitions from the NaCl type to the SnS type[14-16]. This circumstance can serve as indirect evidence favoring the similarity of the structures of SbIII, BiIII, and SnS. An analysis of the interatomic distances shows that the transition causes significant changes in the character of the interaction in these substances. Thus, one short interatomic distance appears in SbIII (Table II) and apparently in BiIII, there and three short interatomic distances in IV-VI compounds (of the SnS type). These distances are close to those assumed for the covalent bond. This suggests that the features of the variation of the R(p) dependence in the polymorphic transitions SbII → SbIII and type NaCl → type SnS are directly connected with the distortion of the crystal structure and the appearance of strong interactions in it. A similar explanation was offered for IV-VI compounds in[17], where it was assumed that the distortion of the crystal structure of the compounds in question is accompanied by a change in the structure of the energy bands, leading to a decrease of the number of carriers per unit volume and of the mobility.

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1) We have in mind the shortest distances.

2) If we choose the origin not at the symmetry center but at the center of the atom, as was done in [12], then the positions of the atoms in BiII are 000, $\frac{1}{2}\,\frac{1}{2}$ 0, $\frac{1}{2}$ 0 $\frac{1}{4}$ and 0 $\frac{1}{2}\,\frac{1}{4}$.

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