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POLYMORPHIC TRANSFORMATIONS IN THE ANTIMONY-BISMUTH SYSTEM AT HIGH PRESSURES

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A section of the p-T-x phase diagram was determined for the Sb_xBi_{1-x} alloy system at room temperature. The limits of the existence (under equilibrium conditions) of phases I, II, II′, and III were determined by two methods: x-ray diffraction and electrical resistance. The following crystal structures were attributed to the various phases: As-type structure to phase I, primitive cube to phase II, monoclinic Bi II to phase II′, and monoclinic Sb III to phase III. The compressibilities of Sb, $Sb_{0.9}Bi_{0.1}$, and $Sb_{0.8}Bi_{0.2}$ were determined by x-ray diffraction in the 0—85 kbar range.

UNDER normal conditions, Sb-Bi alloys form a continuous system of substitutional solid solutions at all concentrations. The first investigations of this system under high pressures at room temperature were carried out by Bridgman,[1] who determined the pressure dependences of the electrical resistance and of the volume. Bridgman used resistance discontinuities to establish that Sb_xBi_{1-x} alloys with $x < 0.035$ underwent the I → II → III sequence of phase transitions, which was well known because of its occurrence in pure Bi. The alloys with $x \geq 0.035$ were transformed directly from phase I to phase III, bypassing phase II. Further increase in the concentration of Sb raised the pressure at which the I → III transition occurred and the transition pressure became less and less definite. The maximum pressure reached by Bridgman in his resistance measurements was insufficient to observe the phase transition in Sb at 83 kbar, which he deduced from the pressure dependence of the volume.[2]

The purpose of our investigation was to determine the crystal structures and the approximate limits of the existence of the high-pressure phases of the Sb-Bi alloy system. It is known that elements of the VB group, which includes Sb and Bi, undergo a series of phase transitions at high pressures. The results of previous investigations enabled us to describe the sequence of crystal structures generated by these transitions in the following way: phase-centered orthorhombic structure (the structure of black P[3] under normal conditions) → rhombohedral structure of the As type (the structure of black P at high pressures[4] and of As, Sb, and Bi under normal conditions[3]) → primitive cube structure (the structure of black P[4] and of Sb—denoted by Sb II—at high pressures[5-7]) or monoclinic Bi II structure (the structure of Bi at high pressures) → monoclinically distorted structure of the SnS type [the high-pressure structures of Sb (Sb III) and Bi (Bi III)[9]]. Recent investigations of the superconductivity of As also demonstrated the existence of two polymorphic transitions at pressures of about 105 and 140 kbar[10] but no data on the crystal structures were obtained in this investigation. Thus, different sequences of high-pressure structural transitions in group VB elements had been observed so far only for the Sb II and Bi II crystal structures which seem to be intermediate between the As-type structure and the monoclinically distorted SnS-type structure (Sb III).

Fairly extensive experimental data are now available on the influence of pressure on the As-type crystal structure.

It is known that this structure is characterized by two parameters: the rhombohedral angle α_r and a parameter u, which represents the displacement of an atom from the center of a rhombohedron along a threefold axis (in the hexagonal setting, the angle α_r is replaced by the ratio of the unit cell parameters c/a but the parameter u remains the same). In the special case of $\alpha_r = 60°$ ($c/a = \sqrt{6} = 2.449$) and $u = 0.25$, the As-type structure transforms into the structure of a primitive cube. Consequently, it can be regarded as a "rhombohedrally distorted" primitive cube in which the degree of geometrical distortion is governed by the deviation of the actual values of α_r and u from the values typical of a cube. The values of these parameters are listed for some elements in Table I.

Measurements of the hydrostatic compressibility of Sb and Bi single crystals along axial directions[14,15] indicate that the ratio c/a decreases with increasing pressure (the angle α_r increases). This result has been confirmed by x-ray diffraction studies of Sb. A comparison of the x-ray diffraction and compressibility data is given in Fig. 1. Similar conclusions apply to the P modification which has the As-type structure. The ratio of the unit cell parameters for this modification is $c/a = 2.608$ ($\alpha_r = 57°15'$).[4] We obtained the x-ray diffraction pattern of P at a higher pressure (the pressure was deduced from the change in the interplanar spacings). We found that $c/a = 2.528$ ($\alpha_r = 58°40'$). The results of x-ray diffraction measurements, carried out on As using copper radiation under hydrostatic conditions and the method described in[16], are included in Fig. 1: they also show that the ratio c/a decreases when the pressure is increased.

It has recently been reported that the displacement parameter u of Sb and Bi increases when the pressure is raised.[17] Thus, we may assume that the influence of hydrostatic compression on the As-type structure is a gradual relief of the "distortions," so that this struc-

Table I. Parameters representing deviations of the As-type structure of group VB elements from the primitive cube structure

Element*	α_r	c/a, hexagonal setting	u	Element*	α_r	c/a, hexagonal setting	u
P, black [4]	57°15′	2.608	0.21—0.22	Sb [12]	57°07′	2,617	0,233
As [11]	54°10′	2.803	0.226	Bi [13]	57°24′	2,609	0.234

*The parameters of black P are given for the range 83 kbar ⩽ p < 111 kbar.

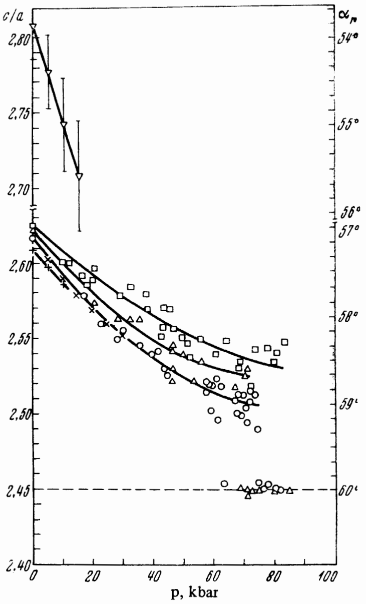

FIG. 1. Pressure dependences of the ratio c/a of As, Sb, Bi, and alloys $Sb_{0.9}Bi_{0.1}$, $Sb_{0.8}Bi_{0.2}$. ▽) As; ○) Sb; △) $Sb_{0.9}Bi_{0.1}$; □) $Sb_{0.8}Bi_{0.2}$. Bridgman's results are included for the sake of comparison: X) Sb [15]; +) Bi [14].

ture approaches that of a primitive cube and the pressure-induced structural changes are basically similar to those observed for all the elements in the VB group.

The Sb_xBi_{1-x} alloys normally crystallize also in the As-type structure. The dependences of the crystal lattice parameters of these alloys on their composition have been investigated quite thoroughly.[18,19] These investigations show that the behavior of the volume of these alloys is almost thermodynamically ideal. However, the dependence of the lattice parameters on the composition exhibits small (and opposite in sign) deviations from Vegard's law.[19] Consequently, the rhombohedral angle α_r is not a linear function of the concentration of antimony and the deviation of the angle α_r from 60° is greatest (the value of c/a is largest) for x = 0.7. This can be seen clearly from Fig. 2, which is based on the results given in[19]. Measurements of the displacement parameter u of the Sb_xBi_{1-x} alloys in the $0 \leq x \leq 0.3$ range show that the room-temperature value of this parameter is practically independent of the concentration of antimony.[18]

Samples of the Sb_xBi_{1-x} alloys with x ranging from 0 to 1 in steps of 0.1 were prepared, at our request, at the Institute of General and Inorganic Chemistry of the USSR Academy of Sciences. Polycrystalline ingots of the required composition were grown by fusing together the stoichiometric amounts of the two components

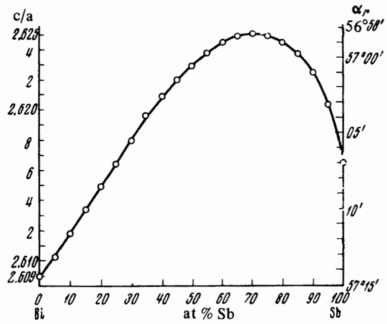

FIG. 2. Dependences of the ratio c/a and of the rhombohedral angle α_r on the composition in the Sb-Bi system, based on the results given in [19].

(99.999% purity) and prolonged annealing of the resultant products.

So far, we have obtained x-ray diffraction data on the phase transitions and compressibilities of Sb and two alloys: $Sb_{0.9}Bi_{0.1}$ and $Sb_{0.8}Bi_{0.2}$. A comparison of the lattice parameters, deduced from the powder diffraction patterns recorded by means of a DRON-1 unit under normal conditions, with those given in[19] demonstrated that the compositions of our alloys did not differ by more than ±0.01 from the nominal values, i.e., the compositions were nominal within the limits of the accuracy reached in the determination of the lattice parameters (Table II).

Our high-pressure investigations were carried out at room temperature using the method described in[7]. The samples were mixed with NaCl, and the compressibility of rocksalt was used to estimate the pressure on the basis of a semi-empirical equation of state calculated by Decker.[21] 1) The average error in the determination of pressure by this method was ±2.0 kbar at pressures below 60 kbar, and it increased linearly to ±6 kbar at 120 kbar. The high-pressure values of the unit cell parameters were calculated in the same way as the parameters under normal conditions (see footnote to Table II).

Our pressure dependences of the unit cell parameters (hexagonal setting) of Sb, $Sb_{0.9}Bi_{0.1}$, and $Sb_{0.8}Bi_{0.2}$ are presented in Figs. 3—5. The continuous lines in these figures represent quadratic dependences of the type

$$-\Delta X / X_0 = \alpha \cdot 10^{-7} p - \beta \cdot 10^{-12} p^2, \qquad (1)$$

where X is the parameter (a, c, or V) which depends on the pressure; p is the pressure in bars; α and β are coefficients calculated from the experimental data by

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1) A systematic error was made in our earlier investigations: [7,9] the pressures were overestimated because of the method used to calculate the bulk compressibility of NaCl.

Table II. Parameters of the unit cells of Sb, Bi, and their alloys under normal conditions (hexagonal setting)

Parameter, Å	According to [12,13]	According to [19]	Our results*	Composition x of our alloys found by comparison of parameters with [19]
		Antimony		
a	4.3084	4.3085	4.3074±0.0005	
c	11.274	11.2732	11.271±0.004	
c/a	2.6167	2.6165	$2.616_8 \pm 0.001_2$	
		Alloy $Sb_{0.9}Bi_{0.1}$:		
a		4.3313	4.3324±0,0008	0.896±0.006
c		11.3588	11.357±0.009	0.903±0.008
c/a		2.6225	$2.621_4 \pm 0.002_5$	
		Alloy $Sb_{0.8}Bi_{0.2}$		
a		4.3542	4,3551±0.0006	0.796±0.007
c		11.4282	11.434±0.008	0,790±0.011
c/a		2.6246	$2.625_4 \pm 0.002_3$	
		Bismuth		
a	4.5461	4.5465	4.5452±0.0005	
c	11,8629	11.8616	11.860±0.004	
c/a	2.6094	2,6089	$2,609_3 \pm 0,001_2$	

*The parameters were calculated from 11 reflections obtained using a DRON-1 unit and K_α copper radiation. Powder samples, mixed with NaCl (for calibration), were used. The average value of a given parameter was calculated by weighting each measurement with the effective angle of a pair of reflections in the way suggested by Zaslavskiĭ. [20]

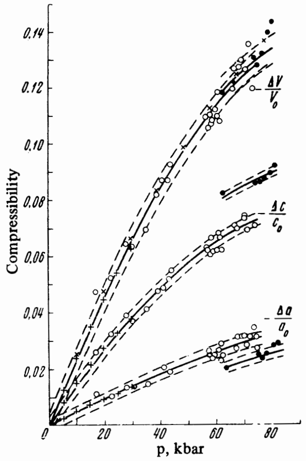

FIG. 3. Linear and bulk compressibilities of the rhombohedral and cubic phases of Sb: ○) rhombohedral phase; ●) cubic phase. Bridgman's results: +) [15]; X) [2].

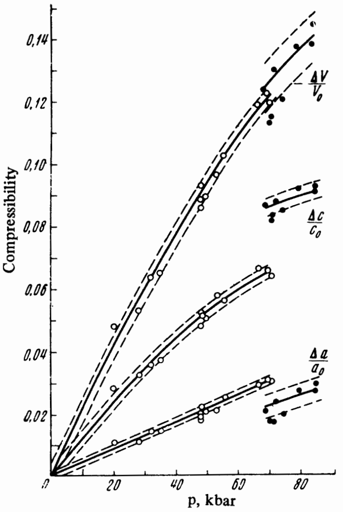

FIG. 4. Linear and bulk compressibilities of the alloy $Sb_{0.9}Bi_{0.1}$: ○) rhombohedral phase; ●) cubic phase.

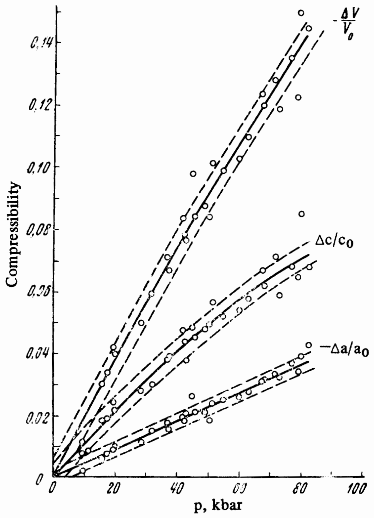

FIG. 5. Linear and bulk compressibilities of the alloy $Sb_{0.8}Bi_{0.2}$ in the As-type phase.

the least-squares method. The numerical values of these coefficients for all the curves are listed in Table III. The dashed curves in these figures show the rms deviations of the experimental results from the mean curve.

The pressure dependence of c/a is given in Fig. 1. The corresponding equation is of the form

$$\frac{c}{a}=\frac{c_0}{a_0}(1-\alpha\cdot 10^{-7}p+\beta\cdot 10^{-12}p^2). \qquad (2)$$

The coefficients α and β for this equation are also listed in Table III.

It is evident from the dependences obtained that the compressibility of the investigated substances decreases and the rate of increase in the angle α_r slows down when the concentration of Bi is increased.

The phase transitions in $Sb_{0.9}Bi_{0.1}$ are fully analogous to the transitions in pure Sb: a polymorphic transition of the first kind at about 65 kbar transforms the structure to that of a primitive cube and an x-ray diffraction line corresponding to the strongest reflection of the monoclinic Sb III structure appears at p ~ 75 kbar. The cubic cell parameter at 75 ± 3 kbar is 2.978 ± 0.005 Å for Sb and 3.001 ± 0.006 Å for $Sb_{0.9}Bi_{0.1}$. No x-ray diffraction patterns of the cubic modification were obtained for the $Sb_{0.8}Bi_{0.2}$ alloy, in spite of the fact that the range of pressures in which this phase could exist was investigated particularly carefully. Some of the experiments indicated the simultaneous presence of the rhombohedral and monoclinic phases, which was never observed in the case of Sb and $Sb_{0.9}Bi_{0.1}$. The strongest reflection of the monoclinic structure was observed for $Sb_{0.8}Bi_{0.2}$ at ~72 kbar.

The polymorphic transitions which we investigated were characterized by a fairly wide range of coexistence of two adjacent phases (this was due to supercooling, which resulted in the retention of one phase in the equilibrium range of existence of the next phase). Thus, the rhombohedral modification (the As-type structure) could sometimes be observed in Sb right up to 75 kbar, whereas in other experiments the pure cubic structure was found at pressures as low as 65 kbar. Between these two pressures, a mixture of both modifications

Table III. Coefficients of analytic expressions for the compressibility (1) and the lattice parameter ratio (2) of Sb and Sb-Bi alloys

	$-\Delta X/X_0$: $-\frac{\Delta a}{a_0}$	$-\Delta X/X_0$: $-\frac{\Delta c}{c_0}$	$-\Delta X/X_0$: $-\frac{\Delta V}{V_0}$	c/a *
Sb with As-type structure				
α	4,9	14.8	25,4	9.8
β	1.2	7.0	10,1	5,5
± σ **	0.002	0.002	0.004	0,007
Sb with primitive cube structure				ja
α	3.2	20.6	26.6	
β	0.1	12.4	12.7	
± σ	0.002	0,002	0.005	
$Sb_{0.9}Bi_{0.1}$ with As-type structure				
α	4.3	13.6	21,9	9.8
β	—	6.0	6.5	6.4
± σ	0.001	0,002	0,003	0.008
$Sb_{0.9}Bi_{0.1}$ with primitive cube structure				
α	3.3	20.2	24.3	
β	—	11.1	9.1	
± σ	0,003	0.003	0.008	
$Sb_{0.8}Bi_{0.2}$ with As-type structure				
α	4.55	11.5	19.6	7,9
β	—	3,0	3.0	4.6
± σ	0.002	0.004	0.006	0,008

*The values of c_0/a_0 under normal conditions are listed in Table II.
**Here, σ is the rms deviation of the experimental points from the smooth curve.

Table IV. Ranges of existence of high-pressure phases and their mixtures in Sb and in Sb-Bi alloys (pressures in kbar)

Substance	Structure of high pressure phase*: 1	2	3	4	5
Sb	0÷75	61÷84	64÷81	74÷90	90÷130 and higher
$Sb_{0,9}Bi_{0,1}$	0÷74	67÷82	69÷85	75÷95	86÷112 and higher
$Sb_{0,8}Bi_{0,2}$	0÷80		72÷83 **		83÷110 and higher

*Structures of high-pressure phases:
1) rhombohedral As-type phase;
2) rhombohedral As-type + cubic (Sb II);
3) cubic (Sb II);
4) cubic (Sb II) + monoclinic (Sb III);
5) monoclinic (Sb III).
**Rhombohedral As-type structure + monoclinic structure (Sb III).

could be observed. Two structures were found to coexist also in the Sb II → Sb III transition, and phase III sometimes appeared at pressures lower than the maximum pressure in the cubic modification range. Similar results were also obtained for the polymorphic transitions in the two alloys being investigated. Table IV gives the range of pressures deduced from a considerable number of experimental runs: 47 experiments on Sb, 35 experiments on $Sb_{0.9}Bi_{0.1}$, and 23 experiments on $Sb_{0.8}Bi_{0.2}$, in the pressure range 55–115 kbar.

Thus, we found that the phase diagram of the Sb_xBi_{1-x} system included, in addition to a narrow range of existence of a phase of the Bi II type, a range of pressures in which a phase of the Sb II type (primitive cube) was observed.

Fuller information on the system being investigated was obtained by measuring the electrical resistance up to ~80 kbar.[2] Figure 6 shows the dependences $R(p)/R_0$ for Bi, Sb, and three alloys with x = 0.2, 0.8, and 0.9. These dependences were obtained by increasing and lowering the pressure. The volume hysteresis loop, plotted on the basis of Bridgman's data,[1] is given for x = 0.2. The dependence $R(p)/R_0$ observed for $Sb_{0.2}Bi_{0.8}$ was typical of the majority of our samples. However, when the concentration of Sb was increased, the discontinuity corresponding to the I → III phase transition decreased in amplitude. The onset of the transition became very indistinct during the rising pressure cycle. We assumed the transition occurred at the midpoint of the range of pressures in which the slope of the fall of the resistance was steepest. The transition pressures

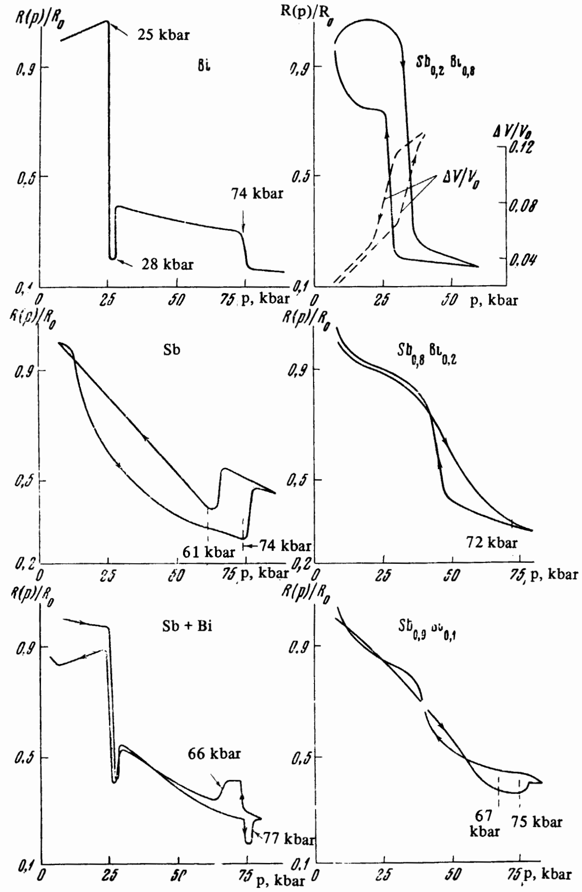

FIG. 6. Typical pressure dependences of the electrical resistance of Sb_xBi_{1-x} samples.

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[2] The pressure calibration of the chamber employed was based on discontinuities of the electrical resistance of Bi, Tl, and Ba, and the corresponding pressures listed in [22], i.e., the calibration was based on the compressibility of NaCl.

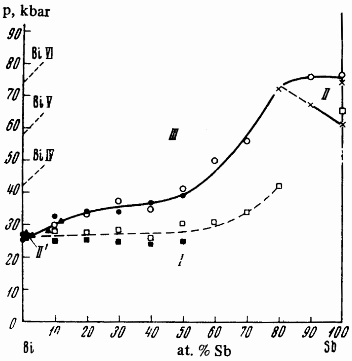

FIG. 7. Typical pressure-composition section of the phase diagram of the Sb-Bi alloy system at room temperature: I) rhombohedral phase with the As-type structure; II) cubic phase with the structure of a primitive cube (Sb II); II′) monoclinic phase of the Bi II type; III) monoclinic phase of the Sb III type. Experimental points: X) x-ray diffraction data; O), □) electrical resistance data obtained during rising and falling pressure cycles, respectively; ●), ■) Bridgman's results [1] obtained by measuring the volume during rising and falling pressure cycles, respectively; ▲) electrical resistance results from M. A. Il'ina and E. S. Itskevich.

found in this way were in reasonable agreement with Bridgman's data[1] on the pressure dependence of the volume in the I → III and III → I transitions in alloys with $0.1 \leq x \leq 0.5$, provided the transition was assumed to occur at the midpoint of the range of pressures in which the slope of $\Delta V/V_0$ was steepest. Our preliminary x-ray diffraction results indicated that a phase transition in $Sb_{0.5}Bi_{0.5}$ produced a monoclinic structure of the Sb III type. The As-type structure was restored when the pres- pressure was removed.

The fall of the resistance of $Sb_{0.8}Bi_{0.2}$ with increasing pressure was so smooth (Fig. 6) that we were unable to localize the I—III transition. We found that the pressure of ~72 kbar, representing the transition to the Sb III structure deduced from x-ray diffraction data, was in no way related to the dependence $R(p)/R_0$.

A comparison of the pressure dependences of the electrical resistance of Sb and $Sb_{0.9}Bi_{0.1}$ (Fig. 6) showed that the rise of the resistance typical of the II → III phase transition, reported earlier by other investigators,[23,24] was clearly exhibited also by $Sb_{0.9}Bi_{0.1}$. The absence of such a rise in other alloys, in which the direct direct I—III transition took place, indicated that this effect was associated with the presence of the intermediate phase II, which had the structure of a primitive cube (Sb II). The vertical dashed lines in Fig. 6 indicate the pressures at which the primitive cube and Sb III phases appeared in the x-ray diffraction patterns.

Simultaneous measurements of the resistance of samples of Sb and Bi connected in series (Fig. 6) demonstrated that the Sb II → Sb III transition pressure found in this way was somewhat higher than the pressure at which the strongest reflection of the Sb II structure appeared in the x-ray diffraction patterns. The hysteresis loop of this phase transition was approximately 11 kbar wider than the hysteresis loop of the Bi V → Bi VI transition.

Bridgman's pressure dependences of the volume[1] and our x-ray diffraction and electrical resistance results were used to plot a typical section of the p-T-x phase diagram of the Sb_xBi_{1-x} alloy system at room temperature. The limits of the existence of phase II′ and of the I → III transition shown in Fig. 7 were found to be in good agreement with the electrical resistance results obtained by M. A. Il'ina and E. S. Itskevich (private communication) for Sb_xBi_{1-x} alloys with x = 0.01, 0.03, 0.08, and 0.12. There were no grounds for assuming that the crystal structure of phase II′ suggested by Bridgman[1] was in any way different from the structure of Bi II.[8] Similarly, phase II with the structure of a primitive cube (Sb II) was observed close to pure Sb and the limit of the range of existence of this phase was a little less than 20 at.% Bi. The I → III transition altered the As-type structure to the structure of monoclinically distorted SnS (Sb III).

The results obtained indicated that Sb-Bi alloys behaved, in the investigated range of pressures, as a single homogeneous substance, in spite of the fact that the structures of antimony and bismuth were different at pressures above 25 kbar.

The authors are deeply grateful to V. K. Nikitina, of the Institute of General and Inorganic Chemistry, for the preparation of the alloys.

Note added in proof (August 27, 1970). When this paper was sent to press, the authors received a letter from Dr. Daggin (Australia) concerning the problems discussed in the third paragraph of the present paper. Dr. Daggin informed us of his discovery of a high-pressure monoclinic phase of arsenic which had the same structure as Bi II. The range of existence of this phase in the p-T diagram is not yet known.

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