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PHASE TRANSITIONS IN ANTIMONY AT HIGH PRESSURES

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Two reversible phase transitions in antimony have been detected by x-ray diffraction studies: Sb I → Sb II (at 70 kilobars to the primitive cubic structure) and Sb II → Sb III (at 85 kbar to the close-packed hexagonal structure). It is found that the first transition takes place as a result of gradual removal of distortions in the initial type A7 structure.

AN x-ray diffraction structure analysis made at 30, 50, 90 and 100 kilobars has shown[1] that antimony experiences in this region of pressures two reversible phase transitions: one at $p \approx 50$ kbar—to a primitive cubic structure, and the second at 85—90 kbar—to a close packed hexagonal structure.

By using the same procedure as before[2-4], we made a detailed x-ray diffraction investigation of Sb at room temperature and at pressures up to 100 kbar. We worked with single-crystal antimony (99.999% pure), having a type A7 structure with parameters $a = 4.297$ Å, $c = 11.244$ Å, and $c/a = 2.617$.

Figure 1 shows x-ray patterns of the initial phase of Sb, taken at different pressures. The parameters of this phase, in terms of the hexagonal and rhombohedral axes, are listed in Table I for pressures up to 50 kbar. On the basis of the results obtained, we calculated the values of $\Delta a/a_0$, $\Delta c/c_0$, and c/a for different pressures p, and plotted the corresponding pressure dependences of these quantities, as shown in Fig. 2; we show also for comparison Bridgman's data (the ratio c/a was calculated in this case from his data for linear compressibilities of Sb).

It turned out that the "x-ray diffraction" dependences of $\Delta a/a_0$ and $\Delta c/c_0$ lie much higher than the curves plotted from Bridgman's data[5], and that the values of c/a lie in both cases on the same straight line (Fig. 2). If we assume that the relations a(p) and c(p) are linear, then the latter condition leads to the relation

$$(\Delta a / a_0)_{\text{xray}} - (\Delta a / a_0)_{\text{Br}} = (\Delta c / c_0)_{\text{xray}} - (\Delta c / c_0)_{\text{Br}} = K, \tag{1}$$

according to which the results of both methods differ from each other by a certain constant K, the value of which depends on p (an investigation has shown that the x-ray diffraction data and Bridgman's data coincide for $p \geq 70$ kbar, for which we therefore have $K = 0$). The discrepancy between the data on the compressibility of antimony in the region of low values of p is apparently

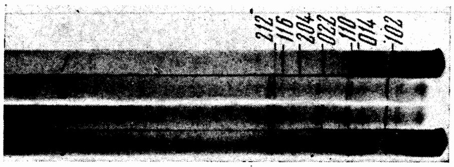

FIG. 1. X-ray patterns of antimony at different pressures (unfiltered Mo radiation): 1 – one bar, 2 – 40 kbar, 3 – 45 kbar, 4 – 60 kbar.

Table I. Parameters of initial phase of Sb at different pressures

p, kbar	a, Å	c, Å	c/a	a_R, Å	α
12	4.295	11.119	2.589	4.460	57°34′
13	4.235	10.930	2.581	4.416	57°17′
16	4.224	10.883	2.576	4.373	57°47′
21	4.211	10.793	2.563	4.341	58°1′
27	4.205	10.698	2.544	4.313	58°20′
32	4.274	10.858	2.540	4.379	58°24′
36	4.194	10.663	2.542	4.301	58°22′
40	4.182	10.601	2.534	4.280	58°30′
46	4.180	10.532	2.519	4.261	58°45′
I bar	4.297	11.244	2.617	4.495	57°7′

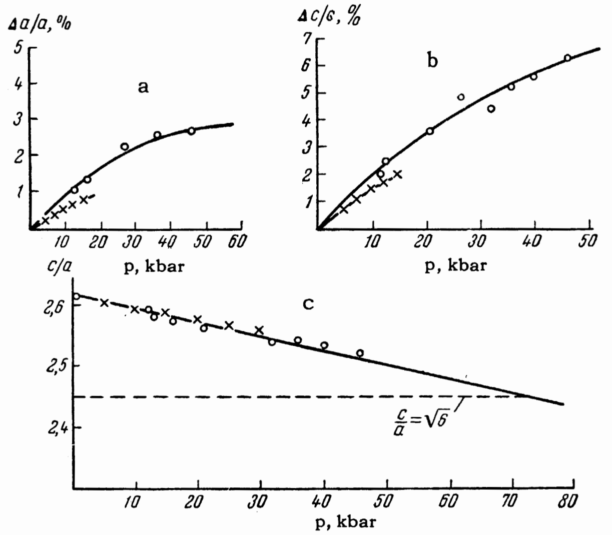

FIG. 2. Pressure dependences for the initial phase of Sb: a – $\Delta a/a_0$ vs. p, b – $\Delta c/c_0$ vs. p; c – c/a vs. p. The x-ray diffraction data are designated by circles, and the Bridgman data are designated by crosses.

the consequence of a certain systematic error in the determination of the pressure in the x-ray diffraction experiments. Since an analogous procedure[2-4] has yielded for tellurium[6] data which coincide with the results of Bridgman, it is quite probable that the discrepancy between the results obtained for antimony can be the consequences of the distribution of the pressure in the antimony sample itself.

FIG. 3. X-ray patterns of antimony for different pressures. a) (unfiltered molybdenum radiation): 1 – one bar, 2 – 70 kbar (cubic phase); 3 – 70 kbar (cubic phase); 4 – 75 kbar (cubic phase); b) (filtered molybdenum radiation): cubic phase of Sb at p = 70 kbar.

Table II

d, Å	hkl	Primitive cubic lattice of Sb	
		a, Å*	J
3.009	100	3.009	strong
2.112	110	2.988	medium
2.719	111	2.977	medium
1.498	200	2.996	medium
1.330	210	2.974	medium
1.220	211	2.988	weak
0.994	300	2.983	very weak
0.942	310	2.978	very weak
0.898	311	2.980	very weak
0.831	320	2.998	very weak
0.795	321	2.976	very weak

* $a_{av} = 2.986 \pm 0.009$ Å.

From an examination of Table I it also follows that the rhombohedral cell angle α increases with increasing pressure. It is known that the structure Sb I (type A7, $\alpha = 57°34'$ and u = 0.233) can be obtained by slightly distorting the primitive cubic structure ($\alpha = 60°$ and u = 0.25). Thus, it is quite obvious that the high pressure (the increase in α) leads in this case to a gradual removal of the distortion of the Sb lattice, so that its structure approaches the primitive cubic one. This assumption is verified by the experiment. Indeed, at p = 60—75 kbar we obtained for Sb x-ray diffraction patterns corresponding to the primitive cubic lattice (Fig. 3). Table II gives data for p = 70 kbar (d—distance between planes, hkl—Miller indices of the reflecting plane, a—lattice constant, J—reflection intensity): a = 2.986 Å, $\rho = 7.6$ g/cm^3, $\Delta V/V_0 = -12.0\%$; according to Bridgman's data p = 70 kbar and $\Delta V/V_0 = -12.4\%$ (V_0—volume of cell per atom at p = 1 bar). By comparing the x-ray diffraction patterns of the initial phase with Sb at different p and the x-ray pattern of the cubic phase we note that with increasing pressure the lines (110) and (014), (212) and (116) come pairwise closer together, and at p = 60—70 kbar they merge with each other; consequently, as expected, we find that upon transition $c/a = \sqrt{6}$.

By plotting c/a against p in the form of a straight line in Fig. 2c, we can approximately estimate the pressure, at which the transformation takes place, in the following fashion: we continue the line c/a = f(p) until it crosses the line $c/a = \sqrt{6}$ (parallel to the pressure axis); the point of intersection corresponds to a transition of the initial antimony into cubic antimony at p = 70 ± 5 kbar.

It must be noted that it was impossible to establish by x-ray diffraction the presence of a jump in the dependence of c/a on p, since the distance between the corresponding lines (110), (014), (212), and (116) could not be determined in practice even at pressures 50—60 kbar. However, the behavior of this dependence up to 50 kbar, together with Bridgman's volume measurements, makes it possible to assume that antimony has a continuous transition from the A7 structure into the primitive cubic structure (without a jump in volume).

The second transition in Sb, first observed by

Table III

hkl	d_{calc}, Å	d_{meas}, Å	J
100	2,92	2,82	very weak
002	2,67	2,67	strong
101	2,56	2,56	medium
102	1.97	1.98	very weak
110	1.69	1,72	very weak
103	1.52	1,56	very weak
200	1.46	—	
112	1.42	1,41	medium
201	1.41		
004	1,33	1.32	weak
202	1.28	1,27	very weak
104	1.21	1.21	very weak
113	1,22	1,23	very weak

Bridgman[7] (p = 83 kbar) with the aid of the volume method, and then by Vereshchagin et al.[8] by the jump in the electric resistivity (p = 90 kbar) was recorded by us by x-ray diffraction. The photographs taken at pressures 80—100 kbar (Fig. 4) indicate a radical change in the structure: the x-ray patterns do not show the lines of the initial and primitive cubic phases. Corresponding to the new phase are the lines listed in Table III, which can be indexed on a close packed hexagonal structure with parameters (p = 90 kbar) a = 3.369 Å, c = 5.33 Å, c/a = 1.58, and ρ = 7.7 g/cm^3. It must be emphasized that both phases, cubic and hexagonal, exist simultaneously in the pressure region 75—85 kbar.

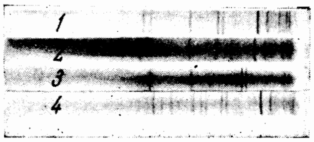

FIG. 4. X-ray diffraction patterns of antimony at different pressures (unfiltered molybdenum radiation): 1 – one bar, 2 – 60 kbar (cubic phase), 3 – 90 kbar (hexagonal phase), 4 – 1 bar (after removal of the pressure).

Thus, the primitive cubic lattice exists in a very narrow interval, not exceeding 10—15 kbar. Indeed, the transition into the cubic phase occurs at p = 70 kbar, while the hexagonal structure, according to our data, occurs already at 75—80 kbar; the "cubic" lines vanish at 85—90 kbar.

We must note once more (see [1]) the presence of some disparity in the distribution of the intensities of the lines on the x-ray pattern of the hexagonal antimony, compared with those usually observed in structures of this type, for example in magnesium. Thus, the relative intensities of the lines (010), (002), and (101) in antimony are: very weak, strong, and medium; for magnesium the sequence is medium, medium, and strong.

It must also be noted that the (110) reflection is exceedingly weak in our case, and in several x-ray patterns it is completely lost in the background. The violation of the normal distribution of intensities is apparently a consequence of absorption by the specimen, which is more noticeable at small angles and is also due to the presence of an orientation effect and the distortion of the crystal lattice as a result of the deviation of the experimental conditions from the conditions of pure hydrostatics. Similar phenomena were observed also by Jamieson[3].

By averaging our data we obtain for the primitive cubic structure a = 2.986 Å and for the hexagonal structure a = 3.346 Å and c = 5.296 Å. Comparing the volume of the unit cell per atom in each phase, we find that the transition from the cubic into the hexagonal phase occurs with a volume jump $\Delta V/V_0 = (V_{cub} - V_{hex})/V_{cub}$ = 3.6%, which is in good agreement with Bridgman's 3.7% [5]

The phase transitions in antimony are accompanied by an increase in the coordination number. In the first transition from the rhombohedral into the primitive cubic structure, it becomes equal to 6 (in lieu of 3), and upon transition into the hexagonal—to 12. Accordingly, the atomic radius of antimony amounts to 1.49 Å for a coordination number 6 and 1.66 Å for 12.

Table IV lists the dimensions of the rhombohedral cell and the values of a for As, Sb, and Bi at atmospheric pressure.

We see from Table IV that there exists a monotonic sequence in the variation of the lattice parameters with increasing atomic number: α and u increase with increasing Z, and consequently the cell distortion decreases; the structure approaches primitive cubic (α = 60°, u = 0.25).

The results of investigations of antimony and black phosphorus[11] indicate that the pressure acts on them in the same direction. Indeed, black phosphorus has at p > 83 kbar an A7 structure, identical to the structures of As, Sb, and Bi; this structure is converted into primitive cubic at p = 111 kbar. Thus, the high pressure removes the distortion in the A7 structure in two cases, in antimony and in black phosphorus, so that we can

Table IV

Parameter	Bi [9]	Sb [10]	As [10]
u	0,234	0,233	0,226
a, Å	4,746	4,507	4.131
α	57.24°	57.1°	54.2°

speak generally of a similarity in the behavior of the elements of the arsenic subgroup at high pressure.

On this basis we can expect analogous transitions into the primitive cubic structure to occur in arsenic at $p \approx 80$ kbar, starting from its position in the subgroup between P and Sb, and for Bi (from the point of view of the same reasoning) at a lower pressure; the latter follows from the foregoing analogy: elements with larger Z should experience transitions at lower pressure, owing to the presence of smaller lattice distortions.

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