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INVESTIGATION OF THE CRYSTAL STRUCTURE OF ANTIMONY AT HIGH PRESSURES

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The linear and volume compressibilities of the rhombohedral phase of antimony are measured in the pressure range from 0 to 80 kbar. It is shown that the phase transition to the primitive cubic structure is a first-order transition. It has been established that a phase transformation from the primitive cubic structure to a distorted hexagonal close-packed structure takes place at p ≈ 90 kbar.

X-RAY investigations of antimony at high pressures[1,2] have shown the presence of two phase transitions: from the rhombohedral A7 structure (As type) to the primitive cubic structure at $p \approx 70$ kbar, and then to a hexagonal close-packed structure at $p = 85$–90 kbar. The pressure dependence of the parameters of the rhombohedral cell was measured up to 46 kbar; it was shown that in this pressure range the rhombohedral angle α_r increases continuously. The pressure of the transition to the primitive cubic structure was determined by linear extrapolation of the $\alpha_r(p)$ dependence to 60° (in terms of the hexagonal axes to $c/a = \sqrt{6}$).

The variation of α_r under the action of pressure coincided with the $\alpha_r(p)$ dependence obtained by recalculating the linear compressibilities of antimony measured by Bridgman[3] on a single crystal up to ~30 kbar. However, the linear compressibilities themselves obtained by these two methods differed appreciably. In[2] the discrepancy was explained by the presence of a systematic error in determining the pressure in the x-ray experiments[1]. The assumption of the possibility of a continuous transition from the rhombohedral A7 type structure to the primitive cubic structure also remained unproved. Because of this and in order to check and refine the previously obtained data, we undertook to repeat the x-ray investigation of antimony at high pressures in the same camera as in[1,2].

The same antimony was used in the experiments as in[1,2]. A decrease of the diameter of the sample to 0.16–0.18 mm and a dilution of the antimony powder with amorphous boron with a 2 : 1 ratio of their weights in order to decrease the absorption improved the diffraction pattern and increased the resolution of the lines on the x-ray patterns under pressure. Admixture of NaCl powder to the mixture of antimony and boron made it possible to measure the pressure in each specific experiment up to 60 kbar within an accuracy of ± 1 kbar and at $p > 60$ kbar within an accuracy of ± 2 kbar. The pressure was determined from the x-ray pattern on the basis of Bridgman's data[4] on the volume compressibility of NaCl.

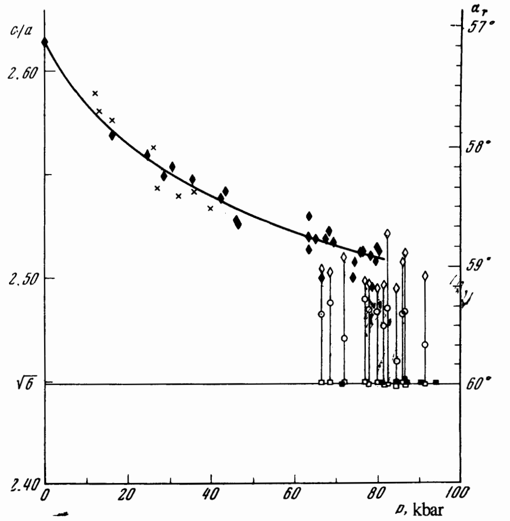

FIG. 1. The variation of the rhombohedral angle α_r (c/a in terms of the hexagonal axes) with pressure: ◆ – for the rhombohedral phase, ■ – for the cubic phase, ◇ – ▫ – ▫ – for a mixture of the rhombohedral and cubic phases, X – data from [2].

We obtained about 50 x-ray patterns of antimony in the 0–120 kbar range of pressures. The parameters of the rhombohedral structure were calculated on the Ural-2 computer by the least-squares method in three successive approximations with the reflections weighted as follows:

$$p_{hkl} \sim \frac{(\sin^2 \vartheta_{hkl})_{\text{calc}}}{\left|(\sin^2 \vartheta_{hkl})_{\text{meas}} - (\sin^2 \vartheta_{hkl})_{\text{calc}}\right|}.$$

Principal attention was accorded to the investigation of the transition from the rhombohedral to the primitive cubic structure in the pressure range of 60–100 kbar. Figures 1–4 show the pressure dependence of the rhombohedral angle α_r (the c/a ratios in terms of the hexagonal axes), the variation of the length of the edge of the rhombohedron a_r, as well as the linear and volume compressibilities. The perfectly clear observed deviation of the $\alpha_r(p)$ dependence from linearity leads to the circumstance that in the majority of cases the rhombohedral phase continues to exist up to pressures of ~80 kbar with $\alpha_r \approx 59°$ ($c/a \approx 2.51$). The transition to $\alpha_r = 60°$ ($c/a = \sqrt{6}$) occurs jumpwise; the lowest determined transition pressure is 73 kbar. In all we obtained seven points with a rhombohedral

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[1] As was shown in [2], assuming a linear change in the compressibility with pressure and with the presence of systematic deviations in the linear compressibilities themselves $(c/a)_X = (c/a)_{Br}$ if these deviations are equal for both parameters:

$$(\Delta a/a_0)_X - (\Delta a/a_0)_{Br} = (\Delta c/c_0)_X - (\Delta c/c_0)_{Br} = K(p)$$

and under the condition that

$$\left|\left(\frac{\Delta a}{a_0}\right) + \left(\frac{\Delta c}{c_0}\right)\right| \gg \left|\left(\frac{\Delta a}{a_0}\right)\left(\frac{\Delta c}{c_0}\right)\right|.$$

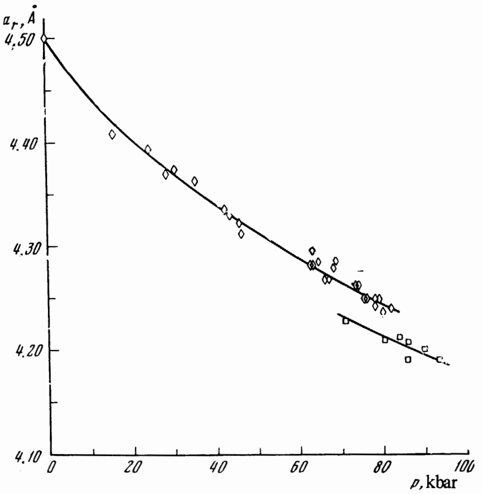

FIG. 2. The variation of the length of the rhombohedron edge with the pressure: ◇ – rhombohedral phase, □ — cubic phase.

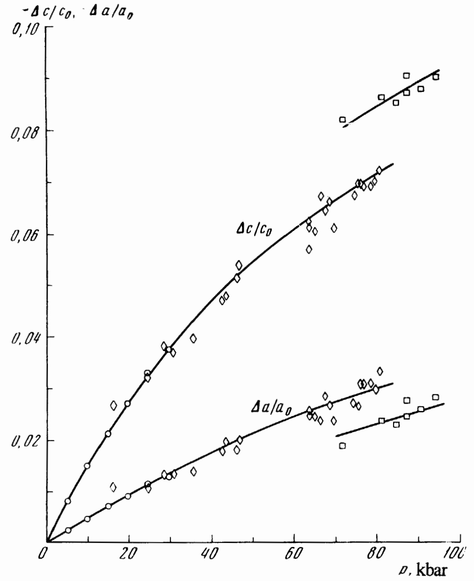

FIG. 3. The variation of the linear compressibilities with the pressure: ◇ – rhombohedral phase, □ – cubic phase, ○ – Bridgman's data.[3].

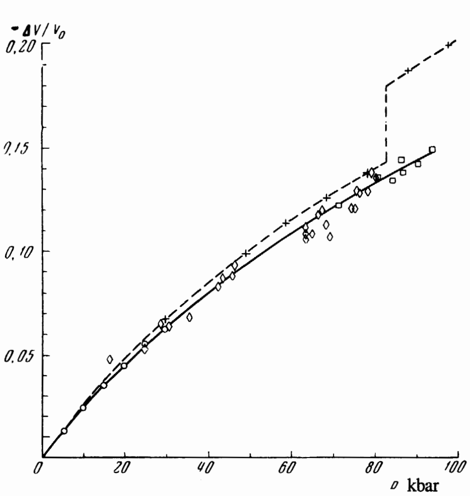

FIG. 4. The variation of the volume compressibilities with the pressure: ◇ – for the rhombohedral phase, □ – for the cubic phase, ○ – Bridgman's data according to [3], + – according to [9].

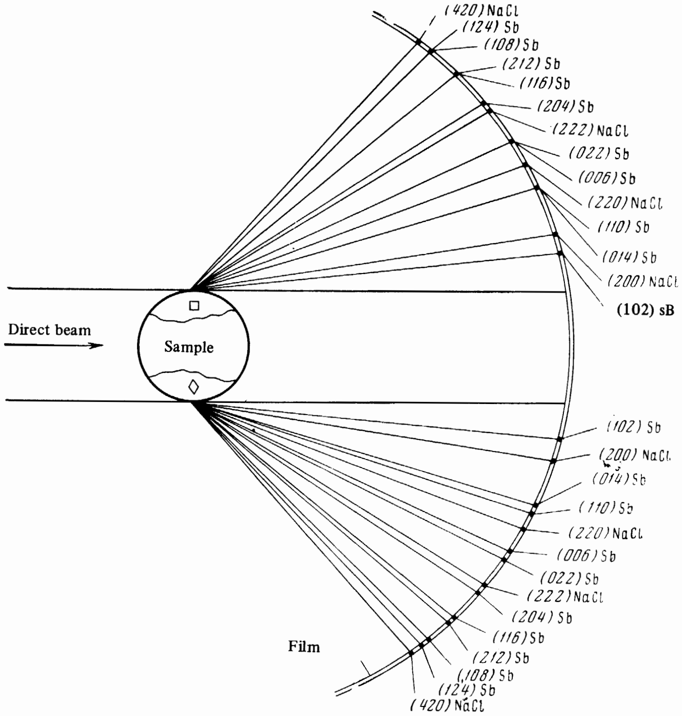

FIG. 5. Schematic diagram of the diffraction pattern of antimony with a partial phase transition to the cubic structure: □ – cubic phase, ◇ – rhombohedral phase.

angle corresponding to the primitive cubic structure.

In addition, about ten experiments in the 70–90 kbar range yielded values 59° < α_r < 60°. In all these instances several reflections having unreasonably large deviations from values calculated in accordance with the entire aggregate of lines were excluded during the weighting. A careful consideration of the corresponding x-ray photographs showed that in these experiments the diffraction patterns are characterized by coalescence of the doublets of the (014) and (110), (006) and (022), (116) and (212), and (108) and (124)[2)] reflections on one side of the direct x-ray beam, indicating a transition to the cubic structure, and the retention of these on the other side of the beam. Taking into account the practically complete absorption of the radiation within the thickness of the sample, such a diffraction pattern can be explained by assuming that only part of the volume of the sample goes over into the cubic phase (see Fig. 5). The presence of NaCl reflections on the diffraction photographs made it possible to calculate each side of the diffraction pattern independently of the order side and to obtain the parameters of the cubic ($\alpha_r = 60°$) and rhombohedral ($\alpha_r \approx 59°$) phases in the region in which they coexist. The partial transition is most probably explained by the kinetic properties of the given phase transition. The $a_r(p)$ dependence (Fig. 2) also exhibits a jumplike change at the transition to the cubic phase.

[2)] The indices of the reflections correspond to a choice of unit cell in terms of hexagonal axes.

The jumplike change of the parameters and the presence of a two-phase region attest to the fact that the observed transition is a first-order phase transition.

The distortion of the intensities of the reflections under the conditions of quasihydrostatics does not make it possible to determine the value of the shift parameter u which amounts to 0.233 in antimony at normal pressures and should have a value of 0.25 in the case of the primitive cubic structure.

According to Falikov's considerations[5], antimony crystallizing with the rhombohedral structure with the parameters $\alpha_r = 60^\circ$ and $u \neq 0.25$ should have dielectric properties, whereas at $\alpha_r = 60^\circ$ and $u = 0.25$, i.e., when it is primitive cubic, it has the properties of a good metal. It would be interesting to investigate the electronic spectrum of antimony at 70–85 kbar, but thus far this region is unaccessible for such experiments. The information available at present on the change of the electrical conductivity of antimony at high pressures at room temperature [6,7] indicates the presence of a rapid fall of the electrical resistance in the 60–85 kbar region and of a sharp increase at the transition to the "hexagonal" phase.

Figure 3 shows the pressure dependence of the linear compressibilities of antimony. The use of NaCl as an internal manometer made it possible to remove the previous discrepancy[2] with Bridgman's data.[3] At the transition to the cubic structure one observes a jumplike change of the unit-cell parameters; the c parameter descreases and the a parameter increases. The jump in pressure dependence of the $\Delta a/a_0$ parameter is less distinct than in the case of $\Delta c/c_0$. However, the systematic deviation of points corresponding to the cubic phase from the averaged curve for the points of the rhombohedral phase makes it possible to conclude that it exists. The spread of the points near the transition does not make it possible to determine with sufficient accuracy the jumps of the parameters; it can be assumed that the relative increase of the a parameter is about half the relative decrease of the c parameter. It is hence clear that the jump in the volume at the transition is extremely small, since $\Delta V/V = 2\Delta a/a + \Delta c/c$. According to our estimates $\Delta V/V$ does not exceed 0.5 percent and lies entirely within the range of the error of the measurements.

The pressure dependence of $\Delta V/V_0$ obtained by us (Fig. 4) is in good agreement with the measurements of Bridgman[3] carried out on a single crystal. Bridgman's data [8] on the volume compressibility of antimony up to 100 kbar exceed somewhat our and his own data for a single crystal.[3] Such a discrepancy is apparently not accidental but is a result of the effect of the macroporosity of the polycrystalline sample on the results of the compressibility measurements by the volume method. This phenomenon was first pointed out by Jacobs.[9]

The phase transition observed by Bridgman [8] in antimony at p = 83.6 kbar and also determined in [7] from the electrical resistance was interpreted in [2] as a transition from the primitive cubic structure to the hexagonal close-packed structure. However, at present it is perfectly clear that the diffraction pattern includes "superfluous" reflections which do not correspond to the hexagonal close-packed structure. The presence of distrotions in this phase was first pointed out in [10].

It should be noted that corresponding fully to the discrepancy with Bridgman's data on the volume compressibility the pressure of the transition to the distorted hexagonal close-packed structure also shifted to higher pressures. According to our data the transition to this phase occurs at $\sim$90 kbar, a mixture of the "hexagonal" and cubic phases being frequently observed. Measurements of the electrical resistance [7] of parallel joined wires of antimony and bismuth under pressure also attest to the fact that the transition to the "hexagonal" phase in antimony occurs at a pressure about 5 kbar higher than the BiVI-BiVII transition.

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