Physics

S. S. KABALKINA, Corresponding Member of the USSR Academy of Sciences L. F. VERESHCHAGIN,

1963

SovietRxiv

Abstract

Full Text

Physics

S. S. KABALKINA, Corresponding Member of the USSR Academy of Sciences
L. F. VERESHCHAGIN,
V. P. MYLOV

PHASE TRANSITIONS IN ANTIMONY UNDER HIGH PRESSURE

It is known that antimony is a structural analog of bismuth. It is natural to suppose that under high pressure both substances behave identically. However, according to Bridgman' s data, in the pressure interval up to 100 kbar there are five phase transitions in bismuth ([1]), whereas in antimony there is only one—at $p = 85$ kbar. Apparently, the same transition in antimony was recorded from the jump in electrical resistance ([2]) at $p = 90$ kbar.

We have carried out a preliminary x-ray study of the structure of antimony at pressures $p = 30$; 50; 90 and 100 kbar. The photographs were taken in a new x-ray chamber,* which is now being successfully used for work at pressures up to 100 kbar and higher ([3–5]). As has already been reported ([5]), the chamber was calibrated with respect to p by recording the jumps in the electrical resistance of bismuth during phase transitions.**

Table 1

d, Å	hkl	Simple cubic lattice	Simple cubic lattice
d, Å	hkl	a, Å	I
2.94	100	2.94	strong
2.09	110	2.95	medium
1.715	111	2.97	medium
1.48	200	2.96	weak
1.33	210	2.97	medium
1.21	211	2.96	weak

$a = 2.96 \pm 0.01$ Å

The study showed that the x-ray patterns of antimony at zero pressure and at $p = 50$ kbar differ from one another. The photograph at $p = 50$ kbar contains a considerably smaller number of lines, although the general appearance of the original diffraction pattern is preserved. It appears that at high pressure some lines have merged with one another. Indeed, at atmospheric pressure four strong

lines of approximately equal intensity are found on the x-ray pattern (their hexagonal indices are (110), (014), (212), and (116)); on the photograph at $p = 50$ kbar only two remain: the line (110) merges with (014), and (212) with (116). Altogether, under these conditions it was possible to record six lines, which can be indexed in a primitive cubic lattice with cell parameter $a = 2.96 \pm 0.01$ Å, $\rho_{\text{calc}} = 7.8$ g/cm^3. The corresponding data are given in Table 1.

Thus, apparently, at $p \simeq 50$ kbar antimony undergoes a reversible phase transition, which is accompanied by transformation of the initial rhombohedral lattice into a primitive cubic one. The nature of the transition remains unclear, i.e., whether we are dealing with a transition of the second or first order. The fact that Bridgman did not observe a volume jump in Sb up to 85 kbar argues in favor of the first assumption. A definitive answer may be obtained by x-ray determination of the dependence $c/a = f(p)$. The initial lattice has $c/a = 2.617$; from the condition of overlap of the reflections (110) and (014), (212) and (116), it follows that at the moment of transition $c/a = \sqrt{6} \simeq 2.44$. It is necessary to determine whether c/a changes continuously with pressure or discontinuously, and at what minimum pressure—

* The main part of the chamber is a pellet pressed from powdered boron, with a channel for the specimen.
** The pressure values were taken according to the Kennedy scale ([6]).

the condition $c/a = \sqrt{6}$ is fulfilled. Photographs at $p = 90$ and 100 kbar confirmed the presence of a reversible phase transition in antimony at 85-90 kbar ([1,2]). They indicate a radical change in structure; the lines of the initial and primitive cubic phases are absent from the roentgenograms. The new phase is represented by four sharp lines and one very weak line, indexed in the closest-packed hexagonal structure with parameters: $a = 3.33$ Å, $c = 5.27$ Å, $c/a = 1.58$, $\rho_{\text{calc}} = 8.0$ g/cm^3 (Table 2).

It is necessary to note the presence of a certain discrepancy in the intensities of the lines on the roentgenogram of hexagonal antimony (at 90-100 kbar) in comparison with those usually observed in such structures, for example in magnesium.

Table 2

hkl	d_{calc}, Å	d_{obs}, Å	*I*
010	2.88	2.88	very weak
002	2.64	2.63	strong
101	2.53	2.53	medium
012	1.95	1.97	medium
110	1.67	no	diffuse
110	1.67	1.71 (?)	diffuse
112	1.41	1.40	medium

hkl	d_{calc}, Å	d_{obs}, Å	I
201	1.39	1.40	medium

Thus, the relative intensities of the first three lines (010), (002), and (101) in antimony are: very weak, strong, medium; whereas for magnesium they are: medium, medium, and strong. The pattern observed in antimony is similar to the data for α-lanthanum ([7]), in which the (002) reflection proves to be the strongest and (010) the weakest. The authors of ([7]) believe that the disturbance of the normal distribution of intensities is a consequence of absorption by the sample, more significant at small angles, and of the presence of an orientation effect. In our case one must also take into account distortion of the crystal lattice as a result of nonhydrostatic pressure. The picture is complicated by the presence of boron diffraction bands and a considerable background (incoherent scattering of boron), superposed on the lines of the substance under study. According to Bridgman' s data, the transition in antimony at 85–90 kbar is a first-order transition with a volume jump $\Delta v/v = 3.7\%$. Our data do not yet make it possible to estimate the net volume jump in Sb during the transition from the primitive cubic to the closest-packed hexagonal structure. For this, a roentgenogram of a mixture of both phases is necessary, obtained during an incomplete phase transition in the sample.

Phase transitions in antimony are accompanied by an increase in the coordination number. In the first transition, from the rhombohedral to the primitive cubic structure, the coordination number becomes equal to six (instead of three); in the transition to the closest-packed hexagonal structure, it becomes twelve. Correspondingly, the atomic radius of Sb for coordination number six is 1.48 Å ($p = 50$ kbar), and for twelve it is 1.64 Å ($p = 90$ kbar).

Thus, the results of the X-ray analysis have shown that Sb at $p = 90$ kbar has a close-packed hexagonal structure, characteristic of many typical metals under ordinary conditions.

Institute of High Pressure Physics
Academy of Sciences of the USSR

Received
13 VI 1963

REFERENCES

1. P. W. Bridgman, Proc. Am. Acad. Art. Sci., **74**, 425 (1942).

2. L. F. Vereshchagin, A. A. Semerchan et al., DAN, **136**, No. 2 (1961).

3. J. C. Jamieson, A. W. Lawson, J. Appl. Phys., **33**, No. 3, 776 (1962).

4. J. C. Jamieson, Science, **139**, No. 3556, 762 (1963).

5. S. S. Kabalkina, Z. V. Troitskaya, DAN, **151**, No. 5 (1963).

6. Kennedy LaMori, *Progress in Very High Pressure Research*, N.Y.–London, 1961, p. 304.

7. J. C. Lennan, McKay, Zs. anorg. Chem., **208**, 275 (1932).

Note: Figure translations are in progress. See original paper for figures.