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# Structure Determinations on Sb up to 85 × 10$^2$ MPa*

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## Abstract

High-pressure single-crystal structure determinations were performed on Sb in the *A*7 crystal structure type in the pressure range 63 to 85 × 10$^2$ MPa. The *A*7 structure initially approaches simple cubic, but then levels off. The transition from the *A*7 to the primitive simple-cubic structure, which was reported to occur in this pressure range by some previous workers, was not found. A transition to an undetermined structure was found at 86 × 10$^2$ MPa, a transition pressure reported by several workers.

## Introduction

In this paper, we describe crystal structure determinations for Sb in the pressure range 0–86 × 10$^2$ MPa. The structure of Sb under ambient conditions is the *A*7 rhombohedral type with space group $R\bar{3}m$ (Donohue, 1974; Wyckoff, 1963; Barrett & Massalski, 1967). There are six atoms per hexagonal unit cell, located at position 6(*c*) with one parameter, *z* (*International Tables for X-ray Crystallography*, 1952). In the *A*7 structure, the atoms are arranged in puckered layers, as can be seen in Fig. 51-1 of Donohue (1974). Within a puckered layer each atom has three neighbors with bond lengths $A_1$ and bond angles $\theta_1$. Each atom also has three next-nearest neighbors with bond lengths $A_2$ and bond angles $\theta_2$, located on the adjacent puckered layer. The *A*7 structure may be regarded as a distorted primitive simple-cubic structure. It would be true simple cubic if $A_1 = A_2$ and $\theta_1 = \theta_2 = 90°$, or, equivalently, if $c/a = \sqrt{6} = 2{\cdot}46$ and $z = 0{\cdot}250$.

There has been considerable experimental interest in the high-pressure crystallographic behavior of Sb. Bridgman (1924, 1925, 1949) measured the compressibilities in the **a** and **c** directions. Several authors have reported X-ray powder diffraction measurements of *a* and *c* at quasi-hydrostatic pressures up to about 90 × 10$^2$ MPa (Kabalkina, Vereshchagin & Mylov, 1963; Kolobyanina, Kabalkina, Vereshchagin & Fedina, 1968; Vereshchagin & Kabalkina, 1964; Kolobyanina, Kabalkina, Vereshchagin, Michkov & Kachan, 1970; Kabalkina, Kolobyanina & Vereshchagin, 1970; Kasper, 1969; McWhan, 1972). These authors agree that the ratio $c/a \rightarrow \sqrt{6}$ with increasing pressure and that there is a definite phase transition around 86 × 10$^2$ MPa. Kabalkina and co-workers report (after extensive experimental work) a transition around 70 × 10$^2$ MPa to the primitive simple cubic structure, while this transition is not observed by McWhan (1972).

The only previous determinations of *z* are by Morosin & Schirber (1969) who attained a maximum pressure of 3 × 10$^2$ MPa, and by Schiferl (1977), who attained a maximum pressure of 26 × 10$^2$ MPa. Both sets of measurements are in excellent agreement and show $z \rightarrow 0{\cdot}250$ with pressure.

The present work, which achieves the maximum of pressure where the *A*7 phase can be maintained, was intended to explore how closely the *A*7 structure approaches the simple cubic before it finally snaps into that structure, if indeed it could be made to do so.

## Experimental

The crystal structure determinations were made with a gasketed diamond-anvil cell designed for use on a Picker FACS-1 four-circle automatic diffractometer

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(Schiferl, Jamieson & Lenko, 1978). The 4:1 methanol:ethanol pressure medium (Piermarini, Block & Barnett, 1973) was used to ensure hydrostatic pressures. Pressures were measured before and after each run, using the ruby-fluorescence technique (Barnett, Block & Piermarini, 1973; Forman, Piermarini, Barnett & Block, 1972). Two single-crystal Sb samples prepared by the method of Schiferl (1977) were used in separate runs.

Our main interests were (1) to explore the nature of the *A*7 structure just before it transforms at high pressure, and (2) to attempt the simple cubic phase. It would have been desirable to collect data over the full pressure range 0–$86 \times 10^2$ MPa for this purpose. However, data had to be collected during the short time that one of us (DS) was visiting the University of Chicago. For this reason, we began our measurements above $60 \times 10^2$ MPa.

The high-pressure crystallographic techniques are described in detail elsewhere (Schiferl, 1977; d'Amour, Schiferl, Denner, Schulz & Holzapfel, 1978). The radiation was graphite-monochromatized Mo $K\alpha$. At each pressure, several X-ray reflections were scanned to check for strain or other damage to the sample. No damage was found below the phase transition at $86 \times 10^2$ MPa. Both Sb samples became polycrystalline upon passing through this phase transition. No studies were made on the new phase.

The lattice constants *a* and *c* of the *A*7 phase were determined from diffractometer measurements with the least-squares orientation program of Lenhert & Henry (1970). Twelve reflections were used; these spanned the maximum ranges of $\chi$ and $\varphi$ permitted by the geometry of the diamond cell and included a few reflections measured at $-2\theta$.

The atom position parameter *z* was determined from the intensities of approximately 80 reflections, of which about 35 were not symmetry-related. Equivalent reflections were averaged after being corrected for X-ray absorption by the diamond cell and the sample itself. Refinements were performed using the *LASL* system of crystallographic programs developed primarily by A. C. Larson. The X-ray scattering factors of Doyle & Turner (1968) and the anomalous-scattering factors of Cromer & Liberman (1970) were used. The refinements minimized $w(\Delta F)^2$ with $w$ determined from counting statistics. As a check, the refinement was repeated with unit weights, but the resulting values of *z* were not significantly different.

## Results and discussion

We did not observe the transition reported by Kabalkina and co-workers (Kabalkina *et al.*, 1963; Vereschchagin & Kabalkina, 1964; Kolobyanina *et al.*, 1968, 1970; Kabalkina *et al.*, 1970) from the *A*7 to the simple cubic at pressures below $86 \times 10^2$ MPa. We observed instead that the *A*7 approaches but does not attain the simple-cubic structure with pressure. At $86 \times 10^2$ MPa, we observed a transition to an unknown structure. The transition pressure of $86 \times 10^2$ MPa corresponds almost exactly to that of the transition reported by all other authors (Bridgman, 1941, 1949; Kasper, 1969; Kabalkina *et al.*, 1970; Kolobyanina *et al.*, 1970; McWhan, 1972).

Kabalkina & Kolobyanina (1979) have pointed out that the transition to the simple-cubic phase in Sb is very sluggish; they observed the complete transformation to simple cubic in only 6 cases out of 30. They suggest that the transition is very sensitive to shear stresses; thus, the exact nature of the quasi-hydrostatic environment and the powder mixture of Sb, B, and NaCl may be critical. They believe that McWhan (1972) might very well not see the simple-cubic phase in a few runs, and that our single-crystal

Table 1. *Crystallographic parameters of* Sb *as a function of pressure*

| *P* ($\times 10^2$ MPa) | *a* (Å) | *c* (Å) | *c*/*a* | *z* | $A_1$ (Å) | $A_2$ (Å) | $\theta_1$ (°) | $\theta_2$ (°) |
|---|---|---|---|---|---|---|---|---|
| 0 | 4·308 (0)[a] | 11·274 (0)[a] | 2·617 (0) | 0·23349 (31)[a] | 2·908 (4) | 3·355 (5) | 95·58 (30) | 79·89 (13) |
| 0 | – | – | – | 0·23357 (6)[b] | – | – | – | – |
| 0 | 4·319 (2) | 11·276 (2) | 2·611 (1) | ≡0·23349 (31)[a] | 2·914 (4) | 3·360 (5) | 95·65 (31) | 79·99 (14) |
| 3 | 4·302 (8)[c] | 11·224 (22)[c] | 2·609 (3) | 0·23389 (4)[b] | 2·906 (3) | 3·339 (5) | 95·50 (13) | 80·21 (12) |
| 7 | 4·292 (8)[c] | 11·157 (22)[c] | 2·599 (3) | 0·23475 (20)[d] | 2·907 (5) | 3·314 (5) | 95·16 (25) | 80·72 (14) |
| 12·5 | 4·282 (8)[c] | 11·065 (22)[c] | 2·584 (3) | 0·23575 (20)[d] | 2·907 (5) | 3·283 (5) | 94·87 (25) | 81·41 (14) |
| 15 | 4·275 (8)[c] | 11·024 (22)[c] | 2·579 (3) | 0·23580 (60)[d] | 2·901 (8) | 3·274 (9) | 94·92 (60) | 81·53 (28) |
| 26 | 4·252 (8)[c] | 10·840 (22)[c] | 2·549 (3) | 0·23790 (60)[d] | 2·900 (8) | 3·210 (9) | 94·28 (60) | 82·94 (28) |
| 63 ± 1 | 4·214 (1) | 10·569 (1) | 2·508 (1) | 0·23966 (16) | 2·881 (2) | 3·137 (2) | 94·00 (16) | 84·40 (7) |
| 68 ± 1 | 4·210 (1) | 10·530 (2) | 2·501 (1) | 0·24009 (14) | 2·887 (2) | 3·125 (2) | 93·89 (14) | 84·70 (6) |
| 71·5 ± 1·5 | 4·198 (1) | 10·485 (2) | 2·498 (1) | 0·24071 (14) | 2·878 (2) | 3·106 (2) | 93·65 (14) | 85·05 (6) |
| 77 ± 2 | 4·196 (1) | 10·455 (2) | 2·492 (1) | 0·24098 (16) | 2·878 (2) | 3·098 (2) | 93·60 (16) | 85·05 (6) |
| 85 ± 1 | 4·172 (7) | 10·385 (2) | 2·489 (4) | – | – | – | – | – |

References: (*a*) Barrett, Cucka & Haefner (1963). (*b*) Morosin & Schirber (1969). (*c*) Kolobyanina *et al.* (1970). (*d*) Schiferl (1977).

Table 2. *Observed and calculated structure factors for* Sb *at high pressures*

| | | | $63 \times 10^2$ MPa | | $68 \times 10^2$ MPa | | $72 \times 10^2$ MPa | | $77 \times 10^2$ MPa | |
|---|---|---|---|---|---|---|---|---|---|---|
| $h$ | $k$ | $l$ | $F_o$ | $F_c$ | $F_o$ | $F_c$ | $F_o$ | $F_c$ | $F_o$ | $F_c$ |
| 0 | 0 | 9 | 69 | 73 | 66 | 70 | 62 | 66 | 58 | 65 |
| 0 | 2 | 7 | 59 | 58 | 57 | 55 | 54 | 52 | 52 | 51 |
| 1 | 1 | 9 | 64 | 62 | 61 | 59 | 56 | 56 | 57 | 55 |
| 1 | 0 | 10 | 79 | 88 | 80 | 89 | 83 | 92 | 82 | 93 |
| 0 | 3 | 6 | 99 | 101 | 99 | 100 | 101 | 102 | 101 | 102 |
| 1 | 2 | 8 | 89 | 88 | 88 | 88 | 92 | 90 | 91 | 91 |
| 0 | 2 | 10 | 75 | 76 | 76 | 76 | 79 | 79 | 81 | 80 |
| 0 | 0 | 12 | 63 | 64 | 65 | 64 | 68 | 68 | 72 | 69 |
| 2 | 0 | 11 | 56 | 55 | 54 | 52 | 51 | 50 | 48 | 49 |
| 0 | 3 | 9 | 42 | 46 | 42 | 44 | 39 | 42 | 39 | 40 |
| 3 | 0 | 9 | 46 | 46 | 44 | 44 | 42 | 42 | 40 | 40 |
| 1 | 3 | 7 | 36 | 36 | 34 | 35 | 31 | 33 | −33 | 32 |
| 1 | 0 | 13 | 62 | 56 | 58 | 53 | 58 | 51 | 57 | 49 |
| 1 | 2 | 11 | 50 | 48 | 47 | 46 | 45 | 44 | 44 | 43 |
| 2 | 2 | 9 | 40 | 40 | 38 | 38 | 36 | 36 | 35 | 35 |
| 0 | 4 | 8 | 63 | 58 | 63 | 58 | 62 | 59 | 66 | 60 |
| 0 | 2 | 13 | 49 | 49 | 44 | 46 | 43 | 45 | 43 | 44 |
| 1 | 3 | 10 | 56 | 50 | 57 | 51 | 59 | 53 | 60 | 53 |
| 3 | 0 | 12 | 42 | 43 | 43 | 43 | 46 | 46 | 46 | 46 |
| 0 | 3 | 12 | 45 | 43 | 46 | 43 | | | 46 | 46 |
| 0 | 0 | 15 | 45 | 48 | 44 | 46 | 43 | 45 | 43 | 44 |
| 2 | 1 | 13 | 41 | 43 | 41 | 41 | 39 | 40 | 38 | 39 |
| 2 | 2 | 12 | 40 | 38 | 39 | 38 | 38 | 41 | 39 | 41 |
| 1 | 1 | 15 | 44 | 43 | 43 | 41 | 41 | 40 | 40 | 39 |
| 0 | 4 | 11 | | | 32 | 32 | 31 | 30 | | |
| 1 | 3 | 13 | 29 | 34 | 30 | 32 | 29 | 31 | 28 | 31 |
| 3 | 0 | 15 | 31 | 34 | 30 | 32 | 30 | 32 | 28 | 31 |
| 0 | 3 | 15 | 32 | 34 | 31 | 32 | 33 | 32 | 30 | 31 |
| 2 | 0 | 17 | 35 | 34 | 34 | 32 | 33 | 31 | 33 | 31 |
| 0 | 0 | 18 | −31 | 15 | −24 | 16 | −29 | 18 | −30 | 19 |
| 2 | 2 | 15 | 29 | 31 | 28 | 29 | 27 | 28 | 26 | 28 |
| 1 | 2 | 17 | −24 | 30 | 23 | 29 | 24 | 28 | 24 | 27 |
| 1 | 0 | 19 | 27 | 29 | 25 | 28 | 25 | 27 | 25 | 27 |
| 2 | 1 | 19 | −21 | 24 | −20 | 22 | 20 | 22 | −20 | 22 |
| 0 | 0 | 21 | −22 | 22 | 20 | 21 | −21 | 21 | −21 | 21 |

samples under hydrostatic pressure would fail to transform.

The results for the unit-cell parameters and structure refinement of the $A7$ structure are presented along with earlier work in Table 1. The thermal parameters were influenced considerably by absorption-correction errors and are therefore not reported here. The estimated standard deviations are given in parentheses, but there is also a systematic error in the lattice constant $a$ at zero pressure and possibly at high pressure due to miscentering. The observed and calculated structure factors given in Table 2 are in good agreement. The values of $R$ were: 5·8% at 63 × $10^2$ MPa, 5·7% at 68 × $10^2$ MPa, 5·4% at 71·5 × $10^2$ MPa and 6·5% at 77 × $10^2$ MPa.

The values of $c/a$ are compared with those obtained by earlier workers in Fig. 1. The values of McWhan (1972) (open squares) were converted from his plot of $c/a$ *versus* $(V - V_0)/V_0$ using the least-squares fit of Kolobyanina *et al.* (1970) and Kabalkina & Kolobyanina (1979) for $V/V_0$; the scatter of their individual data points is about the same as that of McWhan (1972).

The bond distances $A_1$ and $A_2$ are shown as a function of pressure in Fig. 2. The bond angles $\theta_1$ and $\theta_2$ are shown *versus* pressure in Fig. 3. For pressures up to 26 × $10^2$ MPa, these quantities are calculated with the $z$ parameters of Morosin & Schirber (1969) and Schiferl (1977) and the lattice constants of Kolobyanina *et al.* (1970).

Within each puckered layer, the effects of pressure are small. Increasing pressure from 0 to 77 × $10^2$ MPa reduces $A_1$ by less than 1% and reduces $\theta_1$ by only 2°. This behavior is characteristic of covalent bonding, which favors rather rigid bond lengths and bond angles.

Rapid changes in $A_2$ and $\theta_2$ with pressure come about as adjacent puckered layers are pushed much closer together. However, both $A_2$ and $\theta_2$ level off with

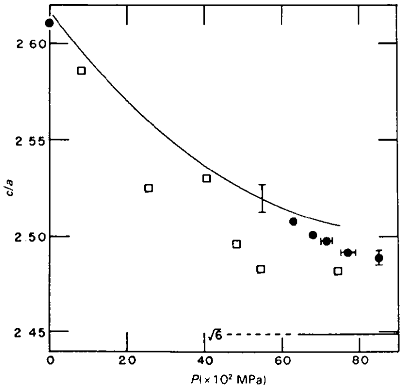

Fig. 1. Ratio $c/a$ as a function of pressure. The present results are shown by the solid circles; the absence of error bars indicates that they are smaller than the circles. The results of McWhan (1972) are shown by the open squares with no error bars assigned. The solid line is from Kolobyanina *et al.* (1970); the error bar indicates the standard deviation of the fitted curve.

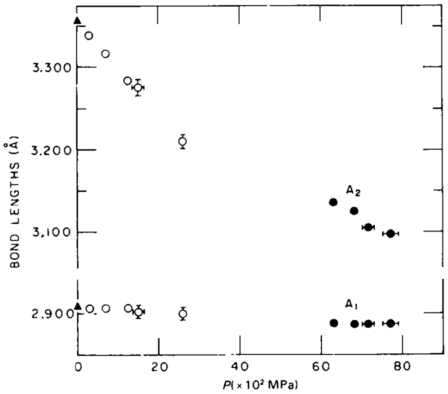

Fig. 2. Bond distances $A_1$ and $A_2$ as a function of pressure. Solid circles represent the present work; solid triangles are from Barrett *et al.* (1963); open circles are from earlier high-pressure work summarized in Table 1. Absence of error bars indicates that they are smaller than the symbols for the points.

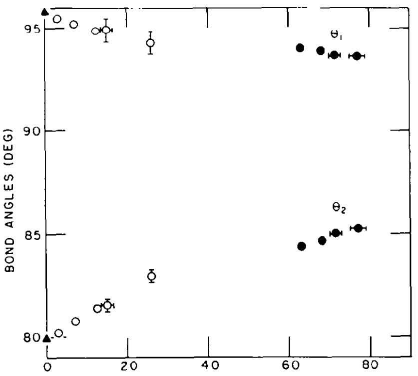

Fig. 3. Bond angles $\theta_1$ and $\theta_2$ as a function of pressure. Solid circles represent the present work; solid triangles are from Barrett *et al.* (1963); open circles are from earlier high-pressure work summarized in Table 1. Absence of error bars indicates that they are smaller than the symbols for the points.

pressure. Long before $A_2$ becomes equal to $A_1$, or $\theta_2$ becomes equal to $\theta_1$, as would be required for a continuous transformation to the simple cubic, the 86 × 10² MPa transition intervenes.

The work of Kabalkina and co-workers indicates that if phase equilibrium could be maintained, a jump to the simple-cubic structure would occur at even lower pressure. It is not surprising that a transition from the *A*7 to the simple cubic be discontinuous. Black P shows such a discontinuous transition (Jamieson, 1963). Moreover, Cohen, Falicov & Golin (1964) have shown that the nature of the bonding in the simple-cubic and *A*7 phases is fundamentally different. The bonding in the simple-cubic phase is purely *sp* metallic, but in the *A*7 it is predominantly covalent. It *is* surprising that drastic changes in structure and bonding induced by this transition are not accompanied in Sb by a large volume change similar to that observed in the corresponding transition in black P.

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