

Structural Systematics of the High-Pressure Phases of Phosphorus, Arsenic, Antimony and Bismuth

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Abstract

New structural systematics of the high-pressure phases of the title elements are given on the basis of the results obtained in our diffraction studies and the results from the literature. Although the structural transition sequence with increasing pressure appears to be different for the four elements, reinterpretation of the structure data has shown that it is expressed in a systematic way as follows

P	A17–A7–PSC	
As	A7–PSC–	dist. BCC–BCC
Sb	A7–	dist. BCC–BCC
Bi	A7–dist. PSC–	dist. BCC–BCC.

Notations used are A17 (orthorhombic layered structure), A7 (rhombohedral layered structure), PSC (primitive simple cubic structure), dist. PSC (monoclinic structure which is regarded as a distorted PSC), BCC (body-centered cubic structure) and dist. BCC (tetragonal structure which is regarded as a distorted BCC). Phosphorus lacks the post-PSC phases, but it is likely that the same transition sequence as that of arsenic is seen under extremely high pressure. Discussion is made on how the network of the densest atomic plane changes through the structural transition sequence.

1. Introduction

Phosphorus, arsenic, antimony and bismuth crystallize in accordance with the $(8 - N)$ rule, N being the group number of the elements, in the structure with atomic coordination number 3. This structure is the rhombohedral A7 structure for the latter three elements, while it is the orthorhombic A17 (black P) structure for phosphorus. Both structures are characterized by the presence of extended puckered layers of atoms with significantly larger distances between atoms on the adjacent layers than the distances in the layer. The difference between the A7 and A17 structures lies in the mode of layer puckering (Hulliger, 1976; Kikegawa & Iwasaki, 1983).

A number of studies were made on the effects of pressure on the crystal structure of the four elements and it was found that they are wealthy in high-pressure polymorphic phases. The trend in the structural phase transitions with increasing pressure is first a decrease in the layer character of the structure, as expected, but the structures forming subsequent to the layered structure appear to be different for different elements. Moreover, there were several phases whose existence was known, but whose structure had been left undetermined.

We carried out a series of X-ray and synchrotron radiation diffraction studies under high pressure on the elements and, in addition to finding a new structural phase transition in arsenic (Kikegawa & Iwasaki, 1987), succeeded in determining the crystal structure of the several phases of antimony and bismuth (Iwasaki & Kikegawa, 1990; Iwasaki, Chen & Kikegawa, 1995; Chen, Iwasaki & Kikegawa, 1996, 1977). We also reinterpreted the structure data published in the literature (Chen, Iwasaki & Kikegawa, 1997; Iwasaki, 1997). Recently, Greene, Luo & Ruoff (1995) found the formation of new phases in arsenic at very high pressures. With all the structure data presently available to hand, we made an attempt to establish the structural systematics of the high-pressure phases of the group VB elements. In the following first the crystal structures of the phases of each element are described and a table is then given showing the structural systematics. Finally, we discuss how the network of the densest atomic plane changes through the structural phase transitions.

2. Structure of the high-pressure phases

2.1. Phosphorus

Jamieson (1963) found that the A17 structure of phosphorus is transformed upon compression into the A7 structure, thus confirming that all four elements have the A7-type layered structure in common. He also found that it is further transformed into the primitive simple cubic (PSC) structure. It is notable that this structure remains stable over a wide range of pressure from 10 to at least 33 GPa (Kikegawa & Iwasaki, 1983), in spite of

the low packing fraction of atoms. The highest pressure at which the PSC phase was observed to be stable was extended to 80 GPa (Akai, Nagatomo, Endo, Akahama & Narita, 1983). There has been no study showing the existence of a post-PSC phase.

2.2. Bismuth

Bismuth is the element best studied among the four. The *A7* structure of BiI is stable up to 2.55 GPa and the second phase forms, whose structure is not PSC but monoclinic, named BiII (Brugger, Bennion & Worlton, 1967). It may also be regarded as a layered structure with atomic coordination number 3, but the layer character is considerably diminished (Hulliger, 1976). It was shown (Chen, Iwasaki & Kikegawa, 1996) that if the near-neighbor distance is redefined in such a way that it includes the distances in the range 1.0–1.1 in relative magnitude, each atom in the BiII structure is surrounded by six atoms and therefore it can be regarded as a distorted PSC (dist. PSC) structure.

BiII is stable in a limited pressure range and is transformed into BiIII, which has a rather complicated diffraction pattern. Using high-energy synchrotron radiation to obtain diffraction patterns of improved quality, we determined the structure to be tetragonal with relatively large lattice parameters (Iwasaki, Chen & Kikegawa, 1995; Chen, Iwasaki & Kikegawa, 1996). It can be regarded as a distorted body-centered cubic (dist. BCC) structure. It was also shown that the phase BiIII',* which forms at pressures higher than the existing range of BiIII, has the same crystal structure as that of BiIII (Chen, Iwasaki & Kikegawa, 1996).

With a further increase in pressure, BiIII' is transformed at 7.7 GPa into the phase BiV,* with a BCC structure (Schaufelberger, Merx & Contre, 1973). It is stable up to at least 40 GPa (Aoki, Fujiwara & Kusakabe, 1982).

It is to be noted that phase BiV* located on the high-temperature side of the BiIII region in the P-T phase diagram has monoclinic crystal structure and is regarded as another type of dist. BCC structure (Chen, Iwasaki & Kikegawa, 1997)†.

2.3. Antimony

With the application of pressure to the *A7* structure of antimony, the lattice parameters are gradually changed so that the structure approaches closely the PSC structure at 6.4 GPa, but no clear indication of the

formation of this structure was found (Iwasaki & Kikegawa, 1986). The phase forming subsequent to the *A7* phase, designated as SbII, is isotypic to BiIII (Iwasaki & Kikegawa, 1990) with a small difference in the degree of distortion.

At 28 GPa SbII is transformed into the phase having the BCC structure (Aoki, Fujiwara & Kusakabe, 1983). It is stable up to at least 43 GPa.

2.4. Arsenic

The *A7* structure of arsenic is the most stable against compression and it is around 32 GPa that a structural phase transition takes place (Kikegawa & Iwasaki, 1987). The structure of the post-*A7* phase is PSC, as is the case with phosphorus. The transition pressure was later redetermined to be 25 GPa (Beister, Strossner & Syassen, 1990).

The PSC structure remains unchanged up to ~48 GPa and a new phase, designated as AsIII, forms whose structure was identified to be of the orthorhombic α -Np type (Greene, Luo & Ruoff, 1995). However, Iwasaki (1997) showed that although the α -Np structure can explain the observed *d* values, it does not provide intensities of the diffraction peaks which are compatible with the observed ones. Instead, it was shown that the tetragonal BiIII or SbII structure is more appropriate with respect to the *d* values as well as the intensities for a structure model of AsIII.

A third structural transition takes place at ~97 GPa and a phase having the BCC structure forms (Greene, Luo & Ruoff, 1995).

3. Structural systematics of the high-pressure phases

Having reviewed the crystal structures of the high-pressure phases of phosphorus, arsenic, antimony and bismuth, we are in a position to express the sequence of structural phase transitions in a systematic form.

Table 1 shows the results. As mentioned above, the *A7* structure forms in all four elements. It is transformed with increasing pressure into the PSC structure in phosphorus and arsenic, while that structure does not form in the heavier two elements. However, in antimony the *A7* structure approaches the PSC structure so closely that 'a slightly distorted PSC structure' forms (Iwasaki & Kikegawa, 1986). In bismuth the dist. PSC structure forms subsequent to the *A7* structure. The mode of distortion is, however, different (Chen, Iwasaki & Kikegawa, 1996). These facts show that the stability of the PSC structure decreases with increasing atomic number and it appears only as a quasi-form in antimony and bismuth.

The structure forming next in the sequence is the dist. BCC structure in arsenic, antimony and bismuth, which is further transformed into the BCC structure. Phosphorus appears to lack the post-PSC phases, but the

* Phase designations follow those adopted by Pistorius (1976).

† According to the results of resistometric measurements (*e.g.* Homan, 1975), the existing range of pressure for BiIII becomes narrower with decreasing temperature, terminating at a triple point at 160 K. The measurements also suggested the existence of two new phases of cryogenic temperatures at pressures higher than 6 GPa. Since no confirmation by diffraction was made, they are not taken into account in the present study.

Table 1. *Structural systematics of phosphorus, arsenic, antimony and bismuth*

P	A17-A7-PSC	
As	A7-PSC-	dist. BCC-BCC
Sb	A7-	dist. BCC-BCC
Bi	A7-dist. PSC-	dist. BCC-BCC.

Notations used are A17 (orthorhombic layered structure), A7 (rhombohedral layered structure), PSC (primitive simple cubic structure), dist. PSC (monoclinic structure, which is regarded as a distorted PSC), BCC (body-centered cubic structure) and dist. BCC (tetragonal structure, which is regarded as a distorted BCC).

transition sequence in the other three elements suggests that the dist. BCC and BCC structures form, although the relevant pressure is extremely high.

The general trend in the structural phase transitions in the Group VB elements is summarized in the following way: the structures belonging to the PSC family, A17, A7, PSC and dist. PSC, are stable at lower pressures and they are transformed into those belonging to the BCC family, dist. BCC and BCC.

There have been many theoretical investigations of the stability of various crystal structures forming in the group VB elements. Most attention has been paid to the relative stability of the A7 and PSC structures in phosphorus (Schiferl, 1979; Chang & Cohen, 1986a; Sasaki, Shindo, Niizeki & Morita, 1988), arsenic (Mattheiss, Hamann & Weber, 1986; Needs, Martin & Nielsen, 1986; Chang & Cohen, 1986b) and antimony (Chang & Cohen, 1986b). The formation of the A17 structure in phosphorus was attacked by Schiferl (1979) and Chang & Cohen (1986a), but no investigation was made as to why it does not form in the other three elements. Shindo, Sasaki & Orita (1989) extended the total energy calculation to the BCC structure in arsenic and antimony and obtained successful results for its relative stability to the PSC structure. A similar investigation was made on bismuth by Aoki, Fujiwara & Kusakabe (1982). No investigation has, however, been made on the dist. BCC structure nor to establish a generalized view of the stability of the phases in the four elements. It is left as a future task.

4. Sequence of the structural phase transitions seen through a change in the network of the densest atomic planes

Crystal structure is considered as a stacking of atomic planes with a definite interplanar spacing d . For the crystal structures having a high symmetry, such as PSC, BCC *etc.*, all kinds of atomic planes are planar and the magnitude of the structure factor $|F(hkl)|$ is the same. In this case the densest atomic plane, the plane with the largest number of atoms per unit area, is that with the largest d value. This plane is $\{100\}$ for the PSC structure and $\{110\}$ for the BCC structure. For the

crystal structures with complicated atomic arrangements, many atomic planes are in general puckered or corrugated and, therefore, $|F(hkl)|$ is smaller. It is possible, however, to find in such crystal structures an atomic plane which is almost planar with a relatively large d value. It shows the strongest (or appreciably strong) peak in the low scattering angle region in a powder diffraction pattern.

Comparison of the diffraction patterns of various phases of the group VB elements shows that the strongest (or appreciably strong) peak in these patterns is located at the corresponding position throughout the sequence of the high-pressure phase transitions. It is, for example, the 012 reflection of the A7 structure of BiI ($d = 0.3280$ nm at 0.1 MPa), the 200 reflection of the monoclinic structure of BiII ($d = 0.3129$ nm at 2.6 GPa), the 211 reflection of the tetragonal structure of BiIII ($d = 0.2860$ nm at 3.8 GPa) and the 110 reflection of the BCC structure of BiV ($d = 0.2673$ nm at 9 GPa). The atomic planes that have produced these reflections must be planar or nearly planar and therefore have the largest number density of atoms in the plane. The fact that the d value of the densest plane *gradually* decreases through the sequence of the phase transitions suggests that the number density gradually changes.

Figs. 1(a)-(f) depict the network of the two successive most dense atomic planes of the A17, A7, PSC, dist. PSC, dist. BCC and BCC structures forming in the group VB elements projected onto the plane. For the sake of comparison, that of the BiIV structure is shown in Fig. 1(g). The lines connecting atoms represent the near-neighbor distances and the broken lines represent longer distances. It is seen that for the PSC and A7 structures the network of the densest plane, Figs. 1(c) and (b), respectively, is square or almost square and the two successive planes stack immediately above each other. For the A17 structure, Fig. 1(a), a similar situation holds, although the network is somewhat distorted in the $[001]$ direction. The network of the plane of the dist. PSC structure, Fig. 1(d), is considerably distorted and the two successive planes are slightly shifted in the plane relative to each other. In the BCC structure the network of the plane, Fig. 1(f), is rhombic and the two successive planes stack with a definite parallel shift above each other. A similar situation holds for the dist. BCC structure, although the network is distorted, Fig. 1(e). The network of the BiIV structure, Fig. 1(g), looks somewhat different from those of the others, but it can be derived from the (110) plane of the BCC structure by introducing a different type of distortion.

It is not unreasonable to assume that the densest atomic plane of a high-pressure phase forms parallel to the densest plane of the preceding phase on the structural transition. It is possible then to see the possible movements of atoms by following the change in

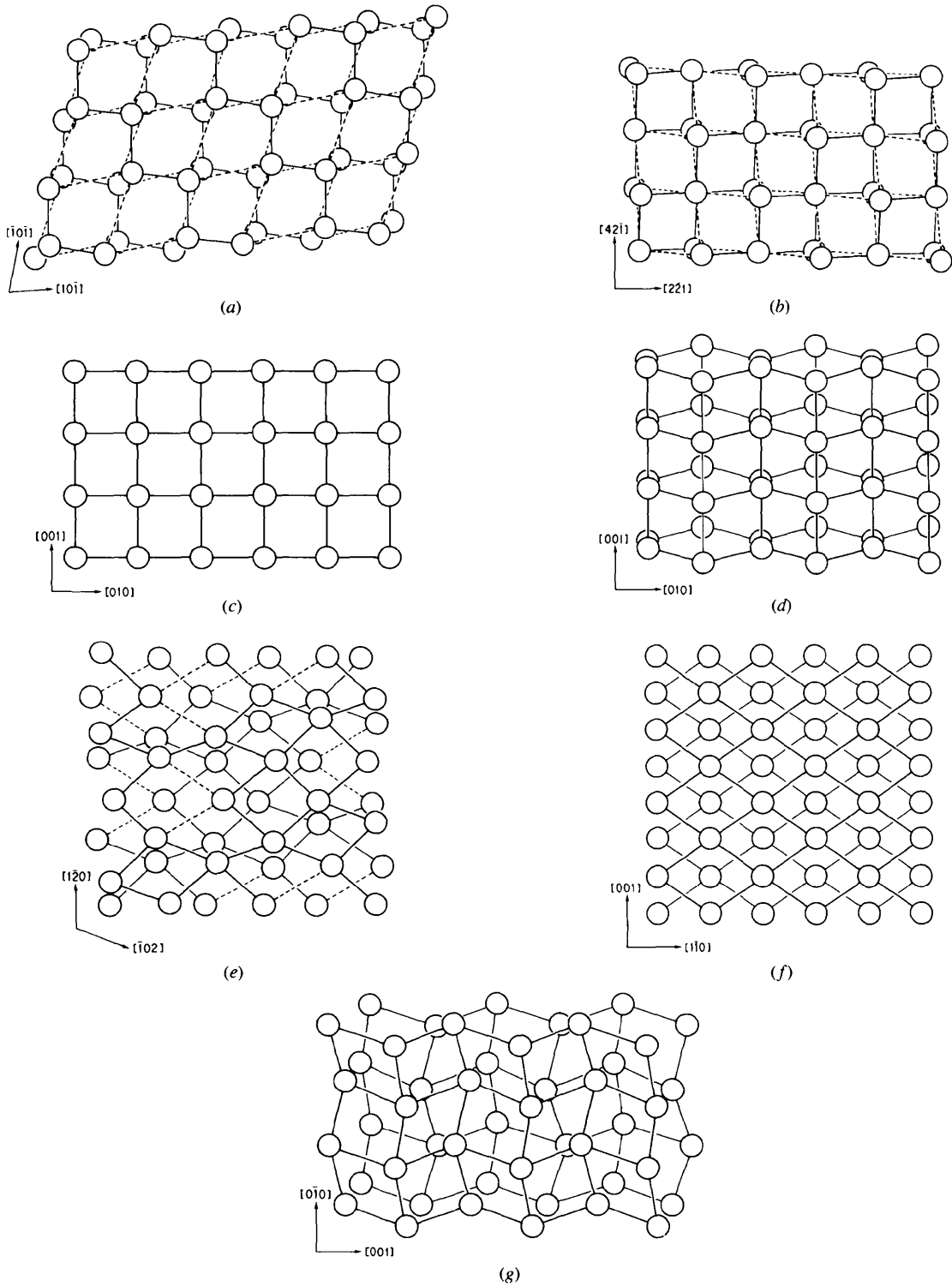


Fig. 1. Network of the densest atomic plane of the solid phases forming in phosphorus, arsenic, antimony and bismuth. (a) (010) plane of the A17 (black P) structure; (b) (012) plane of the A7 structure; (c) (100) plane of the primitive simple cubic (PSC) structure; (d) (100) plane of the distorted PSC structure of BiII; (e) (211) plane of the distorted body-centered cubic structure (dist. BCC) of BiIII; (f) (110) plane of the BCC structure; (g) (100) plane of the BiIV structure. The solid lines connecting the atoms represent the near-neighbor distances and the broken lines represent longer distances.

network of the densest plane. For instance, it is seen in the sequence A7-dist. PSC-dist. BCC-BCC of bismuth how displacements of atoms proceed from the almost square network (A7) to the rhombic network (BCC) via the formation of intermediate networks.

Comparison of the networks of the densest atomic planes in Fig. 1 further suggests that in the structure analysis of a high-pressure phase, knowledge of the network of the densest plane of the preceding phase helps to construct a model of the network of the corresponding plane of the high-pressure phase, if there is correspondence in the location of the strongest peak between the two phases: the structure of the network of one phase must not be very much different from the other.

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