Sequence of changes in the crystal structure of elements of group IV-B as the pressure rises, accompanied by an increase in the c.n. and in the packing factor φ

Lattice type	A9	A4	A5	A2	A1	A3
C. N.	3	4	6	6.2	6—6	12
φ	0.171	0.340	0.535	0.680	0.740	0.740

silicon, germanium and carbon to have a phase with an fcc or hcp type A3 structure.

9. ELEMENTS OF GROUP V-B

The phase diagrams of elements in this group also exhibit a clear sequence with increasing atomic number; this can be seen even in the very incomplete diagrams available at present.

Under normal conditions, phosphorus has several allotropic forms—white, yellow, and red phosphorus, but the greatest interest lies in the semiconducting modification, black phosphorus, which exhibits properties close to those of elements in group V-B. The orthorhombic crystal structure, with one centered face (8 atoms in a cell, c.n. = 3) of black phosphorus, is characteristic also of one of the allotropic modifications of arsenic.

The stable form of arsenic is so-called metallic arsenic, with the rhombohedral type A7 structure. The remaining members of group V-B—antimony and bismuth—also crystallize in this structure.

Figure 19a shows a part of the P–T diagram of black phosphorus. Its fusion curve has been determined up to 20 kbar,[87] and the boundaries between the modifications are indicated only by points obtained at room temperature. The transition to P II was found from a volume discontinuity at 50 kbar[20], using x-ray structure analysis at 80 kbar;[88] this transition was slow and was accompanied by a strong hysteresis. X-ray-diffraction studies showed that at this transition the orthorhombic layered structure of black phosphorus P I changed to the arsenic type A7 structure. Under further compression, there was another transition at 124 kbar and the resultant P III modification has the primitive cubic structure.[88]

The P–T phase diagram of arsenic is shown in Fig. 19b. Again, only certain parts of the diagram are known with certainty. The fusion curve plotted up to 60 kbar was obtained by differential thermal analysis,[89] and the polymorphic transition to the As II phase was found at 100 kbar; Bridgman's investigations of arsenic showed no volume discontinuities although he found that the volume decrement behaved

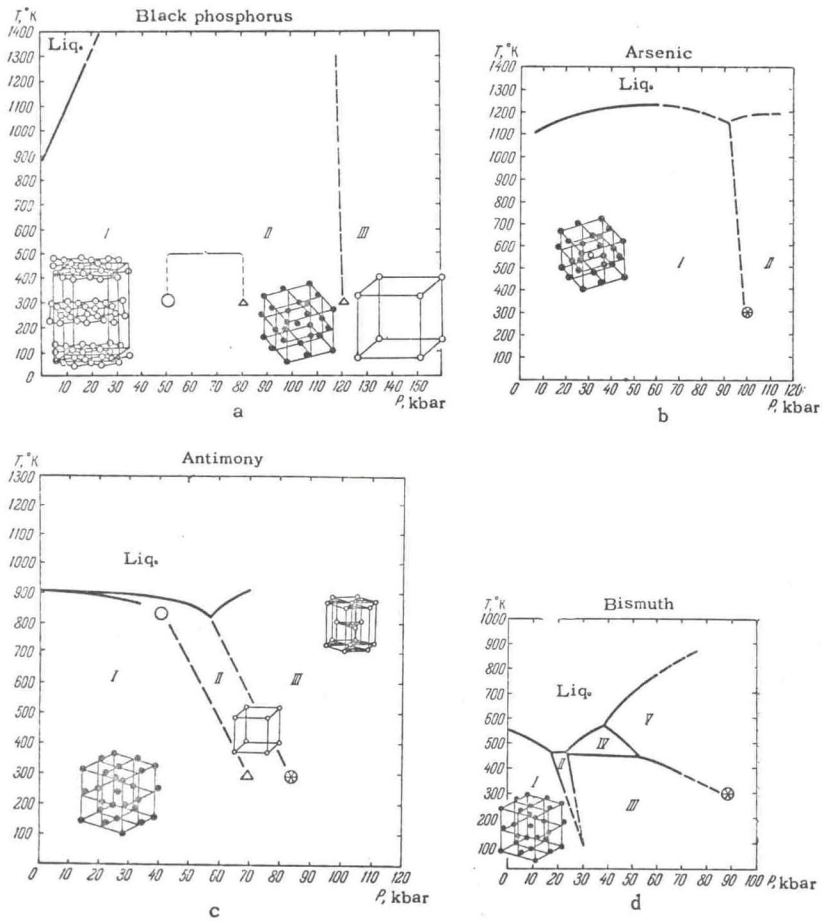

FIG. 19. a) P – T diagram of black phosphorus. The fusion curve was found by the DTA method;[87] the circle denotes conditions under which volume discontinuity was obtained,[20] and the triangles represent the coordinates of the transitions found by the x-ray diffraction method.[88] b) P – T diagram of As. The fusion curve was determined by the DTA method;[89] the "star" denotes the coordinates of polymorphic transition found from an electrical resistance discontinuity.[21] c) P – T diagram of antimony. The upper curve was reported in[89] and the lower in[87]. The circle denotes a hypothetical triple point,[87] the triangle gives the coordinates of a polymorphic transition found by x-ray structure analysis[90] and the "star" is used for the coordinates of a transition found from an electrical resistance discontinuity.[19] d) P – T diagram of bismuth, according to the DTA method.[89]