anomalously at the highest pressures produced by his apparatus, i.e., 100 kbar.[20] Bridgman found that the electrical resistance curve dropped rapidly at 100 kbar, from which he concluded that a polymorphic transition takes place at this pressure.[21] The possible boundary between normal arsenic and its high-pressure phase is shown dashed in Fig. 19b. The present author is of the opinion that the structure of the As II phase is most likely to be cubic primitive; the answer may be found by considering the P–T phase diagrams of antimony and bismuth.

Metallic antimony has the A7 type structure and is an analog of its neighbors in the group—arsenic and bismuth. At present, three modifications of antimony are known. Its fusion curve has been determined up to 70 kbar; it has a negative slope for the first two phases and a positive one for the third (Fig. 19c). One minimum has been found in the fusion curve[89] where it meets the boundary between the two solid phases, Sb II and Sb III. The lower fusion curve shown in Fig. 19c was reported in [87]. It is interesting to note that the author of the latter paper suggested that the P–T diagram of antimony should also have a triple point at the coordinates 37 kbar and 840°K. It is very likely that this hypothetical triple point does indeed exist and is a point at which the boundary between the solid phases Sb I and Sb II meets the fusion curve. The polymorphic transition Sb I–Sb II is accompanied by a very small change in volume and, therefore, it is not detected in "free plunger" apparatus which is used to determine volume discontinuities in polymorphic transitions. However, the existence of this transition was proved by an x-ray diffraction investigation.[90] When the pressure is increased to 70 kbar, the diffraction pattern of the normal modification Sb I disappears and reflections of the high-pressure phase Sb II appear. Analysis of the results shows that this modification has the primitive cubic structure. X-ray analysis also made it possible to establish the structure of the third phase of antimony–Sb III, which appeared at 85 kbar; it was found to have the hcp type A3 structure with the axis ratio $c/a = 1.58$.

The P–T phase diagram of bismuth has been investigated in greater detail than the diagrams of its neighbors. The diagram plotted in Fig. 19d follows [89]. This diagram indicates five polymorphic modifications coexisting in the range of pressures up to 100 kbar. It should be mentioned that Bridgman found eight modifications in this range of pressures.[37] The crystal structure is known only for normal bismuth Bi I—it is rhombohedral type A7. Several attempts have been made recently to obtain x-ray diffraction patterns of the high-pressure phases of bismuth but not all of them have been successful.[16,92–94] This is because the stability zone of the Bi II modification is very narrow. The Debye diffraction patterns obtained were probably the result of the superposition of the patterns of three bismuth modifications, Bi I, Bi II, Bi III, because there is usually a pressure gradient in an x-ray high-pressure chamber. Moreover, it is difficult to obtain x-ray diffraction patterns of bismuth under pressure because of its exceptionally low scattering power, so that weak intensity reflections may be lost completely in the patterns obtained.

Since there are no x-ray-diffraction data on the high-pressure phases of bismuth, all we can do is to offer some suggestions about their structures. For example, it is concluded in [89] that the structure of the Bi II modification is close to the hexagonal type with three atoms in a cell because Bi–Tl alloys have a phase of the substitutional solid solution type, which has the hexagonal disordered structure. Other workers[94] are of the opinion that the lattice of the Bi II phase is very close to the bcc type because eightfold coordination has been found in liquid bismuth near the fusion curve, i.e., each atom has eight nearest neighbors[95], and we can cite other examples when the structure of a high-pressure phase has the same coordination as the liquid near the fusion curve.

Hypotheses have also been advanced about the crystal structures of other modifications of bismuth:[94] Bi II → A2, Bi III → A3, Bi IV → A2, Bi V → A1.

We shall now consider again the P–T phase diagrams of all the elements of group V-B. They have many common features. First, there is the purely outward similarity of the diagrams which is repeated, with slight changes, from neighbor to neighbor. The slope of the fusion curves of the initial phases changes gradually from positive in the case of phosphorus to negative in the case of bismuth; it is likely that the slopes of the boundaries between the solid phases also change gradually from element to element. As the atomic number increases, the P–T diagrams tend to become compressed in the direction of lower pressures and temperatures, so that the diagram of each of these elements can be obtained by expanding or compressing the P–T diagram of its neighbor.

The most remarkable is the feature that the sequence in the crystal structure changes of the polymorphic modifications which is the same for the whole group: orthorhombic lattice with one centered face (black phosphorus P I) → orthorhombic type A7 (P II, As, Sb, Bi) → primitive cubic (P III, As II?, Sb II, Bi II?) → hcp type A3 (Sb III, → Bi III?) → fcc type A1 (Bi V?). This sequence of structures corresponds to an increase in the coordination number of the atomic packing, i.e., an increase in the pressure provides each atom with a tighter environment of neighbors (c.n.: 3 → 6 → 12).

We have placed question marks against some of the modifications in the above sequence—their structures are not yet established and they may not follow the sequence. A discussion of elements of group V-B given in [96] showed that under normal conditions the energetically favored transition was from the cubic primitive to the rhombohedral type A7 structure and that