bismuth could be relatively easily, i.e., at relatively low pressures, transformed into the metallic state with the primitive cubic structure. The A7 structure can be easily pictured by representing two face-centered lattices slightly elongated along the diagonal and displaced by a very small amount with respect to each other; this amount is known as the position parameter u. In the fcc lattice, we can distinguish a unit rhombohedron having a vertex angle of 60°. If the two face-centered lattices are displaced until the position parameter becomes u = 0.250, we obtain a lattice with a unit cell in the form of a primitive cube. Thus, the arsenic A7 type structure represents only a small deviation from the primitive cube; this deviation is less for bismuth and greater for arsenic. High pressures destroy the A7 structure distortion and the lattice becomes primitive cubic.

Thus, if bismuth is placed in a general sequence of elements in group V-B, we may expect the following sequence of structural changes: Bi I—rhombohedral type A7; Bi II—primitive cubic; Bi III—hcp type A3; Bi IV—bcc; Bi V—fcc.

10. ELEMENTS OF GROUP VI-B

Of the VI-B elements, we shall consider only selenium and tellurium because of the great similarity of their properties and because more data are available on their P–T phase diagrams than for the other elements. Under normal conditions, selenium has several allotropic modifications, but the thermodynamically stable form is gray selenium, having the hexagonal type A8 structure; tellurium crystallizes in the same structure.

In the type A8 packing, each atom has two nearest neighbors, one above and one below, both lying on a common vertical, so that the whole structure splits into vertical helical chains.

It is interesting to note that the type A8 (selenium) and type A7 (arsenic) structures are both based on a three-layered cubic packing, but the distortion of the cube is in opposite directions for these two types of structure. In a normal cube, the primitive rhombohedron has the vertex angle of 60°, in the type A7 structure (arsenic, antimony, and bismuth) this angle is less than 60°, while in the type A8 structure it is greater than 60°.

It is evident from Fig. 20a that the P–T diagram of selenium has not been investigated much. The fusion curve has been determined only to 10 kbar,[97] and the polymorphism under pressure is indicated by a kink in the dependence of the volume decrement on pressure at 63 kbar[37] and by electrical resistance discontinuities at 46 kbar[21] and 128 kbar.[98] The first two discontinuities probably represent the same transition Se I → Se II, and the boundary between these phases should be drawn as shown dashed in our figure. The fusion curve of the Se II phase and the phase boundary between Se II and Se III are equally hypothetical.

The P–T phase diagram of tellurium has been determined more fully; it is shown in Fig. 20b. Its fusion curve[99] has been determined up to 50 kbar and it has one deep minimum at 30 kbar, which is the point of intersection of the fusion curve with the equilibrium boundary between the phases Te II and Te III; a maximum in the fusion curve of Te was reported in [100]. The Te I → Te II transition is accompanied by a very small volume change, which is so small that having plotted the phase boundary between the modifications Te I and Te II, Bridgman suggested that his results were not to be taken too seriously.[68] On further increase of pressure, two more transitions take place in tellurium at 45 and 70 kbar; these transitions are accompanied by very marked changes in the volume[137] and the electrical resistance.[101] It is interesting to note that x-ray diffraction analysis showed a polymorphic transition at 15 kbar.[102] It was found that the chain-like type A8 structure of normal tellurium transformed under pressure into the layered structure of the A7 arsenic type; this transition was not accompanied by a volume discontinuity or a change in density.

It is possible that the phase boundary Te I–Te II emerges at the maximum of the fusion curve. Further changes in the structure occur at 45 kbar; this is clear from the Debye diffraction pattern which was obtained for the Te III phase under pressure; it has not yet been possible to interpret this pattern.[102]

If we now compare the P–T phase diagrams of selenium and tellurium, we see that they follow the general

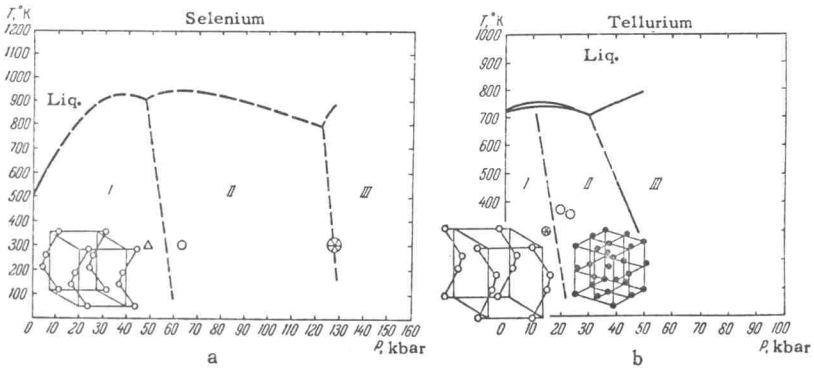

FIG. 20. a) Probable P – T diagram of Se. The fusion curve was determined from volume discontinuities;[97] the coordinates of the polymorphic transitions are indicated as follows: the circle shows a kink in the pressure dependence of the volume decrement,[37] The "star" and the triangle denote electrical resistance discontinuities.[21,98] b) P – T phase diagram of tellurium plotted by the DTA method.[99,100] The "star" denotes the coordinates of the polymorphic transition TeI – TeII, found by the x-ray diffraction method.[102] The circles and part of the phase boundary between TeII and TeIII were obtained by investigating the volume decrement under pressure.[68]