

the structures which is observed in the group as a whole in the transition from element to element. This can be easily understood if the P-T phase diagrams are considered in the same sequence.

Figure 18a shows, by continuous curves, the phase diagrams of carbon in accordance with [76]. The stable form of carbon under normal conditions is graphite and the metastable form is diamond. The boundary between these two phases, according to [76], intersects the fusion curve at 130 kbar and 4100°K, and the fusion curve of diamond has a considerable negative slope, so that the volume discontinuities in graphite, found by means of shock waves, [78] have been assumed to represent melting. The second triple point in the diagram (the point of intersection of the fusion curve with the boundary between the phases diamond and graphite-II) lies at 630 kbar and 1300°K. According to other workers, [77] this point lies at 600 kbar and 2900°K and the boundary between graphite and diamond intersects the fusion curve at 150 kbar and 3300°K. Later, the same workers, having considered in detail the properties of elements in group IV-B and those of the isoelectronic compounds formed of elements of groups III and V, suggested that the P-T diagram of carbon should be somewhat different. [79] Figure 18a shows, as chain lines, the hypothetical boundaries between the phases proposed by these workers. In this case, the volume discontinuities in graphite, found by means of shock waves, [78] will correspond to the polymorphic transition of diamond into graphite-II.

It has also been suggested that the fusion curve of diamond should have a much smaller negative slope and that it should end at the triple point with the coordinates 600 kbar and 2700°K; the graphite-II modification should have the structure of white tin—the tetragonal body-centered type A5 lattice—and a fusion curve with a positive slope. [77] If these hypotheses are confirmed in the future, they will furnish proof of the validity of the conclusions drawn on the basis of analogies between the P-T phase diagrams of elements in the periodic system.

Figure 18b shows the P-T diagrams of silicon and germanium, found by the differential thermal analysis method. [79] The semiconductors silicon and germanium go over to the metallic state at pressures of 200 and 120 kbar, respectively. [81] Experiments showed that the slope of the fusion curve of the high-pressure phase of germanium was positive and the same sign of the slope was proposed for the fusion curve of the high-pressure phase of silicon. The structure of the high-pressure phases of these elements was investigated by x-ray diffraction and the analysis showed that they both have the white tin (type A5) lattice, which is tetragonal body-centered. [82]

As mentioned earlier, metallic or white tin has the tetragonal body-centered type A5 structure with the ratio of the axes  $c/a = 0.545$ . On cooling to 13.5°C, this lattice changes to the  $\alpha$ -Sn modification—gray

tin—which has the diamond type cubic lattice and all the properties of a semiconductor. Figure 18c shows the P-T phase diagram of tin (in accordance with [79]). The stability zone of gray tin lies at negative pressures. The phase boundaries between  $\alpha$ - and  $\beta$ -Sn and the fusion curve of  $\alpha$ -Sn have been calculated. Under pressure,  $\beta$ -Sn transforms into the Sn II modification, [83] which, as shown by x-ray diffraction investigations, has the tetragonal body-centered structure, [25] similar to the bcc type A2 structure. The possibility of a transition from the body-centered tetragonal type A5 structure to the bcc structure in tin has been considered theoretically using the concept of spatial packing [84] and has, in fact, been confirmed.

At atmospheric pressure, lead retains the fcc type A1 structure down to very low temperatures. A polymorphic transition was found in lead at 161 kbar [85] and a study of a series of Pb-Bi alloys gave grounds for assuming that the high-pressure phase of lead had the hcp type A3 structure. [86]

Thus, considering the P-T phase diagrams of elements of the carbon group, we can note a number of characteristic features. First, we see the purely outward similarity in the diagrams. The strongly extended diagram of carbon is followed by the more compressed diagrams of silicon and germanium and the very compact diagram of tin; the "compression" occurs both along the pressure axis and along the temperature axis. The stability zone of the graphite type modification lies at negative pressures for silicon and germanium; the same is true of the diamond-type phase ( $\alpha$ -Sn) of tin. We notice also that the phases having the same structures have the same sign of the slope of the fusion curve, and only the angle of the slope changes from element to element. It would seem that the diagram of each element can be obtained by "expanding" the diagram of the neighbor which follows it in the periodic table.

Thus, having considered the phase diagram of elements in the carbon group, we may say that when the pressure is increased, the polymorphic modifications follow one another in the following sequence: hexagonal layered A9 (graphite)  $\rightarrow$  diamond A4 (diamond, Si I, Ge I,  $\alpha$ -Sn)  $\rightarrow$  tetragonal body-centered A5 (graphite-II, Si II, Ge II,  $\beta$ -Sn)  $\rightarrow$  pseudo-bcc (Sn II)  $\rightarrow$  fcc A1 (Pb)  $\rightarrow$  hcp A3 (Pb II).

The sequence of changes of the crystal structure under the influence of pressure is accompanied by an increase in the c.n. or, we may say, that when structures change under the influence of pressure the packing factor  $\varphi$  increases (this factor is equal to the ratio of the volume occupied by atoms to the total volume of a unit cell). This can be seen clearly in the adjoining table.

The observed sequence of phase diagrams suggests that the same order will apply to the sequence of changes in the high-pressure modifications in all elements of the carbon group, i.e., we may expect tin,