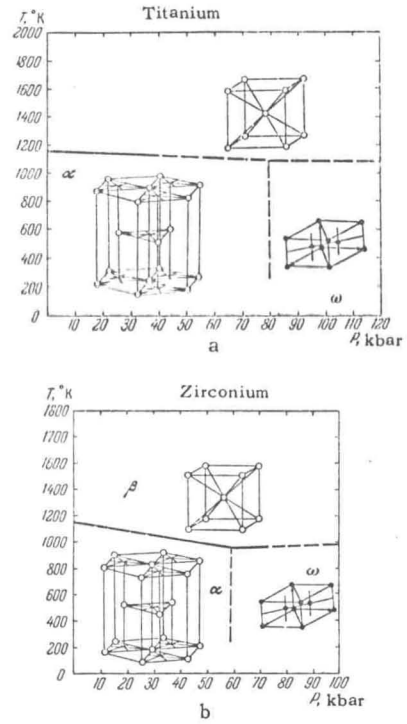

FIG. 17. Phase diagrams of Ti and Zr (according to the DTA method[71]).

nium and zirconium have much in common and, although their fusion curves have not yet been determined (they lie at fairly high temperatures), they should be similar. In elements of this subgroup, the melting points and the $\alpha-\beta$ transition temperatures increase, and the pressures of the $\alpha-\omega$ transitions decrease along the sequence from Ti to Hf. However, it should be mentioned that on the basis of this sequence, one would expect hafnium to exhibit polymorphism at pressures less than 60 kbar but no volume or electrical resistance discontinuities have been observed for this metal and the x-ray structure analysis under pressure showed no change in the structure. This point will be resolved when the boundaries between the polymorphic modifications of hafnium in the P–T field are determined.

8. ELEMENTS OF GROUP IV-B

Elements of the carbon group exhibit a gradual change in their physical properties with increasing atomic number: these properties change from metalloid in carbon, through semiconducting in silicon and germanium, to metallic in tin and lead, which are superconducting at low temperatures. The crystal structure also changes gradually from element to element. Under normal conditions, carbon has the hexagonal layered structure of graphite (type A9), whilst silicon and germanium have the cubic diamond (type A4) structure, white tin (β-Sn) has the tetragonal body-centered structure (type A5) and lead the fcc structure (type A1). This sequence of structures in the carbon group can be expressed symbolically by A9 → A4 → A5 → A1. All elements of this group undergo polymorphic transitions when there is an increase in the pressure or a change in temperature. It is found that the high-pressure modifications exhibit the same sequence in

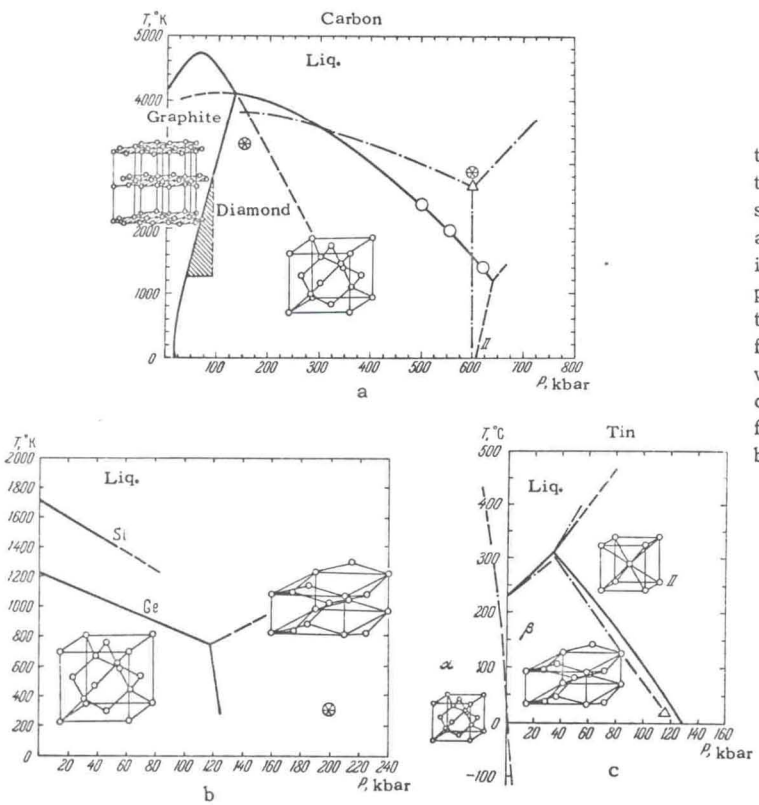

FIG. 18. a) P – T phase diagram of C.[76] The "stars" denote the triple points in the diagram reported in[77]; the circles denote the coordinates of the volume discontinuities obtained using shock waves.[78] The dash-dot lines show the phase boundaries and a triangle gives the triple point coordinates, all reported in[79]. The shaded zone is the region in which it is practical to produce synthetic diamonds. b) P – T diagrams of Si and Ge obtained by the DTA method.[79] A "star" denotes the conditions for a polymorphic transition in Si.[81] c) the P – T diagram of Sn was obtained by the DTA method[79] (shown by continuous curves); the dashed curves represent the $\alpha-\beta$ phase boundaries found by calculation;[79] chain curves are the boundaries found by x-ray structure analysis under pressure.[25]