

FIG. 15. P-T phase diagrams of Al, Ga, and In (according to the DTA method^[65]).

The A6 → A1 transition, as shown by x-ray-structure analysis, occurs in metallic indium at atmospheric pressure when the temperature is increased.^[67] It would seem, therefore, that the boundary between the solid phases should be that indicated by the dashed line in Fig. 15c. It is, at present, impossible to find the point where this line intersects the fusion curve.

Thus, considering elements of group III-B, we can see their general tendency to have fcc structures.

Thallium, which follows indium in this subgroup, has a P-T diagram (Fig. 16) different from the diagrams of its neighbors in the same group but resembling strongly the P-T diagrams of zirconium and titanium.

It is evident from this diagram that, in the region up to 60 kbar, thallium has three modifications. The phase stable under normal conditions has the hcp type A3 structure, while the high-temperature phase has a bcc structure. As in the case of titanium and zirco-

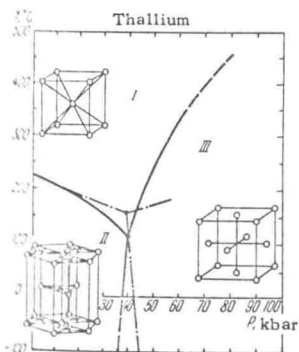


FIG. 16. P-T phase diagram of Tl (according to the DTA method^[65]). Dash-dot lines show the boundaries between phases found by Bridgman using the volume discontinuity method.^[66]

mium, the high-temperature phase of thallium has a higher density than the low-temperature phase, i.e., as the temperature is increased, there is a polymorphic transition with a negative change in volume—the specific volume per atom decreases.

Pressure reduces the temperature of the A3 → A2 transition; the boundary between these two phases has a negative slope. As the pressure is further increased, these two phases change; the atoms become rearranged to form an fcc lattice. The possible structure of the Tl III phase was discussed in^[69] on the basis of thermodynamic data and in^[70] by invoking the concept of the spatial packing of atoms; the authors of both papers concluded that this modification had the fcc type A1 lattice structure. X-ray-structure analysis of this phase under pressure confirmed this conclusion.^[16]

7. METALS OF GROUP IV-A

Titanium, zirconium, and hafnium exhibit polymorphism of a very special type. Their α -phases with the hcp type A3 lattice, which exist under normal conditions, change to the β -form when the temperature is increased and into the ω -form when the pressure is increased. The differential thermal analysis of titanium and zirconium established the boundaries between the α - and β -modifications and, in the case of zirconium, parts of the boundary between the high-pressure ω phase and the α - and β -modifications were also determined. Figure 17a shows the P-T diagram of titanium, and Fig. 17b the P-T diagram of zirconium (in accordance with^[71]).

The high-temperature β -phases of these metals have a bcc structure, like the majority of metals. However, all the transitions referred to are anomalous since they are accompanied by volume discontinuities and the high-temperature β -modification has a higher density than the α -phase.

This observation suggests that the high-pressure phase may have the same structure. The same conclusion was reached by considering the high-pressure phase on the basis of thermodynamic data.^[72] In fact, x-ray structure analysis of these metals, carried out at pressures higher than the transition pressure, showed that the high-pressure phases of titanium and zirconium had a bcc structure.^[73] The high-pressure phase of titanium and zirconium was called the ω -phase by analogy with the structure found in titanium and zirconium alloys.^[74,75] The high-temperature β -phase and the high-pressure ω -phase of these metals are not identical but they may be regarded as isomorphous. As proved for zirconium, the transition between these phases occurs without a change in volume and has no hysteresis; the boundary between the phases is parallel to the pressure axis. It is possible that in the case of titanium the boundary between the analogous phases is also parallel to the pressure axis.

Thus, we may say that the phase diagrams of tita-