

at pressures of 20–25 kbar.^[61] However, it is not clear at all that the metastable phase of gadolinium is formed at this transition. The following suggestion has been made for the sequence of changes in the crystal structure of rare-earth metals during polymorphic transitions under pressure: hcp (type A3) → samarium type → lanthanum (A3') type → fcc (type A1). To confirm or reject this scheme, we would need to carry out x-ray analyses at high pressures.

The rare earths europium and ytterbium are very similar to alkaline-earth metals; this applies both to their chemical activity (they are divalent) and such physical properties as the crystal structure, volatility, refractory properties, thermal expansion, and compressibility.

The similarity of the properties of europium and ytterbium to the properties of alkaline-earth metals is explained by the stability of the half-filled and completely-filled 4f-states of these elements. Their P-T phase diagrams (Figs. 13 and 14) are very similar to the diagrams of alkaline-earth metals.

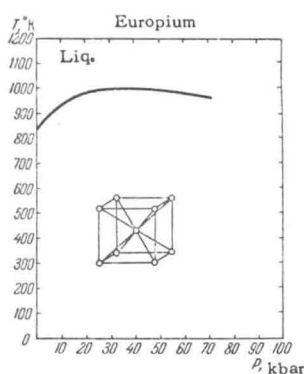


FIG. 13. P-T diagram of Eu (according to the DTA method^[65]).

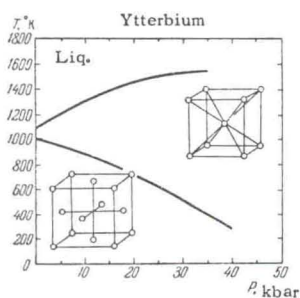


FIG. 14. P-T phase diagram of Yb (according to the DTA method^[65]).

Europium has a fusion curve with a clear maximum, similar to that observed for barium. Like the alkaline-earth barium, europium crystallizes in the bcc type A2 structure. It is assumed that the electrical resistance discontinuity, which is observed in europium at 150–160 kbar,^[62] is due to a polymorphic transition with a change in the bcc lattice to the hcp type A3 lattice, i.e., due to the same structure change as in barium at 59 kbar.^[63]

Since the similarity between these two metals is so great, it seems possible that there is an A2 → A2 transition in europium at a pressure of the order of 30 kbar, similar to that which occurs in barium at 17 kbar.

The rare-earth ytterbium has properties which resemble most those of the alkaline-earth strontium and, as can be seen from Figs. 6 and 14, the P-T phase diagram of this element is very similar to the diagram for strontium.^[63] Under normal conditions, both strontium and ytterbium crystallize in the fcc type A1 lattice, which changes, when the temperature is increased, to a bcc lattice. The P-T diagrams show that the boundary between the α - and β -phases of these elements has a negative slope and that the high-temperature phase is stable also at high pressures. X-ray structure analysis carried out at high pressures definitely confirmed the complete identity of the high-temperature and high-pressure modifications.^[64]

6. METALS OF GROUP III-B

In spite of the fact that fairly complete P-T diagrams are available for group III-B metals up to 70 kbar, this group is most difficult as far as generalizations are concerned. We shall show below that it is natural to consider together aluminum, gallium and indium, and, separately, thallium.

Under normal conditions, aluminum has the type A1 fcc lattice and does not exhibit polymorphism under pressure or when the temperature is increased. This metal exhibits considerable electrical conductivity, which is slightly and monotonically increased by pressures up to 100 kbar.^[20] The fusion curve of aluminum, found by differential thermal analysis,^[65] is shown in Fig. 15a.

Gallium has three modifications in the pressure range up to 100 kbar; its P-T diagram is shown in Fig. 15b. The low-pressure phase has an orthorhombic structure with eight atoms in a unit cell. Each atom in this structure has only one nearest neighbor [the coordination number (c.n.) is 1], i.e., atoms are arranged in pairs—"molecules." The binding between such pairs in the lattice is quite weak and a metal having this structure has a low melting point. When the pressure is increased, the crystal structure changes to the Ga II modification, which, as shown by x-ray structure analysis under pressure,^[66] has the tetragonal face-centered lattice (c.n. = 4.8) with a very small difference between the c- and a-axes, so that the ratio of the axes is $c/a = 1.104$ at 30 kbar; it is worth noting that metallic indium has the same structure (type A6) under normal conditions.

It has been suggested^[65] that the structure of Ga III is the bcc type A2; this hypothesis is very likely to be true since the great majority of high-temperature phases of metals is of this structure. It seems to us that there is another possibility—the structure may be the fcc type A1 because the tetragonal structure of indium differs so little from the fcc structure, that it can assume the latter form under pressure. The tetragonal fcc lattice of indium (type A6, 4 atoms/cell, c.n. = 4) has an even smaller difference between the axes under normal conditions $c/a = 1.077$.