atoms per unit cell and the axis ratio $c/a = 0.706$. In this structure, each atom has two nearest neighbors along the c axis and, therefore, the atoms are linked into narrow rows elongated along this axis. Investigations of the electrical resistance showed no polymorphism in the β-modification of mercury up to 100 kbar.[37]

5. RARE-EARTH ELEMENTS

Rare-earth elements are distinguished by a great similarity of their physical and chemical properties — a consequence of their electron structure. Usually, these metals are divided into two subgroups: cerium (from Ce to Gd) and yttrium (from Tb to Lu); within these subgroups, the properties of the lanthanides show even greater similarity. We shall consider only one of these properties, i.e., polymorphism.

Under normal conditions, all elements in the yttrium subgroup crystallize in the hcp magnesium (type A3) structure with the axis ratio $c/a = 1.6$. The only exception is ytterbium, which has the fcc lattice.

The elements in the cerium subgroup exhibit an even greater variety of crystal structures. α-lanthanum, α-praseodymium, and α-neodymium have the hcp lanthanum-type A3' lattice with $c/a = 3.2$. This structure is characterized by an alternate packing layers of the ABACA... type. Samarium also has the hcp lattice but with a different sequence of layers—ABABCBCACA... —and the ratio $c/a = 7.25$; however, the true structure of samarium is rhombohedral. Metallic cerium, under normal conditions, has two phases: one of them is γ-cerium with an fcc lattice, and the other is the metastable β-cerium phase with the hcp type A3 lattice, whose range of stability in the P–T diagram has not yet been determined. Europium has a bcc lattice.

Most lanthanides, with very few exceptions, are now known to exhibit the temperature polymorphism and all high-temperature modifications have the bcc structure. Many lanthanides also exhibit polymorphism under the action of high pressures. Lanthanides have similar properties and are very likely to have similar polymorphism and display great similarity in the P–T diagrams. Unfortunately, only very few data are available on the P–T diagrams of rare earths.

Figure 11 shows the P–T diagram of cerium. The $\gamma \rightarrow \alpha$ transition in cerium is one of the most remarkable because it is an isomorphic transition; at room temperature, it is accompanied by a considerable sudden change in volume, while the structure of the high-pressure modification remains, as before, fcc.[4]

The reverse $\alpha \rightarrow \gamma$ transition takes place when the pressure is reduced after some delay (hysteresis) but this hysteresis decreases when the temperature is increased. The values of ΔV (volume discontinuity at transition) and ΔQ (heat of transition) both decrease as well. This has suggested that the phase boundary between the α- and γ-modifications ends at the criti-
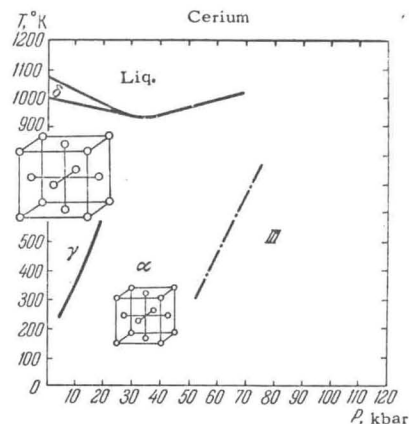

FIG. 11. P – T phase diagram of Ce.[51,53] The $\gamma \rightarrow \alpha$ boundary was obtained by the volume discontinuity method; the probable boundary between the α- and Ce-III phases (dash-dot line) was obtained from the pressure dependence of the electrical resistance.

cal point with the coordinates 280°C, 18.5 kg/cm^2.[50] It must be mentioned that somewhat later an increase in the experimental accuracy made it possible to extend the phase boundary to the coordinate 400°C, 20 kg/cm^2 and it was suggested that this boundary met the fusion curve.[5] However, recent x-ray investigations showed that the (111) reflections of both phases converged as the temperature was increased along the phase boundary. Extrapolation to the point of convergence of the two phases, i.e., to the parameters of a possible critical point, gave the values 350—400°C and 20—22 kbar.[52]

In the $\alpha \rightarrow \gamma$ transition in cerium, we have, so far, the only example of a boundary between two solid phases ending at a critical point.

It is interesting to note that the extrapolation of the phase boundary leads, in this case, to a broad minimum in the fusion curve, which has been found only in cerium.

The chain curve in Fig. 11 represents the boundary between the phases α and Ce III; it was found from irregularities in the pressure dependence of the electrical resistance of cerium.[51] We may assume that the structure of the Ce III modification is compact, most likely hcp.

Lanthanum, praseodymium, and neodymium have very similar properties. As mentioned before, under normal conditions, they have the lanthanum type A3' structure, which is hcp with the ratio $c/a = 3.2$, i.e., approximately twice as large as for normal metals having the type A3 lattice. On heating, the type A3' lattice is replaced by a bcc lattice, as is frequently observed in metals. At atmospheric pressure, lanthanum has one more modification, β-La, which has the fcc type A1 structure. The high-temperature modification, as indicated in the P–T phase diagram in Fig. 12a, is also stable at high pressures. Investigation of its crystal structure confirmed once again the