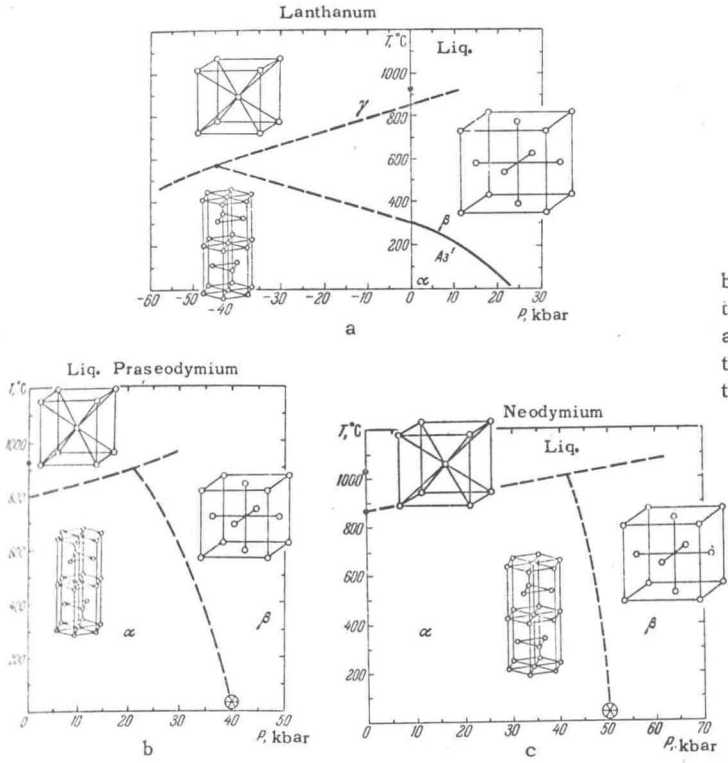

FIG. 12. The P – T diagrams of La, Pr, and Nd. The boundary between the α- and β-phases of lanthanum was found from electrical resistance discontinuities.[54] The P – T diagrams of Pr and Nd are hypothetical. The only reliable features are $T_{m.p.}$, the $\alpha \rightarrow \gamma$ transition temperatures, and the coordinates of the transition from the α-phase to the high- pressure phase.[55]

identity of the high-temperature phase with the high-pressure phase and showed that the lanthanum type structure (A3′) changed under pressure into the fcc type A1 structure.[55]

Exactly the same polymorphism is exhibited by the neighbors of lanthanum—praseodymium and neodymium. The polymorphism of praseodymium was established earlier from the discontinuity in the shear stress[56] and from the discontinuity in the electrical resistance[21] at 50 kbar, but no anomalies were found in the properties of neodymium up to 100 kbar.[20] X-ray diffraction established clearly that, in both these metals, the crystal structure changed from A3′ to A1, as in lanthanum.[55] Unfortunately, the P–T diagrams for these metals are not available but it seems very likely that these close analogs of lanthanum have P–T diagrams very similar to the diagram of lanthanum. These hypothetical diagrams, with phase boundaries shown by dashed curves, are given in Figs. 12b and 12c. It is very likely that the negative slope between the phases A3′ and A1 is retained but it may vary from element to element, and, therefore, while the triple point between the phases A3′, A2, and A1 of lanthanum is in the range of negative pressures, the analogous triple points of Pr and Nd should be in the range of real pressures, and in the case of Nd the triple point should be at high pressures. This form of the P–T diagram may explain why no fcc modification is observed in praseodymium and neodymium at atmospheric pressure.

The question now arises whether these metals have an isotropic transition, similar to that observed in cerium at a pressure of only 7 kbar and accompanied by a rearrangement of the type A1 lattice into a flattened fcc lattice. So far, there are no data to confirm this hypothesis but the existence of such a transition in La, Pr, and Nd seems very likely.

Recently, reports have been published on polymorphism under pressure in gadolinium[57] and samarium.[58] As mentioned earlier, under normal conditions, samarium has a remarkable crystal structure. If it is considered in terms of a hexagonal axis, its unit cell is very much elongated along the c axis; it is filled with atoms in ten consecutive layers. A new phase was found at 40 kbar and 300°C[58], which was retained in the metastable state even after the removal of pressure, and was investigated by x-ray diffraction. Analysis of the Debye diffraction pattern showed that the new phase had the hcp lanthanum A3′ structure.

However, the problem of the stability of this modification of samarium under pressure will be resolved finally only when x-ray analysis is carried out at 40 kbar and 300°C. The point is that metastable forms of various elements may exist under conditions which are far from their stability zone. For example, the metastable phases of carbon[59] or silicon[60] exhibit complex crystal structures; the stability zones of these phases have not yet been found in the P–T phase diagrams of carbon and silicon.

The same applies to gadolinium; a metastable form was obtained at 40 kbar and 400°C. X-ray diffraction analysis showed that the new phase had the samarium-type structure but there were also traces of a phase with the lanthanum type A3′ structure.[57]

Bridgman found both volume discontinuities and anomalies in the electrical resistance of gadolinium