

rule: the tellurium diagram is a compressed variant of the selenium diagram. This suggests that selenium should have the same polymorphism as tellurium, i.e., A8  $\rightarrow$  A7.

It should be mentioned also that these two elements should have a modification with the primitive cubic structure, since polonium, which follows tellurium in the same group, has this structure.

## 11. IRON GROUP

The P-T phase diagram of iron has been investigated over a very wide range of pressures and temperatures. At atmospheric pressure the stable modification of  $\alpha$ -Fe has the bcc structure up to 1179°K, which is then replaced by the  $\gamma$ -Fe phase with the fcc structure. Further heating (to  $T = 1674^\circ\text{K}$ ) changes the fcc phase into the high-temperature form  $\delta$ -Fe, which, like the majority of high-temperature modifications, has the type A2 structure, which is bcc.

Figure 21 shows the P-T phase diagram of iron, which represents the results of analyses of very many investigations.<sup>[103]</sup> The equilibrium curve between the  $\alpha$ - and  $\gamma$ -phases has been investigated by a large number of workers. It has been determined dilatometrically,<sup>[104]</sup> from electrical resistance anomalies,<sup>[105,106]</sup> heats of  $\alpha \rightarrow \gamma$  transition,<sup>[107]</sup> thermal conductivity discontinuity,<sup>[106]</sup> and using shock waves.<sup>[108,109]</sup>

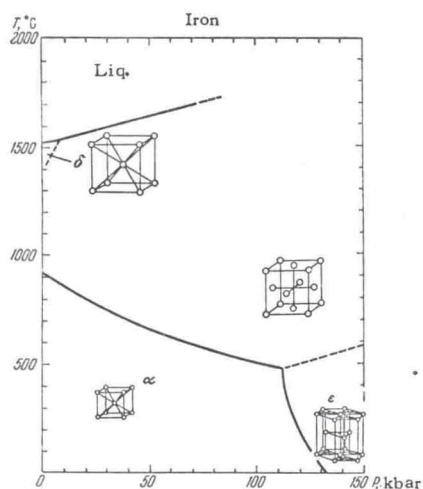


FIG. 21. The P-T phase diagram of iron. The fusion curve was determined by the DTA method.<sup>[110]</sup> The  $\alpha$ - $\gamma$  and  $\alpha$ - $\epsilon$  boundaries were plotted using various methods, and the  $\gamma$ - $\delta$  and  $\gamma$ - $\epsilon$  phase boundaries were calculated in<sup>[103]</sup>.

The sudden change in the slope of this boundary has suggested that the phase diagram has a triple point and that, in addition to the  $\alpha$ - and  $\gamma$ -phases, there is one further modification of iron; it is called  $\epsilon$ -Fe by analogy with the  $\epsilon$ -phase for cobalt.

The existence of this phase was proved by x-ray-structure analysis which showed that  $\epsilon$ -Fe had the hcp type A3 structure.<sup>[103,17]</sup>

The  $\gamma$ - $\delta$  and  $\gamma$ - $\epsilon$  phase boundaries have not been determined experimentally but they have been calculated;<sup>[103]</sup> the fusion curve was determined by the differential thermal analysis.<sup>[110]</sup> The  $\epsilon$ -phase of iron is probably stable to very high pressures; the application of shock waves up to 4000 kbar showed no sudden changes in density.<sup>[111]</sup>

We shall now turn to the neighbors of iron: cobalt and nickel. Under normal conditions, cobalt has two modifications: the hexagonal type A3 ( $\epsilon$ -Co), stable up to 755°K, which is replaced by a high-temperature  $\gamma$ -phase with the fcc structure (type A1) stable right up to the melting point. No polymorphism has been found in nickel; it has the fcc type A1 structure.

As in all cases considered earlier, we can say that the P-T phase diagrams of the iron group are shifted toward lower pressures and temperatures on increase of the atomic number. The fcc and hexagonal phases, coexisting in iron under high pressures, exhibit a transition at atmospheric pressure in cobalt; the temperature of this transition is lower than in iron.

The practical conclusion of such an analysis is that at some pressure we would expect nickel to have an  $\epsilon$ -phase with the hcp-type A3 structure.

The P-T phase diagrams have not yet been constructed for all the elements of the periodic table and, therefore, in generalizing the known facts, we are forced to ignore many interesting substances.

Knowledge of the P-T diagrams allows us to obtain information on transitions which alter the crystal structure; moreover, using the available sequences of polymorphic modifications within each group of the periodic table, we can even now make some predictions of structures which have not yet been investigated by x-ray-diffraction or structures of high-pressure modifications which are difficult to produce. Furthermore, the knowledge of crystal structures of high-pressure phases or at least predictions of such structures will help in the search for new substances under pressure if the properties are known in advance.

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Having considered the P-T phase diagrams of some elements in the periodic table, we have been able to establish that their periodicity applies also to the phase diagrams. We have been able to show that the P-T diagrams of elements in one group are very similar, but they gradually "contract" moving toward lower pressures and temperatures as the atomic number increases. The variety of elements is reflected in the variety of forms of the phase boundaries. The general tendency in the polymorphism of elements produced by the application of pressure is the sequence in which looser crystal structures are followed by more closely packed structures, having higher coordination numbers. Against the background of this general rule, we can point out a number of cases in which the application of pressure alters a structure