cated in the right-hand part of Table II. In the case of La it takes place at $\sigma_c = 1.51$, and in the case of all other rare earth metals at σ_c close to 1.9.

In Ce, all the dynamic experimental data pertain to the low-compressibility high-pressure α phase. As is well-known[22,39], the γ-α electronic transition in cerium occurs at relatively low pressure, 7 kbar. The two isomorphic phases differ from each other in specific volume. The phase-equilibrium line separating them on the P-T diagram at 18 kbar and 280°C is terminated by a critical point, above which strong discontinuities on the dilatometric curves and on the electric resistance curves are not recorded. As established by neutron diffraction[40] and also by measurements of the Hall effect[39], the formation of a dense α phase is due to the transition of its only f electron to the d-band and to the consequent increase of the valence of Ce from 3 to 3.67.

In order to understand the causes of the electronic changes in Ce, we recall[24,41] that the electronic structure of the atoms of rare-earth elements has the following form: closed Xe shell, incomplete 4f layer, and finally, the $6s^2$ and $5d^1$ valence electrons. The 4f electrons are reliably screened by an outer closed layer of the $5s^25p^6$ shell of Xe, inasmuch as the 4f layer has a much smaller average radius. In view of all this, we expect that the 4f electrons in the crystal in the unexcited state are practically not collectivized, do not influence the binding forces, the valence, and the limiting electron density.

A comparison of the interatomic distances in divalent rare earth metals (Eu, Yb), and in trivalent and tetravalent (γ-Ce) shows that under normal conditions the atomic volumes decrease with increasing number of valence electrons[41]. Therefore application of external pressures can stimulate the transition of the 4f electrons to the conduction band, formed by the s-d electrons.

The reasons why such—d transitions at low pressures occur only in the case in Ce are not clear at the present time. In the case of Lu, which has a stable configuration of the filled s-layer, the discontinuous decrease of the compressibility is uniquely explained by the displacement of the outer 6s electrons to the d levels of the fifth layer. Apparently, in other rare-earth metals the formation of low-compressibility electron configurations is connected primarily with the displacement of the s electrons to the 4f and 5d levels, which lie close in energy.

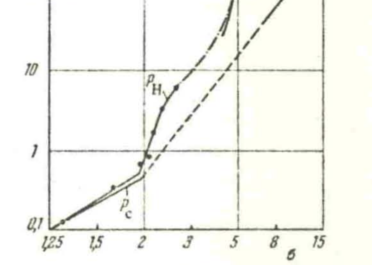

FIG. 20. Extrapolation of shock adiabat and zero isotherm of Sm. —·— —interpolation section of dynamic adiabats; — — —interpolated section of zero isotherm; TF—shock adiabat calculated from the Thomas-Fermi theory [42]; TFC—zero isotherm calculated from the TFC theory.

VII. CONCLUSION

Extensive investigations with the aid of shock waves revealed the main laws governing the compressibility of metals having different electronic structures at high pressures. It turned out that the resistance of metals to compression depends principally on the magnitude of their atomic volumes, or, in other words, on the average electron density on the boundaries of the compressed atoms. There is no direct correlation between the binding energy and the compressibility, and the elasticity of metals is connected with the coupling forces only to the extent that these forces determine the interatomic distances and the atomic volumes.

In many metals, in experiments with shock waves, the shock-compression curves revealed sharp kinks when the density was increased by 1.5–2.5 times, evidencing a discontinuous increase of the elasticity of the metal. The data presented in the present review show that these singularities are observed in practically all metals of the large periods, pertaining to the first five A-groups, i.e., to the alkali, alkali-earth, rare-earth, and transition metals, which occupy the uppermost positions and the decreasing branches of the atomic-volume curve. The atoms of these elements, under normal conditions, have unoccupied or little-filled internal d-shells. The repopulation of the outer s-electrons to the d-levels causes formation of denser and low-compressibility electron configurations with an increased number of the binding d-electrons. The completion of the electron-transition process is naturally associated with the kinks, at which two smooth sections of the dynamic adiabats intersect. The large compressibility in the first compression phase is due not only to the low density of the external s-electrons, but also to their gradual displacement within the atom upon compression, thus decreasing additionally the limiting density of the electron cloud.

There exist causes, indicated in Chapter II, which violate the correspondence between the configurations of the shock adiabats and the equilibrium zero isotherms in the region of electronic transitions. One of these causes is the high temperature of dynamic compression, causing excitation of the electrons and additional smearing of their energy bands. Another cause is connected with possible inertia of the electronic transitions, which apparently have a certain activation energy[33].

Hysteresis phenomena, which characterize the kinetics of electronic transformations and are of independent interest, were observed by x-ray diffraction in the study of Ce[42], and also of Rb[43] (using its electric-resistance curves). The strong disparity between the critical pressures of the transition in the compression and decompression waves was registered in[19] for Ca. These factors lead to a smoothing, on the adiabats, of the singularities characteristic of equilibrium zero isotherms. In particular, under their influence, the steplike form of the compression curve, shown in Fig. 2b and characteristic of first-order