FIG. 3. Plot of pressure vs density: curve 1—out data, curve 2—calculation by statistical theory (log p = 1 denotes $p = 10^6$ atm).

FIG. 4. Plot of $p(1/\delta)$ for K. Line 1-2 is the constant-pressure line of the phase transition.

theory in the calculation of Kalitkin.[3]

For iron, the error in the determination of the normal density reaches 20%. Further progress in this direction calls unconditionally for a more accurate calculation of the exchange pressure. At the present time much effort is expended on developing a procedure for calculating the exchange pressure from the obtained electronic wave functions. The next step forward is to take into account the influence of the exchange on the wave functions themselves. It is proposed for this purpose to find methods of solving the Hartree-Fock equation in crystals. This work is presently also under way.

Inasmuch as the employed quantum mechanical procedure does not describe the Van der Waals forces, the calculation should give a small positive pressure for the close-packed solid Ar at all densities ($\rho_0 = 1.9$ g/cm^3—experimental density of solid Ar), as is indeed the case.

Figure 4 shows the calculated curve of cold pressure in K, the abscissas representing $1/\delta$, which is proportional to the volume. We see on the curve a clearly pronounced minimum at $1/\delta$ = 0.21 and a maximum at $1/\delta$ = 0.29. Such a behavior is distinct proof of the presence of a first-order phase transition, and in reality a jump of density at constant pressure will be observed. This constant-pressure line is shown in Fig. 4. The bounded areas above and below this line should be equal. The transition pressure is here 180,000 atm and a large jump in density, almost by a factor of 2, is obtained. The feasability
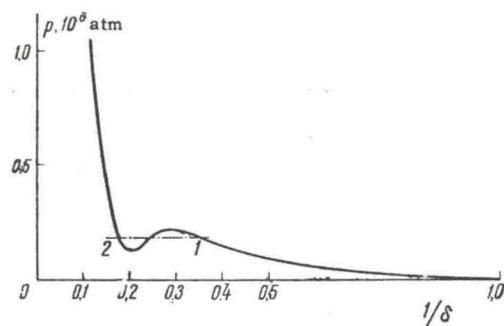
of a first-order phase transition in alkaline metals was considered qualitatively by Arkhipov.[9] The accuracy of the calculation of $p(\delta)$ in K is still insufficient to guarantee the accuracy of these figures, but since this phenomenon is connected with rearrangement of the electron band in K, which we have already mentioned, there is no doubt that such a phase transition in K is possible. It would be very desirable to investigate this question experimentally. The reliability of the electronic phase transition is confirmed also by the fact that the predicted region of negative and small positive Gruneisen coefficient of the electrons, connected with the rearrangement of the band upon compression, was confirmed experimentally, as will be related in detail in the next section.

3. THERMAL ENERGY AND THERMAL PRESSURE OF ELECTRONS

At relatively low temperatures, knowledge of the electronic bands $E(k)$ is sufficient to find the thermal energy and thermal pressure of the electrons. We shall find first the chemical potential μ as a function of the temperature, after which we shall calculate the thermal energy E_T and the thermal pressure P_T.

We introduce the notation

$$E_T = \tfrac{1}{2}\beta T^2, \qquad \gamma_e = p_T V / E_T.$$

The quantity γ_e is called the electron Gruneisen coefficient. Using the thermodynamic relation

$$p_T = T \int_0^T \frac{1}{T^2}\left(\frac{\partial E_T}{\partial V}\right)_T dT,$$

we obtain

$$\gamma_e = -\frac{\partial \ln \bar{\beta}}{\partial \ln \delta}\frac{\bar{\beta}}{\beta}, \qquad \bar{\beta} = \frac{1}{T}\int_0^T \beta dT.$$

At very low temperatures $\bar{\beta} = \beta$ and γ_e $= -\partial \ln \beta/\partial \ln \delta$.

At very low temperatures the calculated value