# CONCERNING THE METAL-DIELECTRIC TRANSITION AND A POSSIBLE PHASE TRANSITION IN A DENSE (STRONGLY NONIDEAL) PLASMA

G. É. NORMAN

Institute of High Temperatures, USSR Academy of Sciences Submitted September 24, 1970; resubmitted December 23, 1970 Zh. Eksp. Teor. Fiz. 60, 1686-1695 (May, 1971)

Approximate formulas are proposed for the free energy of a two- or three-component plasma, the formulas spanning the range of densities from gaseous to metallic. The corresponding equations of state and of ionization equilibrium are analyzed. The proposed model predicts three first-order phase transitions: a vapor-liquid, a metal-dielectric (metallization), and a plasma transition. It is shown that with an increase of the temperature, the dielectric-metal transition changes into the plasma phase transition. Within the framework of the model under consideration, the dielectric-metal transition is found to be a phase transition of the first kind, close to a phase transition of the second kind. The corresponding critical and triple points are discussed.

THE question of what happens to a gas, consisting of atoms, if it is gradually compressed to that state in which the wave functions of the valence electrons of neighboring atoms overlap each other, has been repeatedly discussed in the literature.<sup>[1-6]</sup> It is obvious that as a result of such compression the valence electrons are collectivized, and the substance turns out to no longer consist of atoms but of free electrons and ions. They say that metallization has taken place or, alternatively, a nonmetal-metal transition or a dielectric-metal transition (the opposite transition occurs upon increasing the volume). The basic question is whether metallization occurs smoothly in proportion to the increase of the compression. As long ago as <sup>[1]</sup> and subsequently in <sup>[2,4]</sup> it was conjectured that metallization may be a first-order phase transition.

The other possibility—the possibility of a plasma phase transition—is discussed in <sup>[7]</sup> (also see <sup>[8]</sup>). A plasma consisting of electrons, ions, and atoms is considered for temperatures  $\lesssim 10^4$  °K. It is shown that under the conditions of strong compression (but not up to metallic densities), when the interaction energy of the charged particles among themselves becomes comparable with the energy of their thermal motion, the possibility exists for the plasma to split into two phases: a less dense and a more dense phase (as if there were a plasma "vapor" and a plasma "liquid").

Approximate models covering a wide range of pressures and temperatures are proposed in the present article. Within the framework of these models, metallization is found to be a first-order phase transition. With increasing temperature metallization changes over into a plasma phase transition. The relation between these phase transitions and the usual liquid-vapor phase transition is also clarified.

#### FORMULATION OF THE PROBLEM. PHASE EQUILIB-RIUM CURVES

The basic results of this work are illustrated on Fig. 1, where the phase equilibrium curves are represented schematically for a substance which is a metal under normal conditions (P denotes pressure, V is volume, and T is the temperature). Such curves follow



FIG. 1. Schematic diagrams illustrating the possible nature of the phase equilibrium curves. a, b, c, c', and d denote the critical and triple points; the homogeneous phases are denoted as follows: SS-solid state, L-liquid, G-gas, P-plasma, DP-dense plasma, M and D-metallized and dielectric states; Fig. 1a shows the bi-nodal structure and isotherms of P(V); Fig. 1b shows the equilibrium curves P(T), and Fig. 1c shows the equilibrium curves T(V).

from the models considered in the present work, and their shape will be discussed in more detail below; now, however, we note their basic features.

Point b is the critical point for the vapor-liquid transition which is determined by the forces associated with the interatomic interaction. In the vicinity of the point b the substance consists mainly of atoms. Metallization occurs on the line cc' the substance consists of electrons and ions. Let us consider the isotherm 1 on Fig. 1a: upon a decrease in the volume of the gaseous phase the homogeneous state first of all loses its stability because of the long-range attractive forces acting between the atoms, that is, the substance decomposes into a vapor and a liquid. The liquid, just like the vapor, mainly consists of atoms. With further condensation and approach to the line cc', an appreciable concentration of free charges is established. The interactions of the charged particles with the atoms and with each other lead to a secondary loss of thermodynamical stability of the homogeneous state. The stability of the new, denser metallized state is ensured by the quantum repulsion which is effective in a system of electrons and ions at large densities.

The phase transition associated with metallization on the line cc' takes place upon a relatively small change of the specific volume; apparently this does not depend on the model and is explained by the fact that the electron density in an atom falls off exponentially with distance while the overlap of the electron shells associated with the approach of the atoms increases exponentially with the reduction of the distance. Therefore, under conditions when the ionization is determined by the pressure, the change in the concentration of the free charges from the value when the stability is disturbed to the value when the stability is established may take place at a relatively small distance of approach between the atoms.

At lower temperatures, smaller than the temperature of the point c, the atomic vapor condenses directly into a metallized liquid.

For higher temperatures an appreciable ionization, sufficient in order for the homogeneous system to lose its stability because of the Coulomb interaction, appears at densities which are much smaller than metallic densities. However, as before in order to establish stability, densities close to metallic are required; therefore, in the region between c' and d the specific volumes of the coexisting phases differ markedly from each other (isotherm 2 on Fig. 1a).

Depending on the ionization potential and the roles of the different kinds of interactions, situations may be realized which are different from those shown in Fig. 1. The upper critical temperature for the Coulomb interaction may turn out to be in the region of or below the temperature corresponding to the point c'; then the plasma phase transition will be absent, but the metal-dielectric transition is finished at the critical point. The interactions between charged and neutral particles may displace the triple point c to the right; the possibility of the coincidence of points b and c is of interest; it is impossible to exclude the alternative version when c turns out to be to the right of b in Figs. 1a and 1c. For simplicity, in Fig. 1 we confined our attention to the case when dP/dT > 0 over the entire line cc'd; however, alternate versions are possible when dP/dT < 0.<sup>[7]</sup> Finally, for substances which are dielectrics under normal conditions, the point c falls on the line of equilibrium between the liquid and solid-state phases.

Since the difference between the specific volumes of the two phases on the line cc' is not large, then one can talk about a phase transition of the first kind, similar to a second-order phase transition. In experiments which are not very accurate, the line cc' will not be observed, but the region c' will be perceived as the lower critical point. It should also be kept in mind that the models considered below are very approximate; therefore the line cc' predicted by these models actually cannot be realized in general; in this case the point c' turns out to be the true lower critical point of the plasma phase transition.

The plasma phase transition and its upper critical point d were investigated in <sup>[7]</sup>. However, the model used in <sup>[7]</sup> only took the Coulomb interaction of the free charges into consideration and was suitable only for high temperatures. Therefore, in <sup>[7]</sup> it was not explained what happened to the phase equilibrium curve upon lowering the temperature, or how this is related to the curve for the phase equilibrium between the vapor and liquid states. The contraction of the curves of coexistence to the point c' upon lowering the temperature and the subsequent phase transition cc' are considered in the present article. A two-component model of electrons and ions was used

for the region to the left of cc', and a three-component model of electrons, ions, and atoms was used for the region to the right of cc'.

#### THE TWO-COMPONENT MODEL

We shall use the following three-term equation of state, which is applicable for liquids and solids at high pressures and temperatures:<sup>[9]</sup>

$$\varepsilon = \varepsilon_x(V) + \varepsilon_r(V, T) + \varepsilon_e(V, T), \quad P = P_x(V) + P_r(V, T) + P_e(V, T),$$
  

$$F = \varepsilon_x(V) + F_r(V, T) + F_e(V, T), \quad (1)$$

where  $\epsilon_{\mathbf{X}}(V)$  and  $P_{\mathbf{X}}(V)$  are the elastic components of the energy and pressure, which do not depend on the temperature;  $\epsilon_{\mathbf{T}}(V, T)$ ,  $P_{\mathbf{T}}(V, T)$ , and  $F_{\mathbf{T}}(V, T)$  correspond to the thermal motion of the ions;  $\epsilon_{\mathbf{e}}(V, T)$ ,  $P_{\mathbf{e}}(V, T)$ , and  $F_{\mathbf{e}}(V, T)$  correspond to thermal excitation of the electrons (for the densities and temperatures of interest to us, the electrons are degenerate), and F denotes the free energy. Let us consider methods of calculating the individual terms in Eq. (1).

Under the conditions given below of interest to us, the thermal excitation of the electrons gives a small contribution, and this contribution can be estimated just like for a perfect gas. At relatively low temperatures the thermal motion of the ions is vibrational. Then<sup>[9]</sup>

$$F_{\tau}(V,T) = 3NT \ln (h\bar{\nu}/T), \qquad (2)$$

$$P_r(V,T) = V^{-1} \Gamma(V) \varepsilon_r(V,T), \qquad (3)$$

where  $\bar{\nu}$  and  $\Gamma(V)$  denote the average frequency of the vibrations and the Grüneisen coefficient, which are defined by the relations

$$\nabla = \rho^{\frac{1}{2}} (dP_x / d\rho)^{\frac{\mu}{2}}, \tag{4}$$

$$\Gamma(V) = -\frac{\partial \ln \bar{v}}{\partial \ln(1/\rho)} = -\frac{2}{\Im} - \frac{V}{2} \left(\frac{d^2 P_x}{dV^2}\right) \left(\frac{dP_x}{dV}\right)^{-1}$$
(5)

( $\rho$  is the density). Formulas (2) through (5) are valid for  $T < T_C \cong 2\Delta U/3 \cong U/3$ , where  $\Delta U \cong U/2$  is the height of the potential barrier for motion of the ions, and U is the binding energy.<sup>[9]</sup> For  $T > T_C$  the thermal motion of the ions is translational, and one can take it into consideration in the ideal gas approximation:

$$F_{T}(V, T) = -NT \ln \left[ eV N^{-1} (MT / 2\pi \hbar^{2})^{3/2} \right], \tag{6}$$

where N and M denote the number and mass of the ions. The quantity  $T_c$  increases with increasing density; therefore Eq. (2) is valid for one and the same temperature associated with larger densities, but Eq. (6) is valid for smaller densities; for intermediate densities it is necessary to match the results given by Eqs. (2) and (6).

In the theory of metals, the following result is obtained for  $\epsilon_{\rm X}({\rm V})$ :<sup>[10, 11]</sup>

$$N^{-1}\varepsilon_{x}(V) = \varepsilon_{0}(r_{s}) + 2.21r_{s}^{-2} + 0.284r_{s}^{-1} - 0.88(r_{s} + 7.8)^{-1} + I,$$
(7)

where  $\varepsilon_0(\mathbf{r_S})$  denotes the energy of an electron in a cell of radius  $\mathbf{r_S}$  with the ion at the center; the second, third, and fourth terms correspond to the energy of the degenerate electrons, the energy of the electrostatic interaction between the electrons, and the correlation energy (in the Wigner approximation); I denotes the ionization potential of the atom, and the average distance  $\mathbf{r_S}$  is ex-

pressed in terms of Bohr radii. A convenient approximation for  $\epsilon_0(\mathbf{r}_S)$  is given by  $^{[11]}$ 

$$\varepsilon_0(r_s) = -3r_s^{-1} + r_0^2 r_s^{-3}.$$
 (8)

Thus, the specific properties of the element are taken into account by the single parameter  $r_0$ ; we note that the first term in Eq. (8) can be interpreted as the Madelung energy. Formula (7) is an approximation; if experimental data is available one can use the interpolation approximation of Bardeen:<sup>(11)</sup>

$$N^{-1}\varepsilon_{x}(V) = Ar_{s}^{-1} + Br_{s}^{-2} + Cr_{s}^{-3},$$
(9)

where the coefficients A, B, and C are determined from three points. Formula (9) is more accurate than (7) only in that region where experimental data exists. Formula (7) apparently describes a wide range of variations of  $r_s$ better. We did not begin to introduce certain refinements, which are made in the theory of metals, into formula (7) since these improvements are also valid only for certain ranges of the values of  $r_s$ . In connection with the derivation of formula (7), the presence of the ionic lattice is not very essential; therefore one can anticipate that the utilization of (7) for disordered systems will also give reasonable results.

Knowing  $r_0$  (or A, B, and C) one can evaluate  $\bar{\nu}$  and  $\Gamma(V)$  and then determine all of the quantities in Eq. (1) for the temperatures and densities of interest to us.

## THE THREE-COMPONENT MODEL

Taking into consideration all of the types of interactions, we write down

$$F = F_{ei} - N_a T \ln \left[ eV N_a^{-1} (1 - n_a b - n_i b_i) (MT / 2\pi \hbar^2)^{s/c} \right] - a N_a^2 V^{-1} - a_a N_a N_e V^{-1} - a_a N_a N_i V^{-1} + I N_i,$$
(10)

where  $F_{ei}$  denotes the contribution of the electron-ion subsystem; the different approximations for  $F_{ei}$  are discussed in <sup>[7,12]</sup>. We note that from these expressions it follows that the dependence of  $P_{ei} = -\partial F_{ei} / \partial V$  on V for temperatures smaller than the critical temperature  $\sim 10^4$  °K has a nonmonotonic behavior, which was interpreted in <sup>[7]</sup> as an indication of a phase transition (the nonmonotonic nature itself is a consequence of the competition between the effective Coulomb attraction, which is dominant at large distances, and the quantum repulsion, which is dominant at small distances).

The second and third terms in (10) take the atomatom interaction into account in the van der Waals approximation (b and a are the corresponding coefficients;  $n_a$  and  $n_i$  are the concentrations of atoms and ions); in addition it is customary to take into account the repulsion of atoms and ions at small distances-that is, the coefficient bi is introduced (taking account of the repulsion between electrons and atoms would give a further correction  $n_e b_e$ , but in view of the uncertainties in the values of  $b_i$  and  $b_e$  the corrections  $n_i b_i$  and  $n_e b_e$  in Eq. (10) are combined). In the same way that the coefficient b in the van der Waals equation actually is not equal to four times the volume of the atom, so the coefficient bi may not correspond directly to the mutual impenetrability of the atom and of the ion (electron), but it may be connected, for example, with that volume which is occupied in the plasma by regions, inside of which the microfield attains a value corresponding to destruction of the atom.

The fourth and fifth terms in (10) take into account the interaction between atoms and charged particles (essentially a long-range attraction). According to [13]

$$a_{ae} = \hbar^2 m^{-1} \sqrt{\pi \sigma(T)}, \qquad (11)$$

where  $\sigma(T)$  is the cross section for electron-atom scattering. For the ion-atomic interaction, from (11) it follows that  $a_{ai} \ll a_{ae}$  since in Eq. (11) m denotes the reduced mass of the colliding particles.<sup>1)</sup>

For simplicity, molecules and molecular ions are neglected in Eq. (10).<sup>2)</sup> The equation of state and the equation of ionization equilibrium follow from (10):

$$P = P_{ei} + n_a T (1 - n_a b - n_b)^{-1} - n_a^2 a - n_a n_e (a_{ae} + a_{ai}), \quad (12)$$

$$n_{a} = (1 - n_{a}b - n_{i}b_{i})n_{e}^{2}(2\pi\hbar^{2}/mT)^{3/2} \exp[(I/T) - \varphi], (13)$$

$$\varphi = T^{-1}[\Delta \mu_{ei} + (a_{ae} + a_{ai} - 2a)n_o] + n_a(b - b_i)(1 - n_ab - n_ib_i)^{-1}, (14)$$

where  $\Delta \mu_{ei}$  denotes the change of the chemical potentials due to the nonideal nature of the electron-ion subsystem and the degeneracy of the electrons.

With increasing density the properties of the atoms may change. In particular, this is connected with the appearance of microfields; therefore the coefficients b,  $b_i$ , a,  $a_{ae}$ ,  $a_{ai}$ , and I are in general functions of  $n_i$  and  $n_a$ .<sup>3)</sup> However, taking into consideration the approximate nature of all of the terms in (10) and the uncertainty in the coefficients, which is noted in particular for  $a_{ae}$  and  $a_{ai}$ , we have omitted the corresponding derivatives in Eqs. (12) and (14).

We note the appearance of the factor  $(1 - n_a b - n_i b_i)$ in Eq. (13). One can interpret this factor as a correction which reduces the statistical weight of the atoms.<sup>4)</sup> At comparatively low temperatures an appreciable ionization occurs only when the value of  $n_a b + n_i b_i$  approaches unity. Such ionization can be called ionization by pressure; there remains, however, no place, as it were, for atoms in the system in this case. At high temperatures the ionization is due to the change of the quantity I/T and it occurs when  $n_a b + n_i b_i \ll 1$ . One can call such ionization thermal ionization. The model (10) includes both the limiting as well as intermediate cases.

<sup>2)</sup>For certain systems this assumption may be very essential since the role of strongly bound neutral, positive, or negative molecules (complexes) is very great if they are produced. Let us cite an example from the region of low temperatures: the presence of the strongly bound molecule  $H_2$  leads to the result that the critical temperature of the vapor-liquid transition in hydrogen is two orders of magnitude lower than in the alkali metals; there, where the interaction of the alkali atoms leads to liquefaction, the interaction of the H atoms only leads to the formulation of molecules.

 $^{3)}$ The dependence I(n<sub>i</sub>) can be related to the transformation of the excited levels into the conduction bands and their overlap.

<sup>4)</sup>The reduction of the statistical weight of excited atoms, caused by their finite volume, was considered by Fermi [<sup>18</sup>] within the framework of the van der Waals equation in order to obtain a limitation on the partition function of the atom.

<sup>&</sup>lt;sup>1)</sup>The formula  $a_{ae} = 8\pi e^2 \alpha r_1^{-1}$  is proposed in [<sup>14</sup>] where  $\alpha$  denotes the polarizability and  $r_1$  is the effective radius of repulsion. Even with the uncertainties in  $r_1$  taken into account, the differences from (11) may reach one order of magnitude (formula (11) appears to us to be better founded). The electron-atom interaction is also considered in [<sup>15,16</sup>]. For the ion-atomic interaction  $2a_{ai} = a_{ae}$  [<sup>14</sup>] and  $a_{ai} > a_{ae}$ . [<sup>17</sup>] As is evident from [<sup>13-17</sup>], taking account of the interaction of atoms with charged particles is still extremely ambiguous.

# **RESULTS OF THE CALCULATIONS FOR LITHIUM**

Lithium was selected in view of the simplicity of its electronic structure and the presence of relatively complete information about the parameters which are required for our calculations. The following data was used in the two-component model: in Eq. (8)  $r_0 = 3$ ;<sup>[10]</sup> the values A = -3.14, B = 4.22, and C = 1.93 in Eq. (9) were determined from the following equations: a) the equilibrium value  $r_S^0$  at P = 0 was equated to the experimental value  $r_S^0 = 3.25$ ; b) the value of  $\epsilon_x(r_S^0)$  was equated to the experimental value of the bonding energy, 1.58 eV; c) the value of  $P_x$  ( $\rho/\rho_0 = 0.9$ ) was equated to the value -11.6 kbar, which was measured in <sup>[19]</sup>.

We used formula (9) in order to determine  $\epsilon_{\mathbf{X}}(\mathbf{V})$  for values of  $\mathbf{r}_{\mathbf{S}} \sim \mathbf{r}_{\mathbf{S}}^{0}$ ; for larger values of  $\mathbf{r}_{\mathbf{S}}$  we used formulas (7) and (8). Values of  $\Gamma(\mathbf{V})$  calculated from formulas (7) and (8) are in better agreement with the values found in <sup>[19]</sup> than are the values calculated from formula (9); for example, under normal conditions  $\Gamma = 0.90$ ; <sup>[19]</sup> formulas (7) and (8) give  $\Gamma = 1.05$  but formula (9) gives  $\Gamma = 1.38$ . Therefore, the approximation which follows from (7) and (8) was used in order to determine  $\Gamma(\mathbf{V})$  and  $\bar{\nu}$  for all values of  $\mathbf{r}_{\mathbf{S}}$ . Equations (1) are applied in the literature for  $\mathbf{r}_{\mathbf{S}} \leq \mathbf{r}_{\mathbf{S}}^{0}$ ; however, we are interested in the region  $\mathbf{r}_{\mathbf{S}} \geq \mathbf{r}_{\mathbf{S}}^{0}$ . Therefore, the approximations (7) and (9) are used in such a way that the extrapolation for  $\mathbf{r}_{\mathbf{S}} > \mathbf{r}_{\mathbf{S}}^{0}$  will be normalized in the best way with respect to the experimental data. We note, however, that the utilization of only (7) or (9) would not lead to any fundamental changes in the results. Finally, we shall indicate that  $T_{\mathbf{C}} \cong 5000^{\circ}$ K for normal densities.

The results of calculations of the free energy for three temperatures are shown in Figs. 2-4. In the three-component model for T = 1000 and  $2000^{\circ}$ K only the atom-atom interaction was taken into account; the values of the constants a and b which were used correspond to the following critical parameters for the vaporliquid transition:  $T = 3200^{\circ}$ K and  $n_a = 10^{22}$  cm<sup>-3</sup>.<sup>[20]</sup> For  $T = 6000^{\circ}$ K the Coulomb interaction in the three-component model was taken into account in the Debye approximation.

The dependences of F on V shown in Figs. 2-4 have a nonmonotonic character; they contain regions with negative pressure and unstable regions. Thus, one can talk about phase transitions of the first kind. The points characterizing the states of the coexisting phases are determined by drawing the lowest common tangents. There is a single phase transition in Fig. 2: from the atomic gas into the metallic liquid B; there are two phase transitions in Fig. 3: from the atomic gas C into the atomic liquid D and from the atomic liquid A into the metallized B. Thus, the models under consideration predict that the dielectric-metal transition in a liquid single-component substance is a phase transition of the first kind. The fundamental difference between phase B and phase A consists of the abrupt increase in the concentration of free charges and the formation of a band structure (if one can talk about bands in regard to systems which possess only short-range order).

The influence on curves 2 in Figs. 2 and 3 of the interactions involving the participation of charged particles was also considered. The Debye approximation was taken for  $F_{ei}$ , the value of  $a_{ae}$  was estimated according to formula (11), and it was assumed that  $b_i = b$ 



FIG. 2. The isotherm F(V) for Li with T =  $1000^{\circ}$ K: curve 1 corresponds to the approximation (9) for  $\epsilon_{\rm X}$ (V) and the approximate formulas (7) and (8) for  $\overline{\nu}$ ; curve 2 corresponds to the approximation (10). B and A, D and C-mutally coexisting phases.

FIG. 3. The isotherm F(V) for Li at  $T = 2000^{\circ}K$ : curve 1 corresponds to the approximation (9) for  $\epsilon_{X}(V)$  and the approximate formulas (7) and (8) for  $\overline{\nu}$ ; curve 2 corresponds to the approximation (10). B and A, D and C denote mutually coexisting phases.

FIG. 4. The isotherm F(V) for Li at T = 6000°K: curve 1 corresponds to the approximate formulas (7) and (8) for all quantities; curve 2 corresponds to the approximation (10). B and A denote coexisting phases.

FIG. 5. Phase equilibrium curves for Li. The points b, c, and c' are the same as in Fig. 1. The horizontal line (isotherm) BA corresponds to Fig. 4, the horizontal line BADC corresponds to Fig. 3, and the horizontal line BC corresponds to Fig. 2.





to 2b. It was found that in this approximation the interactions involving the participation of charged particles do not give an important contribution to F in the vicinity of the point A.<sup>5)</sup> Therefore, the results discussed above remain valid. At the same time for  $n_a \rightarrow b^{-1}$  the van der Waals equation always remains stable; taking account of the interactions with charged particles leads to the violation of thermodynamic stability for  $n_a < b^{-1}$ , but to the left of the point A (within the framework of the assumptions which have been made). Such a violation of the stability on curve 2 in Figs. 2 and 3 for a reduction of V naturally supplements the picture of the A-B phase transition, since curve 1 becomes unstable upon an increase of V.

The loss of thermodynamic stability associated with the reduction of the volume along curve 2 in Fig. 4 is due to the interaction of charged particles among themselves. Under these conditions the ionization is thermal; therefore the difference between the specific volumes of phases A and B is appreciable.

The phase equilibrium curves which follow from the models under consideration are shown on Fig. 5. The

<sup>5)</sup>We note that these interactions at the same time may be decisive in connection with the calculation of the electrical conductivity.

isotherms depicted on Figs. 2-4 are marked on these same curves. The basic conclusions which follow from Fig. 5 were already considered by us during the discussion of Fig. 1.

As has already been mentioned, estimates<sup>[13-17]</sup> of the interaction energies of charged particles with neutral particles differ appreciably from each other. There also is considerable uncertainty in estimates of the other types of interactions, for example, in the calculation of the atom-atom interaction for large densities. Therefore, the specific values of the thermodynamic quantities shown in Figs. 2-5 may differ substantially from the real values. Evidently the dielectric-metal phase transition turned out to be shifted excessively to the side of higher densities. At the same time the qualitative nature of the situation hardly changes upon taking more accurate account of the different kinds of interactions. The forces of attraction (charge-charge forces at higher temperatures, and charge-neutral forces at lower temperatures) play the principal role on the line AA. These forces lead to an increase in the degree of ionization and to a loss of thermodynamic stability. Stability is established only at higher densities owing to the quantum effects in a system of charged particles. We note that quantum effects develop in two ways; for example, in formulas (7) and (8) the terms  $2.21 r_s^{-2}$  and  $r_0^2 r_s^{-3}$ , which ensure stability, have different natures: the first is due to the degeneracy of an ideal electron gas, and the second is due to the quantum nature of the interaction between electron and ion at small distances.

In conclusion let us once again mention the crudeness of the models which have been used, and connected with this, the necessity for further investigation of the possibility of phase transitions which differ from the ordinary "vapor-liquid" transition in the gaseous, liquid, and solid states of matter.

### COMPARISON WITH MEASUREMENTS

In the previous section the example of lithium was considered, since it was easiest to perform the calculations for it. However, the investigation of the properties of the phase equilibrium curves which was carried out is of a general nature, and its results can be applied to different elements.

Direct measurements of the equations of state, including the region up to the point b and somewhat above, for the present have been carried out for mercury and cesium.<sup>[3,5,21]</sup> In these experiments a second phase transition in addition to the vapor-liquid transition was not observed. This can be explained by the fact that the dielectric-metal phase transition is similar to a secondorder phase transition (actually the difference of the volumes may be considerably smaller than the result obtained in Fig. 3) and the great difficulties associated with carrying out the experiments did not permit them to achieve the required accuracy in <sup>[3,5,21]</sup>. Temperatures above the point c' have not yet been obtained. Measurements of the specific heat in the neighborhood of cc' and along the curve bc would also be of interest.

Measurements of the electrical conductivity  $\sigma$  were also carried out in <sup>[3,5]</sup>. Some of the anomalies observed in its behavior are interpreted in <sup>[4]</sup> as possible indications of a phase transition. Recently A. G. Khrapak and I. T. Yakubov reached a similar conclusion; from the data<sup>[3,5]</sup> they constructed the dependence of  $\partial \ln \sigma / \partial (T^{-1})$ on the volume; the nonmonotonic behavior of this dependence (in a narrow range of variation of the volume) enabled them to conjecture that in this interval the conductivity in a heterogeneous system was being measured. Thus, the measurements<sup>[3,5]</sup> did not give a direct proof that metallization is a phase transition, but at the same time they gave indirect confirmation of such a point of view.

Attempts to investigate the metallization of xenon under large pressures were undertaken in  $[5,2^{22}]$ . The accuracy of the measurements which were made is considerably worse than in  $[3,5^3]$ ; therefore, it is impossible to say anything yet about whether metallization of xenon is a phase transition.

Above the concepts of a metal and of a dielectric were used somewhat schematically. In fact, to the right of cc' on Figs. 1 and 5 the conductivity does not vanish, but to the left it cannot immediately become metallic. In the transition region the substance may possess semiconducting properties.<sup>[3-5,16]</sup>

I wish to express my sincere gratitude to V. S. Vorob'ev, L. V. Keldysh, A. N. Starostin, and I. T. Yakubov for interesting discussions and for helpful comments.

<sup>1</sup>Ya. B. Zel'dovich and L. D. Landau, Zh. Eksp. Teor. Fiz. **14**, 32 (1944).

<sup>2</sup>R. G. Arkhipov, Zh. Eksp. Teor. Fiz. **49**, 1601 (1965) [Sov. Phys.-JETP **22**, 1095 (1966)].

<sup>3</sup>I. K. Kikoin, A. P. Senchenkov, É. B. Gel'man, M. M. Korsunskii, and S. P. Naurzakov, Zh. Eksp. Teor. Fiz. 49, 124 (1965) [Sov. Phys.-JETP 22, 89 (1966)]; I. K. Kikoin and A. P. Senchenkov, Fiz. Metal. Metalloved. 24,

843 (1967) [The Physics of Metals and Metallography 24, No. 5, 74 (1967)].

<sup>4</sup>N. F. Mott, Rev. Mod. Phys. 40, 677 (1968).

<sup>5</sup> E. U. Franck and F. Hensel, Phys. Rev. **147**, 109 (1966); F. Hensel and E. U. Franck, Rev. Mod. Phys. **40**, 697 (1968).

<sup>6</sup> Marvin Ross, Phys. Rev. 171, 777 (1968).

<sup>7</sup>G. É. Norman and A. N. Starostin, Teplofizika Vysokikh Temperatur 8, 413 (1970) [High Temperature 8, 381 (1970)].

<sup>8</sup>G. E. Norman, in the book: Ocherki fiziki i khimii nizko-temperaturnoĭ plazmy (Outlines of the Physics and Chemistry of a Low-temperature Plasma), edited by L. S. Polak, Izd. Nauka, 1971, p. 260.

<sup>9</sup>Ya. B. Zel'dovich and Yu. P. Raĭzer, Fizika udarnykh voln i vysokotemperaturnykh gidrodinamicheskikh yavleniĭ (Physics of Shock Waves and High-Temperature Hydrodynamic Phenomena), Izd. Nauka, 1966, p. 536 (English Transl., Academic Press, 1966 and 1967).

<sup>10</sup> Frederick Seitz, The Modern Theory of Solids, McGraw-Hill, 1940 (Russ. Transl., Gostekhizdat, 1949, p. 367).

<sup>11</sup> Joseph Callaway, Energy Band Theory, Academic Press, 1964 (Russ. Transl., Mir, 1969, p. 143).

<sup>12</sup> G. Kelbg and W. Ebeling, Institute of Theoretical Physics Preprint, Ukrainian SSR Academy of Sciences, Kiev, 1970. K. Rohde, G. Kelbg, and W. Ebeling, Ann. Physik **25**, 80 (1970). W. Ebeling, G. Kelbg, and R. Sändig, Beiträge aus der Plasmaphysik 10, 507 (1970). <sup>13</sup>A. A. Vedenov, Conference on Quiescent Plasma, Frascati, 1967.

<sup>14</sup>B. L. Timan, Zh. Eksp. Teor. Fiz. 25, 733 (1953).

- <sup>15</sup> A. A. Likal'ter, Zh. Eksp. Teor. Fiz. 56, 240 (1969) [Sov. Phys.-JETP 29, 133 (1969)].
- <sup>16</sup> I. I. Yakubov, Zh. Eksp. Teor. Fiz. **58**, 2075 (1970) [Sov. Phys.-JETP **31**, 1118 (1970)].
- <sup>17</sup> B. M. Smirnov, Dokl. Akad. Nauk SSSR 195, 75 (1970) [Sov. Phys.-Doklady 15, 1050 (1971)].
  - <sup>18</sup> E. Fermi, Z. Physik 27, 54 (1924).
- <sup>19</sup> A. A. Bakanova, I. P. Dudoladov, and R. F. Trunin, Fiz. Tverd. Tela 7, 1615 (1965) [Sov. Phys.-Solid State 7, 1307 (1965)].

<sup>20</sup> I. G. Dillon, P. A. Nelson, and B. S. Swanson, J. Chem. Phys. 44, 4229 (1966).

<sup>21</sup> Yu. S. Korshunov, A. P. Senchenkov, É. I. Asinovskiĭ, and A. T. Kunavin, Teplofizika Vysokikh Temperatur 8, 1288 (1970).

<sup>22</sup> M. Ross, R. N. Keeler, and A. C. Mitchell, Bull. Am. Phys. Soc. 13, 1660 (1968).

Translated by H. H. Nickle 185