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Electric Properties of Liquid Metals and Semiconductors

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An attempt is made to describe from a unified point of view the electric properties of liquid metals and semiconductors, including the critical region of temperatures and pressures for metals. Various models are discussed for the description of the electric properties of liquid metals and semiconductors, for which many experimental and theoretical investigations are known. At temperatures and pressures above critical, the accumulated experimental and theoretical material is not as extensive, but even now certain conclusions can be drawn concerning the character of the metal-dielectric transition during the continuous change from the liquid to the gaseous state.

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INTRODUCTION

INTEREST in liquid metals and semiconductors has greatly increased of late. In addition to the increasing interest in transport phenomena in disordered conductors and in the physics of the liquid-solid and solid-vapor phase transitions, liquid conductors have found concrete practical applications, for example as high-temperature coolants in nuclear power installations, as resistance thermometers operating at high radiation levels, or as the working media in MHD energy converters and in heat converters.

Thus, practical demands have stimulated the investigation of the properties of molten metals and semiconductors in a wide interval of temperatures, from the melting point to the gas phase. Research in such a wide interval of temperatures and corresponding densities is of considerable interest from the scientific point of view. Indeed, variation of the temperature and the density of the metal in a wide range uncovers prospects for the observation of changes in the physical properties of materials and the understanding of the mutual correlation of their different characteristic parameters.

The purpose of the present paper is to cast light on the material accumulated to date, principally on the electric properties of liquid metals in a wide range of temperatures, including the transcritical state, and of semiconductors. Since most investigations of liquid metals are limited to the relatively narrow interval near the melting point and much progress has been attained in this region when it comes to the quantitative interpretation of the data, we deemed it advisable to deal with the research on metals in the low-temperature interval in a separate first chapter.

In the second chapter we report the main results on liquid semiconductors. The material of this chapter, in the authors' opinion, is a very valuable supplement to the preceding chapter because at ultrahigh temperatures molten metals become nearly semiconducting. Knowledge of the main laws governing liquid semiconductors may be useful for the identification and understanding of the property transformation that takes place in metals.

The third chapter deals with metal research in a range of temperatures close to critical and higher, up to the gas phase.

Chapter I was written by V. Ya. Prokhorenko, Chap. II by A. A. Andreev, and Chap. III by V. A. Alekseev.

I. LIQUID METALS

The first theoretical studies of the physics of liquid metals were made by Mott[1,2]. The phenomenological approach developed by Mott was sufficiently fruitful and is being used even now in the free-volume theory[3,5].

Subsequent researches, particularly those of Regel'[5] and Mott[6], have shown that a microscopic quantum-electronic model of liquid metals can be constructed only on the basis of rigorous premises concerning the structure of liquid metals.

The fundamental research on the structure of liquid metals was started in the thirties. Debye, Zernike, Prince, and Danilov have developed a theory for the scattering of x-rays in liquids[7]. The theory yielded an expression for the intensity of coherently-scattered x-rays (in electronic units):

$$I^{coh}_{(el.\,un.)}(k) = Nf^2 \left\{ 1 + \int_0^\infty 4\pi r^2 [g(r) - g_0] \frac{\sin kr}{kr} dr \right\}, \quad (1)$$

where N is the number of scattering atoms, f is the atomic scattering factor, g(r) the atomic density of the molten metal at a distance r from a fixed atom, and g_0 is its average atomic density. The wave number is determined by the scattering angle θ and by the x-ray wavelength λ:

$$k = (4\pi/\lambda) \sin(\theta/2).$$

The Fourier transform of the intensity of the scattered rays yields an expression for the radial distribution function (RDF) of the atoms, which characterizes the structure of the molten metal:

$$4\pi r^2 g(r) = 4\pi r^2 g_0 + \frac{2r}{\pi} \int_0^\infty k \left[\frac{I^{coh}_{(el.\,un.)}(k)}{f^2} - 1 \right] \sin kr\, dk.$$

Further structure investigations of molten metals were continued with emphasis on the determination of interatomic distances and the average coordination numbers from the experimental radial-distribution curves. In addition, models of theoretical RDF were assumed by "smearing" the crystal structures; their comparison with the experimental data has made it possible to assess the degree of variation of the short-range order during the melting of the metal. Later, summarizing the earlier work on the x-ray diffraction studies of molten metals, Radchenko[8], one of the pioneers of this research, classified the investigated object in the following manner:

a) Metals characterized in the solid state by a close-packed structure (Al, Au, Pb, Zn, Cd, Tl, In, and others). The positions of the maxima on the experimental intensity and radial-distribution curves for these metals after melting are in good agreement with the diffraction lines of the closest coordination spheres in the crystals of the corresponding substances. In addition, the experimental radial-distribution curves of the atoms in the liquid metals of this group coincide with the theoretical ones obtained by "smearing" the close-packed structures. It can be concluded on the basis of these facts that metals having a close packing in the solid state retain the short-range order structure on going to the liquid state.

b) Metals with loose packing in the solid state. A similarity is observed between the intensity curves for this group of metals in the liquid state. Immediately beyond the melting point, a secondary maximum is observed on the descending branch of the first maximum of Bi, Ga, Sb, or Ge. In liquid Sn and Hg, only a tendency to the formation of such a maximum is observed. A s slight rise in temperature smooths out the secondary

maximum and causes a considerable change in the intensity curve. An analysis of the radial-distribution curves leads to the conclusion that the short-range order becomes closer (the coordination number increases) when these metals melt.

A considerable contribution to the knowledge of the electronic properties of liquid metals was made by Soviet scientists. In 1931 Kikoin and Fakidov[9] published their results on the Hall constant R of liquid metals. It was shown that R of a eutectic Na-K alloy remains almost unchanged when it melts and is equal to the value calculated with the free-electron model (FEM). The notion that the structure of the melt is close to the structure of the solid is the basis of the fundamental kinetic theory of liquids developed by Frenkel[10]. It was established experimentally that the vanishing of the long-range order during the melting of metals has little influence on their electric properties, namely, the difference between the electric conductivity of two metals in one aggregate state can greatly exceed the change produced in the electric conductivity by melting. On the basis of the available experimental material, Ioffe[11] reached the conclusion that the short-range order plays a decisive role in the determination of the electric properties of substances. Regel' and co-workers[5,12-14] have demonstrated this convincingly for a large group of metals and alloys.

Table I shows the present status of the experimental research on the resistivity ρ, the absolute thermoelectric power α, and the Hall constant R of different metals upon melting. The table lists the most reliable and repeatedly confirmed data. The ratios of the resistivities of the solid and liquid metals and the values of ρ near the crystallization temperature are taken from[15,17]. The ratios of the measured Hall constants of liquid metals R_{liq} to the values of R_0 calculated in the FEM are taken from[18]. The absolute thermoelectric power near the crystallization temperature, α_{liq}, and its change on going to the solid state are taken from the latest original sources. The change ΔK of the coordination number is taken from[28], with the exception of certain elements (Cu, Ag, and Sn from[20] and In from[23]).

The experimental material on the structure and electronic properties of liquid metals can be generalized in the following manner:

1. The resistance ratios of liquid and solid metals are larger the greater the decrease of the coordination number upon melting, and smaller the denser the short-range order. We have in mind, of course, only the general tendency and not an exact correspondence, since the coordination number is by far not the only governing factor in the structure.

2. The temperature coefficients of resistivity of most liquid metals do not change with temperature in the first approximation, and are smaller than in the solid state (with the exception of the metals of the first group of the periodic system, for which $\partial\rho/\partial T$ changes little upon melting). The temperature dependence of $\rho(T)$ of liquid metals of the second group is nonlinear.

3. For the overwhelming majority of the investigated liquid metals, the experimental values of the Hall constant are very close to those calculated by the FEM. Exceptions are Al, Tl, Pb, Sb, and Bi, for which, incidentally, the measured values of R_{liq} can not be regar-

Table I

Ele-ment	ρ_{liq}, $\mu\Omega$/cm	ρ_{liq}/ρ_{sol}	R_0, 10^{-5} cm³/C	R_{liq}/R_0	α_{liq}, μV/deg	Ref.	$\Delta\alpha = \alpha_{liq} - \alpha_{sol}$, μV/deg	Ref.	$\Delta K = K_{liq} - K_{sol}$
Li	25.31	1.64	—	—	21.7	18	6.0	15	1.5
Na	9.57	1.45	25.5	0.93	−7.9	18	0.0	15	0—1.0
K	12.97	1.56	—	—	−14.0	16	2.3	15	0—1.0
Rb	22.0	1.60	--	0.7	−6.3	16	3.8	15	0—1.0
Cs	36.0	1.66	—	—	6.4	16	5.8	15	0—1.0
Cu	21.1	2.04	8.25	1.00	17.7	19	10.0	19	−0.5
Ag	17.2	2.09	12.0	1.02	11.0	19	1.0	19	−0.5
Au	31.2	2.28	11.8	1.00	5.6	19	2.1	19	−1.0
Zn	37.4	2.24	5.1	1.01	0.1	21	−6.3	26	−1.2
Cd	33.7	1.97	7.25	0.98	0.5	21	—	—	—
Hg	90.96	4.94	7.6	0.96—1.20	−3.5	21	−1.5	27	3.3
Al	24.2	2.20	3.9	1.00	−2.6	19	1.0	19	−1.2
Ga	25.8	0.45—3.12	3.95	0.95	−0.5	22	−1.5	22	4.0
In	33.1	2.18	5.65	1.00	−1.2	22	−3.5	22	−0.5
Tl	73.1	2.06	6.27	0.76	−0.5	21	—	—	—
Ge	63.0	0.053	3.40	1.00	−12.0	24	70.0	24	4.0
Sn	48.0	2.10	4.42	1.00	−0.5	21	1.3	26	2.5
Pb	95.0	1.94	5.05	0.38—0.88	−3.4	21	7.5	26	0.2
Sb	113.5	0.61	3.87	1.14	5.6	25	−16.0	26	3.8
Bi	128	0.35	4.30	0.60—0.95	−2.2	25	55	26	4.5

ded as reliable[18]. The available data indicated that R_{liq} is almost completely independent of the temperature.

4. There are no obvious laws governing the change of the absolute thermoelectric power on melting. Semimetals are exceptions, and their melting is accompanied by a sharp decrease of the absolute value of the thermoelectric power. In this case there is a correlation between the temperature region in which the thermoelectric power experiences an abrupt change and the existence of a secondary maximum on the descending slope of the first maximum of the intensity curve. Quantitative calculations[25] of α have revealed that the Fermi surface of most liquid metals can be well approximated by a sphere.

5. The results of measurements of the optical reflection[29,30] are adequately described by the Drude formula. The effective number of the free electrons per atom $n_a = (n/N_a)(m_0/m^*)$ (n is the free-electron concentration, N_a is the number of atoms per cm³, m_0 is the mass of the free electron, and m^* is the effective mass of the electron) turned out to be close to the number Z of the valence electrons (Table II). The observed disparities can be attributed to inequality of m_0 and m^*.

6. Extensive material has been accumulated by now on the thermal conductivity of liquid metals. The first generalizations of the available data[31-33] show that jump-like changes of the thermal conductivity during melting are close to the changes of the electric conductivity, and that the Lorentz number in liquid metals has values very close to that predicted by the FEM. However, the thermal conductivity of liquid metals is insignificantly altered by heating, and consequently a progressive increase of the deviations from the Wiedemann-Franz law is observed with increasing temperature. According to[32], this effect can be attributed in part to the increasing role played by the elastic scattering of the electrons with increasing temperature.

7. Recently, interest has increased in the study of liquid transition metals, including rare-earth metals metals[34-37]. Transition metals, unlike those considered earlier, experience no significant changes in their electronic properties upon melting. Thus, for example, the Hall constants of Sm and Ce do not experience a noticeable jump upon melting and remain positive[37], indicating that the change in the electronic structure of these metals on going to the liquid phase is negligible. The quantum-mechanical approach[28] also turned out to be highly promising for the interpretation of the properties of transition metals.

Modern quantum-electronic theory of liquid metals is based on different notions concerning the structure of the melts.

Gubanov[38], using Glauberman and Tsvetkov's experimental confirmation[39] of the structural-diffusion theory, based his model on a quasicrystalline approach. According to Gubanov, the parameter characterizing the degree of violation of the short-range order in a liquid is very small, and therefore, if a certain deformed coordinate system is introduced, the field of the ionic cores can be regarded as approximately periodic. The solution of the Schrödinger equation in the new system of coordinates is a rather complicated task. The main qualitative result of Gubanov's theory is the statement that the band structure is conserved in the liquid phase. The loss of the long-range order leads only to a certain broadening of the bands of allowed energies and to the appearance of additional scattering mechanisms. The total mean free path l of the electron in a liquid is given by[38]

$$l^{-1} = l_{liq}^{-1} + l_d^{-1} + l_{ph.liq}^{-1} + l_{ph}^{-1};$$

here l_{liq} is the specific "liquid" scattering due to violation of the short-range order; l_d takes into account the scattering by local abrupt disturbances of the structure (this scattering is analogous to the action of impurities and other defects in a crystal); $l_{ph.liq}$ describes the so-called phonon-liquid scattering, which is proportional to the temperature and is due to the less stringent selection rules in the scattering of electrons by phonons; l_{ph} is determined by the usual phonon scattering. Taking

Table II

	Ag	Cu	Hg	Cd	Ga	In	Sn	Pb	Ge	Bi	Sb
n_a	1.13	0.84	2.0	2.13	2.9	3.3	4.68	4.68	4.3	5.3	6.12
z	1	1	2	2	3	3	4	4	4	5	5

into account all the scattering mechanisms, the resistivity of a liquid metal is given by

$$\rho = (3\pi^2 m^{*2}/e^2 \hbar^3 k_F^3)\,(A + Bk_F^2 + Dk_F^4), \qquad (2)$$

where m* is the effective mass of the electron and k_F is the wave vector on the Fermi surface. The parameter A determines the scattering by the local defects and the "liquid" scattering; the parameter B describes the phonon-liquid scattering, and the parameter D the scattering by the phonons.

The parameters in expression (2) for the electric resistivity can be determined in principle if one knows the spectrum and the wave functions of the electrons, but the practical calculation of these parameters is difficult, and the theory gives therefore only qualitative results. It is thus of interest to use a different approach to the problem, which, while not universal, would yield mathematically more concrete results on the basis of the atomic and structure features of a definite group of substances. Attention is called in this connection to the latest researches of Gubanov[40,41], who uses a method of linear combinations of atomic orbitals developed by him to calculate the energy spectrum of the electrons in liquid alkali metals.

In addition to Gubanov's work, Ziman's theory[42-44] has gained wide acceptance in recent years. This theory makes it possible to calculate numerically the kinetic coefficients of liquid metals by using experimental information on their structure. Ziman's theory is based on the concept of the pseudopotential. The pseudopotential (PP) model was developed by Phillips and Kleinman[45] on the basis of Herring's orthogonal plane wave method[46]. The method is based on the fact that orthogonalization of plane waves to the wave functions of the internal shells leads to rapidly convergent expansions for the electronic wave functions. A consequence of such an orthogonalization is that a certain potential, describing the repulsion of the electrons from the ions, is added to the true potential of the crystal lattice. As a result, the total effective potential, called the pseudopotential, turns out to be a small smoothed-out quantity. It is therefore possible to apply perturbation-theory methods to the electrons in the conduction band.

One of the fundamental physical approximations on whi which the PP theory is based consists[47] of subdividing all the electronic states into states pertaining to the internal shells and states of the conduction band, under the assumption that the wave functions of the internal shells are strongly localized. It is assumed in this approximation that the wave functions of the internal shells do not differ from the wave functions of the isolated ions, although the corresponding energy eigenvalues E_α do not coincide with the energies from the isolated atoms. The different corrections that must be introduced in the energy eigenvalues of the internal shell of the ion in order to obtain the corresponding values of E_α in a metal are called by Linn and Phillips[48] the energy shifts of the internal shells. It is shown in[48] that the difference between the pseudopotentials employed by different authors reduce with good accuracy to changes in the energy shifts of the internal shells. At the present time the pseudopotentials of Cohen[49], Heine and Abarenkov[50], Animalu and Heine[51], Harrison[47], Ashcroft[52], Krasko[53], and others are successfully

used to calculate the kinetic properties of liquid metals. These PP, whether derived from first principles or by means of models, have all their shortcomings and advantages when used to calculate concrete properties of a metal. It is therefore useless to speak of the choice of an optimal universal model.

An important feature of PP is that the total scattering potential can be represented by the sum of the PP of individual ions:

$$U(\mathbf{r}) = \sum_i u(\mathbf{r} - \mathbf{R}_i), \qquad (3)$$

where $u(\mathbf{r} - \mathbf{R}_i)$ is the PP produced at the point r by an ion situated at the point $\mathbf{R}_i$. The possibility of representing the potential in the form of the sum of potentials of N individual ions permits its matrix elements to be factorized. Substituting (3) in the definition of the scattering matrix element, we obtain

$$U_{\mathbf{k},\,\mathbf{k}+\mathbf{K}} = V^{-1} \int \exp\,(i\mathbf{k}\mathbf{r}) \sum_i u\,(\mathbf{r} - \mathbf{R}_i) \exp\,[-i\,(\mathbf{k} - \mathbf{K})]\,\mathbf{r}\,dv$$

$$= V^{-1} \sum_i \exp\,(-i\mathbf{K}\mathbf{R}_i) \int \exp\,[-i\,(\mathbf{k} + \mathbf{K})\,(\mathbf{r} - \mathbf{R}_i)]$$

$$\times u\,(\mathbf{r} - \mathbf{R}_i) \exp\,[i\mathbf{k}\,(\mathbf{r} - \mathbf{R}_i)]\,dv.$$

Thus, the scattering matrix element can be represented in the form of a product of the matrix element of an individual ion (form factor) by a sum of plane waves that depend on the ion coordinates, or in other words on the structure of the metal. Changing over to a new variable $\mathbf{R} = \mathbf{r} - \mathbf{R}_i$, we obtain

$$U_{\mathbf{k},\,\mathbf{k}+\mathbf{K}} = S(\mathbf{K})\,U_\mathbf{K}, \qquad (4)$$

where

$$S(\mathbf{K}) = N^{-1} \sum \exp\,(-i\mathbf{K}\mathbf{R}_i),$$
$$U_\mathbf{K} = (N/V) \int \exp\,(-i\mathbf{K}\mathbf{R})\,u\,(\mathbf{R})\,dv. \qquad (5)$$

The problem of electron scattering by a definite structure is perfectly analogous to the problem of x-ray scattering, the only difference being that the form factors used in the first problem are replaced by atomic form factors. Therefore, in accordance with the theory of diffraction in a liquid, we can write down the structure factor for electron scattering:

$$a\,(\mathbf{k}) = N^{-1} \Big| \sum_i \exp\,(-i\mathbf{k}\mathbf{R}_i) \Big|^2 = I^{\text{coh}}_{(\text{el. un.})}/Nf^2, \qquad (6)$$

where $I^{\text{coh}}_{(\text{el. un.})}$ is the intensity of the coherent scattering of x-rays by N atoms of the liquid metal with an atomic scattering factor f. The quantity $I^{\text{coh}}_{(\text{el. un.})}$, given by expression (1), is obtained directly from experiment.

In the first approximation, Ziman[42] assumed that the ions scatter the electrons independently (the quasigas model). Then the mean free path of the electron is given by the formula

$$\frac{1}{l} = \frac{N}{V}\,2\pi \int_0^{2\pi} (1 - \cos\theta)\,F(\theta) \sin\theta\,d\theta, \qquad (7)$$

where $F(\theta)$ is the differential cross section for scattering by each of the N ions through an angle θ in the volume V. The quantum theory of collisions gives for the differential scattering cross section in the Born approximation

$$F(\theta) = \frac{4\pi^2 m^2}{\hbar^4} \Big| \int \exp\,(-i\mathbf{k}\mathbf{R})\,u\,(\mathbf{R})\,dv \Big|^2 = \frac{4\pi^2 m^2}{\hbar^4} \frac{V^2}{N^2} |u_\mathbf{k}|^2. \qquad (8)$$

In the last equation we took into account expression (5) for the matrix element of an individual ion.

Obviously, to take into account the correlation of the scattering in the liquid, it is necessary to introduce in (8) the complete scattering matrix element given by expression (4) with allowance for (6). If we then substitute the expression for the scattering cross section in (7) and change over from the variables θ to wave numbers, we obtain for the mean free path in the liquid metal

$$1/l_{\text{liq}} = (3\pi/2\sqrt{2})\,(Zm^{1/2}/\hbar E_F^{3/2})\,\langle a\,(\mathbf{k})\,|\,u_k\,|^2\rangle,$$

where Z is the valence, E_F is the Fermi energy, and

$$\langle a\,(\mathbf{k})\,|\,u_k\,|^2\rangle = \frac{1}{4k_F^4}\int_0^{2k_F} a\,(\mathbf{k})\,|\,u_k\,|^2\,k^3\,dk. \qquad (9)$$

Substituting the obtained mean free path in the expression for the electric resistivity ρ and the absolute thermoelectric power α, Ziman[54] obtained the following calculation formulas:

$$\rho_{\text{liq}} = (3\pi/2)\,(m/\hbar e^2 E_F)\,(V/N)\,\langle a\,(\mathbf{k})\,|\,u_k\,|^2\rangle, \qquad (10)$$

$$\alpha_{\text{liq}} = -\,(\pi^2 k_B^2 T/3eE_F)\,\{3 - [2a\,(2k_F)\,|\,u_{2k_F}\,|^2/\langle a\,(\mathbf{k})\,|\,u_k\,|^2\rangle]\}, \qquad (11)$$

where k_B is Boltzmann's constant and $a(2k_F)$ and u_{2k_F} are the values of the structure factor and of the form factor of the PP in the region covered by double the Fermi radius.

Thus, in Ziman's theory the resistivity and the thermoelectric power of liquid metals are determined completely by the form factor of the pseudopotential and by the structure factor. For the first of these quantities there exist quite reliable theoretical models and even tables[51] of the u(k) dependence in a wide range of k. The structure factor, on the other hand, is usually obtained from experimental x-ray and neutron scattering intensity curves.

Typical plots of $|u(k)|^2$ and a(k) are shown in Fig. 1. Since the Fermi radius k_F is a function of the atomic density N/V and of the valence Z,

$$k_F = (3\pi^2 ZN/V)^{1/3},$$

the upper limit of integration in (9) shifts towards larger k with increasing valence of the metal. This fact is marked in the figure by vertical lines.

It should be noted that the determination of the intensity of x-rays and neutrons scattered at small angles entails great experimental difficulties; therefore the data on a(k) are regarded as reliable for $k \geq k_p/2$ (k_p is the wave number for the first maximum of the structure factor). For smaller values of k, the values of a(k) are approximated by

$$a\,(0) = kT\,(N/V)\,\varkappa_T, \qquad (12)$$

where $\varkappa_T$ is the isothermal compressibility. Of course, the approximation accuracy is determined to a considerable degree by the accuracy of the experimental investigations of the structure at small scattering angles. Therefore most earlier x-ray investigations of liquid metals, in which little attention was paid to this scattering region, can hardly be used to advantage in calculations of the kinetic properties. This applies in particular to monovalent metals, in which the integral

FIG. 1. Structure factor of liquid metals and the squared form factor of a pseudopotential.
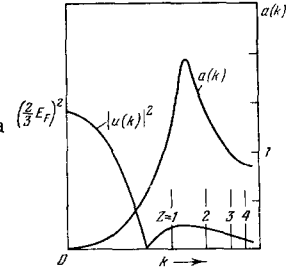
$$\int_0^{2k_F} a(k)k^3\,dk,$$

and hence the scattering factor $\langle a(k)|u_k|^2\rangle$, is determined by the region of small k to a much greater degree than for polyvalent metals, owing to the low value of the upper limit of integration. A computer estimate of the error in the calculation of the resistance[55], obtained by analyzing the rising front of the integral (9), has shown that in the case of polyvalent metals ρ is particularly sensitive to the accuracy with which the structure factor is determined in the region of the first maximum of the a(k) curve. It has been shown, for example, that an error of one degree in the determination of the x-ray scattering angle can lead to as much as a 20% deviation in the value of the resistance.

The requirements imposed by Ziman's theory on the accuracy with which a(k) is determined have stimulated the development of modern neutron-diffraction and x x-ray diffraction investigations of liquid metals. The new structure studies[20,23,56-61] were not only performed with a much smaller instrumental error of the intensity, but also with more accurate atomic scattering factors, corrections for the polarization and incoherence, and other details of the analysis of the experimental scattering curves.

The resistance was calculated with formula (10) in[62] for eleven liquid metals of different valences. The calculations were performed with Heine-Abarenkov pseudopotentials[50] and with experimental a(k) curves obtained by various authors. The agreement between the calculated ρ and the experimental ones was satisfactory for most metals. As shown in[63], the observed disparities can be blamed on imperfections of the employed PP model (particularly neglect of the spin-orbit interaction in heavy elements).

It follows from (11) that to calculate the absolute thermoelectric power it is necessary to have particularly accurate information on the behavior of u_k and a(k) in a region subtended by double the Fermi radius. Kendall[16], on the basis of his precision measurements of the thermoelectric power of liquid alkali metals, calculated α using PP of different authors. The general conclusion of[16] is that the accuracy with which u_{2k_F} is determined in all the models is insufficient for good agreement between the calculated and experimental results. At the same time, the experimental and calculated values of the thermoelectric power can be reconciled within the limits of the permissible error in the determination of the PP (0.01 Rydberg in[51]). On this basis, Cusack[34] regards a semi-empirical determination of u_{2k_F} from relation (11), using the experimental values of α_{liq} and a(k), as acceptable.

Attempts have been made recently[64-66] to find the effective potential of the interaction between the ions directly from the paired radial distribution function obtained by taking the Fourier transform of the experimental scattering intensity (see formula (1)). The results obtained in this direction are as yet debatable. There is no doubt, however, that a direct experimental determination of the effective interaction potential between the ions will become an important method of investigating metals. Thus, the exact knowledge of a(k) of liquid metals is needed both in the theory of kinetic properties and in the general theory of the liquid state. It must be noted with regret that even in the latest investigations the obtained structure factors frequently differ appreciably, especially in the $2k_F$ region, and also in the region of approximation to small values of k. Tables of the function a(k) in the region from 0 to $2k_F$ are among the main requirements for further refinement of the theory of kinetic phenomena in liquid metals.

In addition to experimental attempts to obtain more accurate a(k) curves, work is being done also on theoretical models for these curves. From among such studies, mention should be made of those of Ashcroft[67], who tested his model for the calculation of the resistivity by means of formula (10).

On the basis of the hard-sphere model, Ashcroft calculated the functions a(k) for 23 metals from the Percus-Yevick equations[68]. The criterion for the correct choice of the hard-sphere diameters and the density of their packing was a comparison of the calculated curves with the experimental ones of Gingrich and Heeton[58] for alkali metals and of Furikawa[57] for many others. A comparison with experiment shows that agreement does not always take place, but it can always be obtained by varying the packing density within the range 0.4—0.5. Attention is called here to the following circumstances: for monovalent metals the calculated results in the region of small k turn out to be more accurate than those obtained by extrapolation from experiment; for polyvalent metals this is not so, but it does not matter in their case, where the small-angle scattering region makes a small contribution in the calculation of the kinetic properties. Owing to the simplified ion-interaction scheme assumed in the hard-sphere model, the theoretical curves deviate from the experimental ones; the deviation becomes appreciable above the $2k_F$ boundary even for metals with high electron density.

The good agreement of the hard-sphere model with experiment in the range from 0 to $2k_F$ has enabled Ashcroft to plot a(k) curves for liquid Be, Mg, Ca, Ba, Si, and As, for which there are no diffraction experiments. The theoretical a(k) curves constructed under the assumption that the hard spheres have a constant packing density (0.45) were employed to calculate the resistance by the Ziman formula, using the pseudopotentials of Heine and Abarenkov[50] and of Animalu and Heine[51], and the Cohen pseudopotential[49] for alkali metals. A comparison with experiment shows that in most cases the discrepancies between ρ_{exp} and ρ_{calc} do not exceed 20% if a suitable pseudopotential model is chosen. An undisputed confirmation of the applicability of the hard-sphere model is also the theoretically plotted $\rho(T)$, which agrees sufficiently accurately with the

experimental one. The possibility of plotting the function a(k) = f(T) is based on the variation of the packing density of the spheres with temperature, which can be determined from the temperature dependence of the isothermal compressibility.

Ashcroft's experiment demonstrates the possibility of obtaining a unified method for determining the structure factor, and has therefore been extensively used in recent years. In this respect, the conclusions[69] that the experimental curves a(k) are more useful should be taken as a need for improving the theoretical models of the structure of liquid metals.

One of the important advantages of Ziman's theory is the possibility of calculating the temperature dependence of the kinetic properties. It is obvious from (10) that the factor responsible for the temperature dependence of the resistance is the scattering integral (9). On the other hand, inasmuch as the pseudopotential changes very little with temperature, it follows that $\rho(T) \sim a_k(T)$. The fact that ρ is determined by the temperature dependence of the structure factor explains the peculiarities of the $\rho(T)$ dependence of liquid metals of different groups of the periodic system. It is known that heating of a liquid metal is accompanied by a lowering and broadening of the first maximum of the a(k) curve (Fig. 2). At small k, the value of a(k) is determined only by the macroscopic oscillations of the density and increases linearly with the temperature (12). Accordingly, the resistance of monovalent metals, for which the upper limit of integration in (9) lies much below the first maximum (see Fig. 1), increases almost linearly upon heating, while $\partial \rho / \partial T$ barely decreases after melting. In bivalent metals, the $2k_F$ boundary hardly includes the first maximum of a(k). In this case $\int_0^{2k_F} a(k)k^3 dk$ remains practically unchanged or even decreases with the temperature; accordingly, $\partial \rho / \partial T \approx 0$ or may even become negative for Mg, Zn, and Cd. The scattering integral of liquid metals with valence of three and more increases with temperature; for these metals $\partial \rho / \partial T$ is positive, although it is smaller than for the monovalent metals, and decreases upon melting.

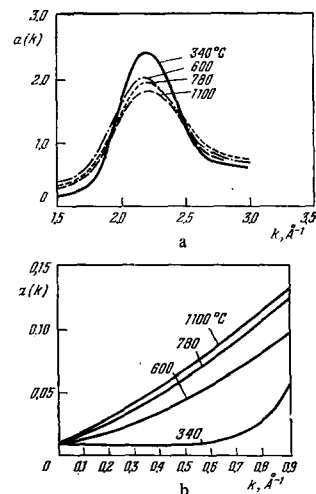Quantitative calculations of $\rho(T)$ entail large experi-

FIG. 2. Temperature dependence of the structure factor for liquid lead [59]. a) a(k) at large k; b) approximation to small k.

mental difficulties in the determination of the temperature dependence of the structure factor. However, the available results[16,58,62,67, etc.] reveal in many cases a satisfactory reproducibility of $\rho(T)$, and also of $\alpha(T)$. Recently much attention has been paid to the investigation of liquid mercury, the electronic properties of which are anomalous. The resistance of mercury, calculated from (10) using the ordinary pseudopotential models, is $\sim \rho_{exp}/3$, and the thermoelectric power of mercury is also anomalously large. The thermoelectric power and the resistance decrease rapidly with increasing pressure[70]. For a qualitative explanation of the excessively large values of ρ of mercury, Mott[71] proposed the possible existence of a minimum in the function of the density of the electronic states in the region of the Fermi energy. Subsequently, however, on the basis of experimental low-temperature investigations of the de Haas—van Alphen effect[72] and of optical absorption[73], Mott[6] expressed doubts concerning the existence of an anomaly in the density of states of liquid mercury, and called attention to its complicated atomic structure. Recently Evans et al.[74] advanced the hypothesis that the anomalous properties of the electron transport in mercury is the result of the energy dependence and of the unusual form of the scattering potential. Structure investigations[75,76] reveal an appreciable asymmetry of the first maximum of the a(k) curve, and also an anomalously large ratio, compared with normal metals, of the wave numbers of the second and first maxima. It is shown in[76] that the hard-sphere model cannot be reconciled with the experimental a(k) function. At the same time, the conclusions in[77] that two short-range order structures exist (α-Hg and β-Hg) cannot be regarded as correct, since variation of the temperature does not influence the experimental plot of the structure factor. The electronic structure of liquid mercury assumed in[74] is apparently correct, since the use of the pseudopotential introduced there, together with the experimental a(k) curve, makes it possible to calculate from (10) values of ρ that agree with experiment at various temperatures[76].

A special problem in the analysis of the electric conductivity in a liquid phase is posed by binary systems. Scattering in a complicated melt can be calculated by taking into account all the possible structure-correlation functions. For a binary melt, any type of short-range order can be expressed by introducing three interference functions: $a_{AA}(k)$, $a_{AB}(k)$, and $a_{BB}(k)$. On this basis, Faber and Ziman[44] obtained an expression for the resistivity of a binary melt

$$\rho_p = \frac{3\pi}{2} \frac{m}{e^2 \hbar E_F} \frac{V}{N} \int_0^{2k_F} |u(k)|^2 k^3 \, dk,$$

where the scattering potential $|u(k)|$, unlike in simple melts, has a more complicated form

$$|u(k)|^2 = C_A C_B |u_A(k) - u_B(k)|^2 + C_A^2 |u_A(k)|^2 a_{AA}(k)$$
$$+ C_B^2 |u_B(k)|^2 a_{BB}(k) + 2C_A C_B |u_A(k)||u_B(k)| a_{AB}(k);$$

here C_A and C_B are the atomic concentrations of the components, and $u_A(k)$ and $u_B(k)$ are the form factors of the pseudopotentials of the atoms A and B.

The common structure factor of a binary melt can always be represented by the expression

$$a(k) = \frac{C_A^2 f_A^2}{\langle f \rangle^2} a_{AA}(k) + \frac{C_B^2 f_B^2}{\langle f \rangle^2} a_{BB}(k) + \frac{2 C_A C_B f_A f_B}{\langle f \rangle^2} a_{AB}(k), \quad (13)$$

where f_A and f_B are the atomic scattering factors of the components and $\langle f \rangle$ is the average atomic factor of the melt,

$$\langle f \rangle = C_A f_A + C_B f_B.$$

To determine the three partial interference functions, it is necessary in principle to perform three independent diffraction experiments[78,79]. For example, one of them should be performed with x-rays and the two others with neutrons of different energies or with neutrons and electrons. We then obtain three different ratios of the atomic scattering factors of the components. From the three experimental a(k), by solving three equations (13), we can obtain the partial structure factors $a_{AA}(k)$, $a_{AB}(k)$, and $a_{AB}(k)$.

Another method of obtaining the partial structure factors, used by Enderby and co-workers[104,105], is to use three isotopes of one of the elements. In this case an investigation of three samples having the same concentration but containing different isotopes also makes it possible to calculate the partial structure factors, but now through the use of only one type of radiation.

Since such diffraction experiments are very laborious and difficult to interpret, their number is limited at the present time. Having no results of such experiments at all for the construction of their theory, Faber and Ziman[44] assume a certain hypothetical simplified model of the melt. In the considered "substitution model" it is proposed that the solvent ion can be replaced by an ion of the solute metal without any change in the mutual placement of the ions, and there is no tendency to form homogeneous "clusters." Obviously, such a model is possible under two conditions:

a) the components are characterized by close values of the atomic volume;

b) the interference functions of the components are the same.

Such a model leads to the following expression for the resistivity of the melt:

$$\rho = \rho_1 + \rho_2. \quad (14)$$

where

$$\rho_1 = \frac{3\pi}{2} \frac{m}{e^2 \hbar E_F} \frac{V}{N} \int_0^{2k_F} [C_A a(k) u_A^2(k) + C_B a(k) u_B^2(k)] k^3 \, dk, \quad (15)$$

$$\rho_2 = \frac{3\pi}{2} \frac{m}{e^2 \hbar E_F} \frac{V}{N} \int_0^{2k_F} C_A C_B [1 - a(k)][u_B(k) - u_A(k)]^2 k^3 \, dk. \quad (16)$$

It is easily seen that the satisfaction of the Nordheim rule (approximate proportionality of the resistivity of the melt on the isotherm to the product $C_A C_B$) is determined by the part ρ_2. At the same time, ρ_1 varies approximately linearly between ρ_A and ρ_B. Thus, the sign and magnitude of the deviation from the linearity of the dependence are determined by the ratio of the quantities $\rho_1(c)$ and $\rho_2(c)$ for a definite system (c is the concentration). It follows from (15) and (16) that the extent of bending of the concentration dependence of the resistance on the isotherm is determined primarily by the deviation of the summary structure factor $\langle a(k) \rangle$ from unity.

Faber and Ziman[44] attempted also to extend the region of applicability of the substitution model to in-

clude dilute solutions of components with different atomic volumes. Low impurity concentrations disturb the structure of the matrix only slightly, and then the dilatation effects can be taken into account by introducing an effective pseudopotential of the impurity. Such an improvement of the model makes it possible to explain qualitatively the satisfaction of the Nordheim rule observed in[80] for dilute solutions of alkali metals. In the case of polyvalent metals, small impurities change the resistivity of the matrix insignificantly[81,82]: in this case ρ_2 is always negligible ($u_A(k) - u_B(k)$ tends to zero at small k, and the factor $1 - a(k)$ deviates little from zero at large k).

Ashcroft and Langreth[83,84], using the Lebowitz solution[85] of the Percus-Yevick equation[68] for a mixture of two types of hard spheres, obtained an expression for the partial structure factors in a binary melt. Assuming then that the ratio of the hard-sphere diameters of the two types of atoms is equal to unity ($\sigma/\sigma_2 = \alpha = 1$), Ashcroft and Langreth[84] arrived at a single structure factor describing the system, meaning to the possibility of using the substitution model. In accordance with the hard-sphere approximation, a simplified model of the pseudopotential was developed in[83,52], in which a certain decisive effective radius R_{eff} is assumed, outside of which the electron-ion interaction is similar to a Coulomb interaction, and inside of which the potential corresponding to the quasi-plane-wave approximation is practically equal to zero. An investigation of the assumed model of the pseudopotential has shown that R_{eff} differs little from the usual ionic radius for many polyvalent metals, and can be calculated from the form factors of the pseudopotential components. The modified substitution model turned out to hold well in the calculation of the concentration dependence of the resistivity of most investigated systems[84,86]. The averaged hard-sphere diameter σ_{AB} and the averaged density σ_{AB} of their packing were obtained by linear interpolation of the corresponding parameters of the pure components. In other cases, agreement between the calculated and experimental values of the resistivity can be obtained with a suitable deviation of the parameter $\alpha = \sigma_1/\sigma_2$ from unity (in particular, $\alpha \approx 0.8-0.9$ for alloys of alkali metals). The substitution model can be used also to calculate the resistivity of molten ternary metallic alloys[87,88].

As is well known, mercury amalgams occupy a special position among binary molten alloys. In contrast to the behavior of the majority of liquid systems, the addition of metals (other than alkali) to liquid mercury results in a sharp decrease of ρ. The concentration dependence of the thermoelectric power is also "strange." In particular, in metls of the In-Hg system the thermoelectric power is also "strange." In particular, in melts of the In-Hg system the thermoelectric power has a maximum at small amounts of In (~ 3 at.%), followed by a sharp decrease[89]. Owing to the unusual behavior of the concentration dependence of the resistivity and of the thermoelectric power, the substitution theory could not be applied to mercury amalgams[90]. At the same time it follows from diffraction experiments that the structure of molten Hg-In and Hg-Tl is described by a single structure factor[90-92]. It is shown[90-92] that such a disparity can be avoided by using the Mott fac-

tor[71] g, which determines the minimum of the density of states at the Fermi level. At the same time, however, a perfectly justified hypothesis was advanced that the pseudopotentials could hardly be invariant relative to the electron density in amalgams. The latest investigations[93] did not confirm the presence of a minimum of the density of states at the Fermi level for molten Hg-In. Ashcroft and Langreth[83] have shown that on the basis of a modified substitution theory, using a "volume-dependent" pseudopotential, it is possible to obtain a $\rho(c)$ dependence that is close to the experimental one for molten Hg-Zn, Hg-In, Hg-Bi, and Hg-Pb, with the ratio of the hard-sphere diameters deviating little from unity. Apparently an even more rigorous agreement can be obtained by taking into account the energy dependence of the pseudopotential for mercury[74].

An analysis of the numerous experimental investigations of the electric properties suggests that molten binary metallic alloys are best subdivided into four principal classes[84]:

1. Alloys of metals of group III with metals of higher groups of the periodic system. The resistivity has a nearly linear dependence on the concentration. These molten alloys can be described by a simple substitutional model in which the part ρ_1 predominates in (14). k_ρ for this class of molten alloys is always smaller than $2k_F$.

2. Liquid mixtures of noble or alkali metals. Such mixtures satisfy well the Nordheimer rule, namely, the isotherms are convex curves. If the substitution model is applicable, the part ρ_2 in (14) is positive and large in absolute magnitude. k_ρ for this class is always smaller than $2k_F$.

3. Amalgams of mercury. The anomalous $\rho(c)$ dependence of liquid alloys of this type was mentioned earlier. A thorough investigation of mercury is needed in order to study the mechanism of scattering in its molten alloys.

4. Molten alloys of Au, Ag, and Cu with polyvalent metals. For such alloys one observes a maximum on the isotherms of the resistivity, and also negative $\partial\rho/\partial T$ in the region of this maximum. In the region where the maximum exists, k_ρ becomes equal to $2k_F$. It is assumed that boundary zone effects exist in these alloys when the boundaries of the Fermi surface approach the first Brillouin zone. The mechanism of these effects need further study.

A current pressing problem is also the investigation of molten alloys based on transition metals, for the purpose of determining the role played by d-electrons in the conductivities of the corresponding liquids.

II. LIQUID SEMICONDUCTORS

The picture of the mechanism of electronic conductivity in liquid conductors would be incomplete were we to confine ourselves to metallic liquids only. No less important for the understanding of the phenomenon as a whole is the study of another extreme group of materials having patently semiconducting or in some cases even dielectric properties. This group includes molten alloys of superconductors with appreciable fraction of ionic components in the chemical-bond forces or else of

molecular-covalent crystals with weak intermolecular coupling. These liquid semiconductors have a unique range of properties due to the features of the energy spectrum and of the electron transport in disordered atomic structures. We note that in a real situation one observes also all the intermediate cases, i.e., effects take place, which constitute a certain intermediate group between liquid metals and liquid semiconductors. An analysis of the transformation of the conductivity mechanisms in this metal—dielectric series raises a number of fundamental questions: What is the role of the collective effect of the electron-electron interaction in the replacement of dielectric properties by metallic ones, how does the structural disorder modify the spectrum of the electronic states or under what conditions is a gap produced in the electronic spectrum when the system becomes disordered, what is the character of the electronic states—is the band mechanism of motion retained or do the electronic states become localized and the motion of the carriers becomes hop-like?

The purpose of the present chapter, however, is not to answer these questions. At the present stage of research in this field, an attempt to do so would apparently be premature. It is advantageous only to summarize the experimental material and to describe those qualitative models on the basis of which the mechanism of the electronic processes is being evaluated at the present time.

1. Experimental investigations of molten semiconductors. Ioffe and Regel'[95] laid the groundwork for the study of the electronic conductivity of molten semiconductors. The data presented in their paper, principally on the electric conductivity, indicate that when certain semiconductors melt they lose their semiconducting properties, whereas others retain the value and temperature dependence of the conductivity typical of semiconductors. Ioffe and Regel' advanced the hypothesis that the retention or loss of the semiconducting properties is due to the conservation or destruction of the short-range order in the atomic structure. In subsequent numerous investigations, this idea was intensively discussed, and many experimental proofs of its validity were obtained, and possible refinements were suggested. Let us examine the change occurring in the properties of the melt on going from metal-like behavior to semiconducting behavior.

The semiconductors that lose their semiconductor properties upon melting are Ge, Si, InSb, and others of the III—V type. The electric conductivity of liquid Ge, for example, and other IV and III—V semiconductors reaches values characteristic of liquid metals ($\sigma > 10^4$ ohm^{-1}cm^{-1}), and has a negative temperature coefficient. The Hall coefficient R corresponds with high accuracy to the value R_0 predicted by the free-electron model. The thermoelectric power and the thermal conductivity in the liquid phase also assume values typical of metals[18,95,98,112].

What causes a semiconductor of the Ge type to go over into the metallic state? Is this the result of the loss of long-range order upon melting, or does a qualitative change take place in the system of interatomic bonds and leads to a radical realignment of the energy spectrum? X-ray diffraction studies of the radial distribu-

tion function, performed for liquid Ge, show that the coordination number changes from 4 to 8 upon melting[96]. This means that the rigid system of covalent bonds of the crystalline Ge is upset by melting, the short-range order changes, and the gap collapses. This result makes liquid Ge an unsuitable object for the study of the influence of disorder on the electronic spectrum. As noted by Gubanov[38], liquid germanium should be compared not with semiconducting crystalline germanium but with some hypothetical crystal having a coordination number 8, which for various reasons (see[38], p. 381) should be a metal.

The conclusions obtained for germanium are apparently valid also for the other IV and III—V substances.

We turn to the following characteristic group of molten semiconductors, which can be placed immediately after the Ge group in the liquid metals—liquid semiconductors series. These are molten tellurides of metals mainly from groups IV and V, for example Bi_2Te_3, Sb_2Te_3, SnTe, GeTe, and PbTe. This group includes also the elementary semiconductor Te. All the foregoing semiconductors (in the solid phase) are crystals with a mixed type of chemical bond: they are either molecular-covalent compounds with a complicated layered structure, for example Bi_2Te_3, or a chain-like structure, for example Te, or else ionic-covalent, such as PbTe and others. Recognizing the crystal-chemical peculiarities of the semiconductors of this group, we can assume a priori that melting of these materials does not lead to a complete dissociation of the system of interatomic bonds, since the deformation of the structure upon melting will be experienced by weaker-molecular or ionic bonds. Thus, there are grounds for hoping for at least a partial conservation of the short-range order in these complex structures. Indeed, structural investigations[97] of Te, performed in a liquid

Table III

Substance	R, 10^{-5} cm^3/C*	R_0, 10^{-5} cm^3/C**	R/R_0	Literature
Ge	—3.6	—3.4	1.06	99
InSb	—6.9	—4.8	1.4	18, 103
Te	—11.4	—3.8	3.0	102, 99
Bi₂Te₃	—8.7	—3.9	2.2	102
Sb₂Te₃	—14	—3.6	3.9	102, 99
SnTe	—12	—4.4		102, 101
PbTe	—10	—4.7	2.4	101
GeTe	—14	—3.8		101
CdSb	—8.3	—5.5	1.5	100
ZnSb	—5.3	—4.5	1.2	100
CuTe	—16	—4	4	102
AgTe	—100	~ —5	~ 20	102
Tl₂Te	—160	—	—	102, 131
In₂Te₃	—200	—	—	103
CuSbSe₂	—7,0·10⁻²***	—	—	125
GeSe	—3,6·10⁻²	—	—	190
Sb₂Se₃	—1,5·10⁻³	—	—	125, 191
Sb₃₆Se₅₄Te₁₀	—1,3·10⁻¹	—	—	125, 191
Sb₃₆Se₅₄Sb₁₀	—1,1·10⁻²	—	—	125, 191
Sb₃₆Se₅₄In₁₀	—4,8·10⁻²	—	—	125, 191
InSe	—10⁻¹	—	—	130

*The values of R are given for temperatures in the immediate vicinity of the melting point (in the interval 20—100°C).

**R_0 is the free-electron-model value calculated under the assumption that the electrons of the valence shell are completely ionized.

***Starting with this substance and below, the values of R are given in cm³/C.

state, show that the chain-like structure is conserved. There are no data whatever, however, for the other molten alloys at present.

Measurements of the electric properties show that, unlike liquid IV and III—V substances, the electric conductivity of the molten alloys of this group has a positive temperature coefficient and its absolute magnitude is of the order of 10^3 ohm^{-1}cm^{-1}, i.e., smaller by 1—2 orders of magnitude than the electric conductivity of liquid metals[35,98]. The positive temperature coefficient of electric conductivity is a specific property of semiconductors, and during the first stage of the investigation, its observation in the liquid phase served as a basis for classifying melts of the Bi_2T_3 type (it is convenient to identify the group by using its most typical representative) as liquid semiconductors[95]. Investigations of the Hall effect, however, lead to an alternative conclusion. The Hall data for the group of liquids in question are summarized in Table III. As can be seen from the table, the Hall constant of the investigated liquids in the group is negative, and its absolute value is close to that predicted by the free-electron model. Some discrepancy in the results, for example for Ge, consists only of a large deviation of the experimental constants from the theoretical one, reaching a factor of 3—4. In the first approximation, however, the agreement with theory of free electrons can be regarded as satisfactory, and this would seemingly indicate that this group of liquids should be regarded as metallic[100,102]. But if these are metals, how is one to explain the positive temperature coefficient of the electric resistivity? Enderby and co-workers[100,102] advanced the hypothesis that an interpretation is possible on the basis of Ziman's theory[42,43,44] by assuming a special variation of the structure factor that determines the intensity of the electron scattering. That such a variant of the interpretation is realistic was demonstrated by Enderby and co-workers[104,105] in a parallel study of the structure characteristics and the electric properties of metallic molten alloys of the Cu- Sn system, certain compositions of which also have a positive temperature coefficient of electric resistivity.

Is the Enderby metallic model the only possible description of the experimental relations? An alternate model of an intrinsic compensated semiconductor was discussed in[101]. Indeed, the small Hall constant may be the result of the compensation of the contributions made to the Hall voltage by carriers of opposite signs? The main argument against the intrinsic-semiconductor model were, however, the difficulties in explaining the equally good compensation for a large group of materials, and furthermore up to values close to the free-electron model. In spite of certain doubtful aspects in in the model of the intrinsic compensated semiconductor, additional experiments were needed for an unambiguous solution of the problem. The most convincing experiments are seemingly those in which the thermal conductivity was measured. For liquids with high electric conductivity ($\sigma \gtrsim 10^3$ ohm^{-1}cm^{-1}), the experimentally observed value of the thermal conductivity can be attributed with good approximation to the thermal conductivity of the electron gas[106,108,112]. If we assume the model of an intrinsic compensated semiconductor, then it would be necessary to expect thermal conductiv-
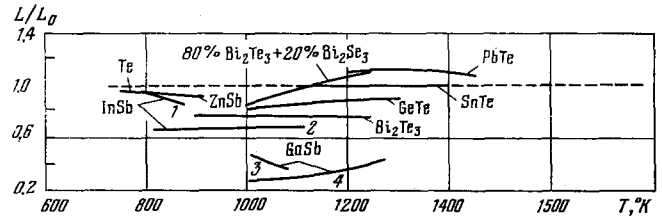

FIG. 3. Ratio of the experimental Lorentz number L to the theoretical L_0 for a degenerate electron gas, for a number of molten semiconductors (from [112]). 1, 2—3, 4—data by different authors.

ity obtained in experiments on the measurement of the thermal conductivity to be much higher than $L_0\sigma T$, where L_0 is the Lorentz number for the degenerate electron gas, owing to the additional contribution from the transport of the ionization energy by the electron-hole pairs or owing to bipolar transport. In a large number of experiments on Te[10,107], Bi_2Te_3[108], and IV—VI compounds[109,110,111] it was shown, however, that there is no bipolar transport of heat in the liquid phase. Figure 3 summarizes the data for the Lorentz number L of alloys of the considered semiconductors, and shows rather satisfactory agreement between the experimental and theoretical values for a degenerate electron gas.

Thus, measurements of the thermal conductivity do not confirm the intrinsic-semiconductor model, and consequently it remains to accept the theory of almost free electrons as the basis for the discussion. However, to what degree are liquid metals such as Bi_2Te_3 "good" metals? How correct is Enderby in explaining the positive temperature coefficient of the electric conductivity only on the basis of the temperature variation of electron scattering? Busch and Guntherodt[18], on the basis of a joint investigation of the Hall coefficient, the electric conductivity, and the structure parameters of binary metallic systems, including such as Bi- Te and also Te, have noted one interesting regularity: a positive temperature coefficient of the electric conductivity appears precisely when the diameter of the Fermi surface in k- space, calculated from data on the Hall effect, $2k_F = (3\pi^2/eR)^{1/3}$, is equal to the wave vector k_p corresponding to the first maximum of the structure factor $a(k)$*. For a qualitative analysis, the wave vector k_p can be identified with the reciprocal lattice vector of the crystal. Consequently, k_p determines the dimensions of the first Brillouin zone, if we use solid-state terminology. From band theory it is known that the role of discontinuities or gaps in the energy spectrum of the electrons is particularly important when the dimensions of the Fermi sphere become comparable with the dimension of the first Brillouin zone. In other words, in this case the "zone effects" control the motion of the electrons. It can be assumed that liquids of the molten Bi_2Te_3 type, for which, in particular, $2k_F = k_p$, exhibit certain properties that would be anomalous in "good" metals, precisely because of the appearance of such "zone effects." Mott[6] introduced, for the description of the singularities of the zone type in the spectrum of metal-like liquids, the concept of the quasigap or mini-

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*)a(k) is the Fourier transform of the radial distribution (for more details see Chap. I).

mum in the density of the electronic states as a function of the energy.

The appearance of "zone effects" in liquids of the group under consideration can apparently also be expected if account is taken of the consideration advanced earlier with respect to singularities of the crystal-chemical structure of the considered group of substances. The mixed type of bond which is characteristic of these substances makes it possible to retain in the liquid phase the short-range structure elements that are typical of a crystalline semiconductor*. Taking into consideration the idea of Ioffe and Regel' that the band scheme is retained if the short-range order is retained, the presence of certain properties that would be anomalous in metals is no longer so unexpected in the case of partial ordering of the semiconducting type. The temperature coefficient of the electric conductivity can be explained in elementary fashion within the framework of such an analysis, as a result of dissociation, with increasing temperature, of the remainders of the solid-state structure and the release of the electrons retained in the molecular complexes by the interatomic covalent bond forces[95]. Within the framework of Mott's model, this picture corresponds to a "washing out" of the quasigap with increasing temperature.

If we assume the foregoing point of view, we still remain with the following question: how can complexes of the molecular type exist and "float" in the free-electron gas? Should not the collective effects of electron screening lead to a complete dissociation of the covalent bonds (as in liquid germanium) and release of all the valence electrons? In other words, what forces hinder the realization of the Mott transition? It is possible that the answer must be sought in the dynamic properties of the liquid, such as disorder and fluctuation instability of the structure, causing the molecular complexes to have a "virtual" character.

Thus, the molten germanium and its analogs, considered above, are in essence metallic, whereas melts of the Bi_2Te_3 type already manifest properties that are anomalous for metals but similar to those of semiconductors. Which materials are semiconductors in the liquid state? Where is the borderline between the metallic state and the truly superconducting one? If we follow the crystal-chemical considerations and make use of Ioffe and Regel's idea that short-order plays a decisive role in the formation of the structure of the energy spectrum, then liquid semiconductors should be sought among molten materials in which the ionic component makes an appreciable contribution to the interatomic-bond forces, or substances having a molecular lattice with weak intermolecular interaction. Examples of the former are certain tellurides, selenides, sulfides, and oxides of metals, such as GeSe, In_2Te_3, Sb_2Se_3, Tl_2S, Sb_2S_3, Bi_2O_3, or V_2O_5; a typical representative of the second group is Se. The electric conductivity of molten

semiconductors of this group does not exceed 10^2 ohm^{-1}cm^{-1}, i.e., it is smaller by 2 or 3 orders of magnitude than the electric conductivity of liquid metals. If we assume that all the valence electrons of these melts participate in the conductivity, then this leads to inadmissibly low values of the mobility, on the order of 10^{-3} cm^2/V-sec according to the most exaggerated estimates. On the other hand, Regel' has already shown[113] that many substances in this group, for example Tl_2S, Bi_2O_3, Sb_2S_3, and Cu_2Te, melt without a noticeable change in either the absolute electric conductivity or its temperature dependence. It is important to note that the electric conductivity of these molten substances always increases with increasing temperature and this dependence is in most cases exponential, i.e., the same as in the case of intrinsic semiconductors. It is obvious that such a behavior of the electric conductivity could not occur if a cardinal realignment of the energy spectrum were to occur during melting, with a loss of the semiconductor band structure. It remains thus to assume that the foregoing materials are semiconductors in the liquid state.

What is the distinguishing feature of these liquid semiconductors? An answer to this question can be obtained only by parallel investigations of aggregates of kinetic coefficients of some particular object. Recently, the most exhaustive investigations were made on Tl_2Te and Sb_2Se_3. The electric conductivity of the former near the melting temperature is ~70 ohm^{-1}cm^{-1}[114], whereas that of the second is ~2 ohm^{-1}cm^{-1}[115]. Investigations were made of the electric conductivity, Hall coefficient, thermoelectric power, and thermal conductivity of these liquid semiconductors. An important fact is also that, in addition to studying stoichiometric compositions, much attention was paid to the investigation of those changes that can be produced in the electric properties by deviations of the composition of the substance from stoichiometric, and the role of alloying with a third element.

In addition to the investigation of Tl_2Te and Sb_2Se_3, many studies were made of other semiconducting liquids. These investigations, as a rule, were confined to measurements of one or two kinetic coefficients, and the results do not always suffice for some general conclusions. The most interesting investigations were made on InSe[116,117], In_2Te_3, Ga_2Te_3[118,103], chalcogenide glasses As_2Se_3-As_2Te_3-Tl_2Te in the liquid phase[119], and Te-Se alloys[120]. The results of many investigations are summarized in[98,6,121,122,33].

Let us return to the results for Tl_2Te and Sb_2Se_3. Apparently, the most remarkable fact observed in these molten alloys is the inversion of the type of conductivity (as revealed by the sign of the thermoelectric power) when the composition of the subject deviates from stoi stoichiometric. It should be noted, however, that this phenomenon is not a general characteristic of semiconducting liquids. For example, it is known that a similar behavior of the thermoelectric power is observed in Tl_2Se and Tl_2S[192] and in Sb_2S_3[124], but not, for example, in In_2Te_3[103] or InSe[193] and in many others. Thus, the isotherms of the electric conductivity and of the thermoelectric power for the Tl-Te system near the stoichiometric composition of Tl_2Te and of Sb_2Se_3 doped with antimony and tellurium, are shown in Figs. 4 and 5. In

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*It is appropriate to recall that in the liquids under consideration the Hall constant is $R \approx (3-4)R_0$, and this excess can be due to partial binding of the electrons in complexes of the molecular type. The true picture is approximately as follows: molecular complexes or clusters "float" in the liquid metal. The Hall effect in such a complicated structure is determined exclusively by the metallic phase, and the Hall constant is a true measure of the concentration of the free electrons.
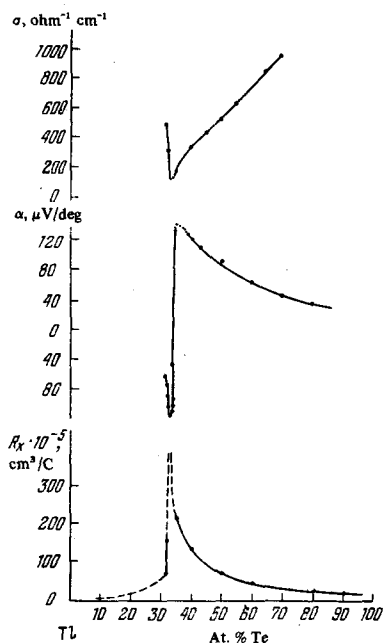
FIG. 4. Isotherms (T = 750°C) of the electric conductivity, of the thermoelectric power [127], and of the Hall coefficient [102] in the Tl-Te system near Tl_2Te (the plotted quantity is $R_X \times 10^{-5}$).

FIG. 5. Isotherms (T = 890°C) of the electric conductivity, thermoelectric power [115], and the Hall coefficient [125] for molten Sb_2Se_3 doped with antimony and tellurium.

the case of Sb_2Se_3, the Se is replaced by Te. The data are quoted from[125] and[115], respectively. If we consider only the shape of the plot of the electric conductivity or the thermoelectric power and disregard the relatively large absolute values of the introduced excess components, then the presented curves are surprisingly similar to those observed for crystalline semiconductors that have a tendency to self-doping (i.e., the doping of which can be effected by violation of the stoichiometric composition). It is important here that the type of conductivity, for example p-type, arises in the case of an excess of the metalloid component, whereas the n-type conductivity corresponds to an excess of the metal. This is precisely what the action of the excess components should be if doping occurs by deviation from stoichiometry. A similar result was obtained also in the case of doping with a third element, for example with indium in the case of Sb_2Se_3[125]. The role of the impurities in Tl_2Te was investigated also in[194] and it was shown that introduction of Ag, Cd, or In ensures an n-type conductivity, whereas Sb and Si cause a p-type conductivity. If we regard the reversal of the sign of the thermoelectric power by various additives as the result of a doping process that has the same nature as in the case of a crystal, then the experiments described above offer convincing proof of the existence of liquid semiconductors. The fact that to effect doping in the liquid phase it is necessary to introduce appreciable amounts of the doping substance can also be readily understood, since the contribution of small amounts of an impurity can be masked by the fluctuations of the density of the electronic states near the band edge in the disordered system. A different point of view concerning the reversal of the sign of the thermoelectric power upon variation of the composition of Tl_2Te was advanced in[102], where it was proposed that a decisive role in this
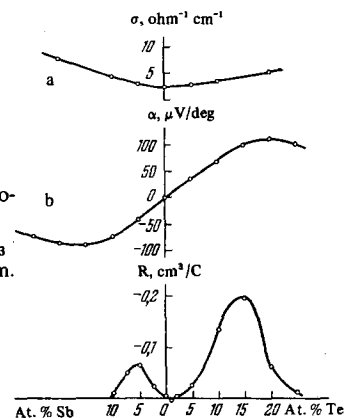
phenomenon can be played by the abrupt change occurring in the energy dependence of the carrier relaxation time when the composition is changed.

The thermal conductivity of molten Tl_2Te and Sb_2Se_3 was also measured. Whereas in the analysis of the properties of liquids with high conductivity the measurements of the thermal conductivity were cited as arguments in favor of the metallic character of the liquid, for the semiconductors in question the data on the thermal conductivity play the opposite role. In the case of Tl_2Te, Mallon and Cutler[195] have shown that the experimental value of the thermal conductivity, with allowance for the "lattice" component, exceeds $L_0 \sigma T$, and have attributed this additional contribution to bipolar heat transport. Measurements of the thermal conductivity of Sb_2Se_3[128] and of other liquid semiconductors, for example $InSe$[117], $InTe$, $GaTe$[129], and others (see the review[112]) also revealed considerable deviations from the Wiedemann-Franz law, which were interpreted in part as being due to the additional contribution of bipolar heat transport[117,112].

Measurements of the Hall effect have introduced some dissonance in the foregoing orderly selection of the experimental facts for liquid semiconductors. The experimental Hall constant of Tl_2Te[100,131,102] actually turned out to be of the order of 2×10^{-3} cm^3/C, i.e., larger by almost two orders of magnitude than the typical values for metals. A rather unexpected fact, however, was that the sign of the effect remained inalterably negative for all the compositions of the Tl-Te system, even for those with positive thermoelectric power ((Fig. 4).

The plots of the Hall effect, of the thermoelectric power, and of the electric conductivity for molten Tl_2Te cannot be explained jointly by using the standard model of a crystalline semiconductor. Sb_2Se_3, unlike Tl_2Te, has a smaller absolute electric conductivity, and its semiconducting properties are more distinctly pronounced. It is possible that measurements of the Hall effect in this molten material will reveal a reversal of the sign of the Hall constant in accordance with the reversal of the sign of the thermoelectric power. Such measurements were performed in[125,191]. Indeed, for nearly-stoichiometric compositions it was observed that the Hall constant decreased (Fig. 5). This decrease can be qualitatively attributed to cancellation of the contributions of carriers of opposite signs. However, for

compositions containing more than 1% of the excess component always have a negative Hall constant, regardless of the sign of the thermoelectric power, and this anomaly in the behavior of the Hall effect is similar to that observed in Tl_2Te. It is appropriate to note here that observation of a negative Hall constant together with a positive thermoelectric-power coefficient is a well known feature of disordered systems. Thus, for example, Male has obtained similar results for glass chalcogenide[119]. A negative Hall constant and a positive thermoelectric power were observed also by Clark[132] in amorphous germanium. This anomalous behavior of the Hall effect points to a peculiar conductivity mechanism in liquid semiconductors. The main cause of this peculiarity is the disordered atomic structure. What is the nature of this peculiarity and to what theoretical premises does it lead?

2. Theoretical model of liquid semiconductor. The purpose of this section is to describe those theoretical concepts that have been proposed for the interpretation of the peculiarities of transport in liquid semiconductors. It is obviously necessary to analyze two questions: the first concerns the changes in the energy spectrum caused by the disordered structure, and the second, which is related to the first, concerns the effect of these changes on the kinetics of carrier motion.

The first investigations of the influence of disorder on the spectrum of the electronic states were apparently those of Fröhlich[133], followed by those of Gubanov[38]. This problem was subsequently tackled by a number of workers[134-136]. The end purpose of the theoretical calculations was to determine the electronic state density function. The totality of the investigations have shown that by virtue of the fluctuations of the interatomic distance and hence of the potential field of the "lattice," the electronic state density function in systems having only short-range order differs from zero below the bottom of the conduction band and the upper edge of the valence band, and has the form of a "tail"*.

To determine the kinetics of carriers moving in the region of the band tail it is necessary to ascertain whether the electronic states in the tail are of the band type or are localized. To answer this question, it is customary to use the results obtained by Anderson for a certain artificial model[137]. Anderson solved the problem of localization of a single solitary electron placed in a band perturbed by a random potential, and showed that at a definite degree of fluctuation of the potential, namely, when the amplitude of the fluctuations exceeds the initial band width, all the states in the band become localized.

Mott[6] has noted correctly that the idealized picture is not realized at least when it comes to amorphous or liquid semiconductors, since the degree of disorder in these systems is insufficient for the Anderson localization. Mott proposes that there should exist in the band structure of semiconductors having only short-range order a certain limiting energy (E_c for electrons and E_v for holes), above which the electronic states are states of the band type, i.e., the motion of the electrons over these states has a band character, and below this limiting energy the states are localized. This intuitive idea

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*The "tail" at the edge of the band is a term universally used in the literature.
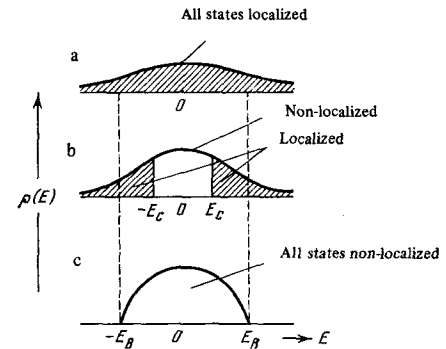

FIG. 6. Scheme for the transformation of the electronic state density function $\rho(E)$ with increasing degree of disorder in the structure [140]. The shaded regions correspond to localized states: a) ideal order in the system, b, c) the degree of disorder increases.
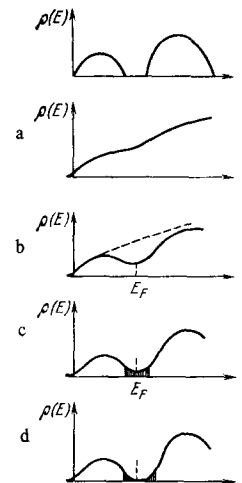

FIG. 7. Electronic state density function in liquid metals (a, b) and semiconductors (c, d) [6]. The shaded sections correspond to localized states. The upper figure pertains to a crystal and is shown for comparison.

of Mott's is presently being diligently developed by a group of theoreticians headed by Cohen[138]. In a number of recent publications by this group[139,140], they report a semiquantitative confirmation of Mott's ideas. The scheme for transforming the electronic state density function $\rho(E)$ with increasing disorder in the system is shown in Fig. 6.

On the basis of Mott's ideas it is easy to present possible variants of the transformation of a band spectrum following violation of the ordering in the system. Figure 7 shows various types of state density functions $\rho(E)$, arranged in increasing order of the degree of coupling of the electrons with the potential field of the atomic structure[6,141].

Case (a) corresponds to complete vanishing of the gap. $\rho(E)$ approaches the $\rho(E)$ dependence corresponding to a gas of free electrons. This case, according to Mott, describes melts of the type of Ge and other metals.

In case (b), the density of states is decreased in the energy interval corresponding to the forbidden band of the crystalline material. This region with the decreased density of states is customarily called a "quasigap." The depth of the quasigap is quantitatively characterized by the ratio $g = \rho(E_F)/\rho(E_{Fb. el.})$. According to Mott, the presence of a quasigap is the cause for the deviations revealed by liquids such as Bi_2Te_3 or Te, and others with an average conductivity on the order of 10^3 $ohm^{-1}cm^{-1}$, from metallic properties. Assuming that

σ increases with increasing g and that g in turn tends to unity with increasing temperature, as a result of the destruction of the short-range order, Mott explains why the liquids have a positive temperature coefficient of electric conductivity of the group intermediate between metals and semiconductors. If $g \leq 1/3$, then, according to approximate estimates by Mott[141,142], the states in the region of the quasigap are localized (Fig. 7, cases b and c). The localization of the states produces special conditions for electron transport. Transport in the region of the localized states occurs more readily by thermally-activated jumps from one local state to the other. The upper limit for the electron mobility in this case is of the order of $10^{-1}-10^{-2}$ cm^2/V-sec[138], whereas the lower limit in the case of the band mechanism of motion is of the order of $1-10$ cm^2/V-sec. Consequently, the mobility on the boundary between the localized and band states should experience an abrupt change amounting approximately to two orders of magnitude. This differential in the value of the mobility has been called the "mobility edge." According to an idea by Cohen[138,143], the principal role in kinetic phenomena occurring in a disordered semiconductor described by a spectrum of the type (c) or (d) is played not by the forbidden gap, which is absent in the general case, but by a certain energy interval bounded by the mobility edge for electrons on the one side and by the mobility edge for holes on the other. Cohen proposed the term "mobility gap" for this gap. According to semiquantitative estimates[141], the electric conductivity of the system at $g \approx 1/3$ does not exceed 10^2 ohm^{-1}cm^{-1}. This is precisely the maximum value of the electric conductivity of substances hitherto classified as liquid semiconductors. Consequently, it is necessary to relate these liquid semiconductors with schemes (c) and (d). Following the previously noted regularity in the enhancement of the semiconducting properties with decreasing electric conductivity, it can be suggested that the scheme (d) corresponds to objects having higher resistivity. An example of a semiconductor described by scheme (c), according to Mott, is molten Tl$_2$Te, whereas the scheme (d), which approaches the standard scheme for a crystalline semiconductor, corresponds more readily to Sb$_2$Se$_3$, the electric resistivity of which is higher by almost two orders of magnitude than that of Tl$_2$Te.

The electric conductivity of liquid semiconductors is determined by a sum of two components—the band component (the carriers are produced by activation through the mobility gap) and hopping (thermally activated jumps over local states within the limits of the quasigap). It might seem that the activation energy of the hopping mechanism should not differ significantly in first approximation from the activation energy for the band motion, for if the local centers are close in energy, they are separated in space, and if they are in the immediate vicinity of one another, which is the condition for the hopping, they are separated in energy by an amount which is comparable in the mean with the half-width of the quasigap. This means that the electric conductivity, in spite of the participation of two independent mechanisms, is described by a single activation energy*.

For liquid semiconductors in the temperature interval $100-300°C$ above the melting point, this agrees with the experimental data. The ratio of the band and hopping conductivities depends on the parameters of the material and, naturally, is a function of the temperature. Attempts at quantitatively analyzing this question with Sb$_2$Se$_3$ as an example were undertaken in[117].

Assuming that the hopping mechanism makes an appreciable contribution to the conductivity, the anomalous Hall data obtained for liquid semiconductors become understandable. Austin and Mott[145] note that there is no sufficiently correct theory of the Hall effect in the case of hopping conductivity in disordered semiconductors. There are only certain assumptions and schematic calculations with simplified models[145-147], which demonstrate that the Hall constant in the hopping mechanism can become negative regardless of the type of carrier. If this is indeed the case, then the behavior of the Hall effect in Tl$_2$Te becomes understandable and serves in turn as a confirmation of Mott's model. The negative sign of the Hall effect for Sb$_2$Se$_3$, obtained in the case of strong doping with tellurium, can seemingly also be understood. Since introduction of the excess component adds a composition disorder to the structural disorder, the density of the local states in the "quasigap" increases. The contribution of the hopping mechanism to the electric conductivity increases simultaneously, and this possibly leads to the negative sign of the Hall effect.

It is quite clear that the foregoing picture of the electronic processes in liquids can be regarded only as obviously qualitative. However, a discussion of simple models for disordered semiconductors, the separation of the principal laws, and standardization of the terminology constitute an important problem at the present stage, since they make up the necessary condition for the construction of a quantitative theory.

III. ELECTRIC CONDUCTIVITY OF METALS AT TEMPERATURES AND PRESSURES ABOVE CRITICAL

In the first two chapters we considered the electric properties of liquid metals and semiconductors in a relatively narrow range of temperatures. Nature, on the other hand, affords a unique possibility of tracing these properties at high temperatures and pressures with continuous decrease of the density of the metal.

The condition for continuous transition from the liquid state into the gaseous state requires that the measurement be performed above the critical point of the liquid-vapor phase transition. Owing to the high binding energy in the metal, this point corresponds to high critical temperatures and pressures. Investigation of this region involves considerable experimental difficulties, which were overcome in part in the last 5—6 years, but reliable results were obtained only for metals having relatively low critical temperatures and pressures. The experimental technique used to measure the electric conductivity and density of metals in this region of temperatures and pressures is described in detail in the review[148]. The critical parameters for Hg, Cs, and Rb, obtained directly from experiment, are listed in Table IV. For certain metals, the critical points lie at

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*)It can be stated in addition that investigations of the high-frequency conductivity[144], performed on amorphous semiconductors, seem to confirm these considerations.

Table IV

Element	T_C, °K	p_C, bar	d_C, g/cm³	Litera-ture
Hg	1733±20	1608±50	—	149
Hg	1753±10	1520±10	5.7±0.2	150
Hg	1763±15	1510±25	4.2±0.4	151, 152
Cs	2057±40	—	0.428±0.012	153, 154
Cs ·	2033±20	115±5	0.40±0.02	157
Cs	2053±20	120±10	0.44±0.05	158
Cs	2049	119	0.445	155
Cs	1993±30	110±10	—	156
Rb	2093±35	—	0.428±0.012	153, 154
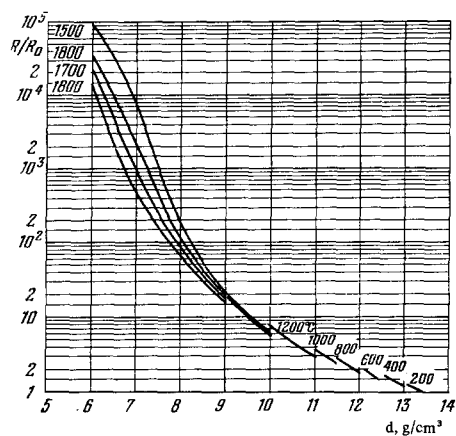
FIG. 8. Isotherms of the relative resistance of mercury as a function of the density [150].
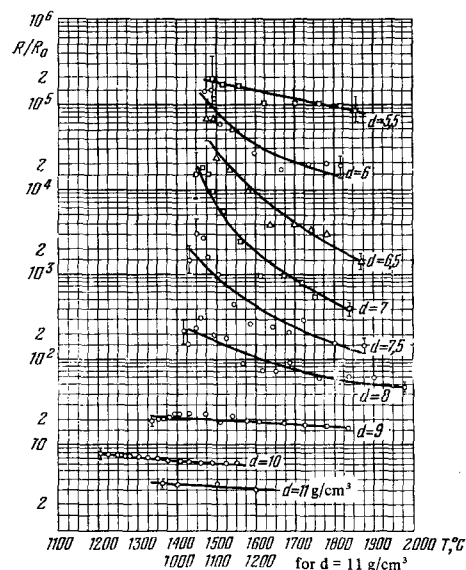

FIG. 9. Dependence of the relative resistance of mercury at constant density (isochores) on the temperature [150].
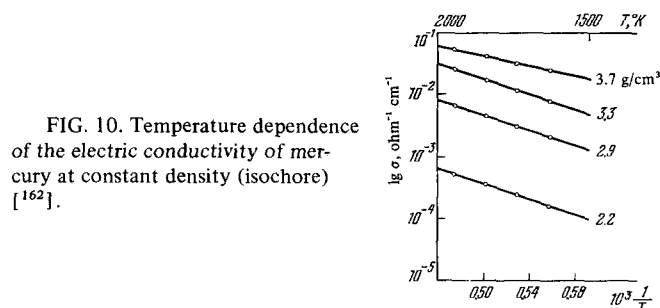
FIG. 10. Temperature dependence of the electric conductivity of mercury at constant density (isochore) [162].
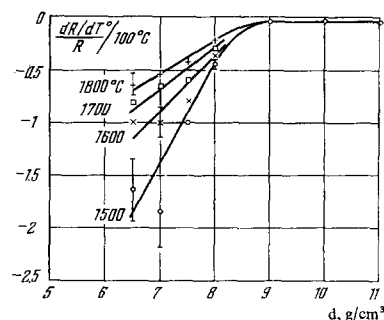

FIG. 11. Temperature coefficient of electric resistivity of mercury as a function of the density and temperature [150].

higher temperatures and pressures, which are difficult to obtain in the measurements. For example, the values predicted for silver are T_c = 7500°K and P_c = 5060 bar[159]. The critical temperatures and pressures of other metals are likewise difficult to attain[160].

The first measurements of the electric conductivity in the region of critical temperatures and pressures were made for mercury by Birch in 1932[149]. Birch has shown that near the critical point there is a sharp change in the electric conductivity (by an approximate factor 10³). For a long time after this study, no experiments were performed in this region at all, and only the work of Kikoin and co-workers in 1965[150,161], Franck and Hensel in 1966[151,152] on mercury, and the work Alekseev in 1967[163-165] and of Renkert, Hensel, and Franck in 1969[156] on cesium marked the first progress in the study of the electric conductivity of metals in the transcritical state. These studies have demonstrated that in this region a 20% decrease of the density of mercury causes the electric conductivity to decrease by a factor 10⁴, and the decrease for cesium is by a factor 10³[156,164,165], whereas in liquid mercury at 20% decrease of density leads to a decrease in the electric conductivity by a factor of 4[166]. The measured values of the electric conductivity cited in[150,161] and in[152,156] differ greatly, but the character of the behavior of the electric conductivity is the same. Figure 8 shows a plot of the electric resistivity against the density for mercury. These data were obtained by a null method and are the most accurate. The electric conductivity of mercury was measured down to 5.5 g/cm³ in[150] and 2.2 g/cm³ in[162]. The values corresponding to a density 3.5 g/cm³ and below were obtained by extrapolation

from the empirical equation of state of mercury. Figures 9 and 10 show the result of measurement of the electric resistivity and the electric conductivity of mercury at constant densities (isochores) for different temperatures. It is seen from the curves that for mercury, down to 9 g/cm³, the electric conductivity depends little on the temperature, and a sharp decrease of the electric conductivity is observed below 9 g/cm³. These isochores were used to calculate the temperature coefficient of electric resistivity of mercury as a function of the density and of the temperature (Fig. 11).

In the case of cesium there are no exact data on the electric conductivity in the region below critical. For densities below critical, the electrical resistance has
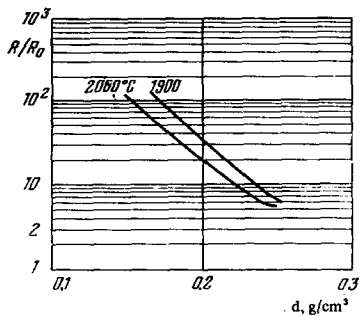
FIG. 12. Relative resistance of cesium as a function of the density
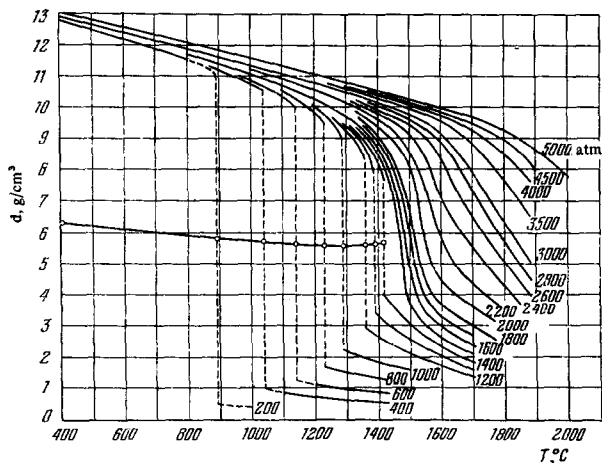[165]. R_0 is the resistance of liquid cesium ahead of the transition re-
gion.

FIG. 13. p-V-T diagram of mercury [150].

FIG. 14. p-V-T diagram of cesium [157].

FIG. 15. Dependence of the
relative resistance of mercury
on the reciprocal density [167].

an exponential dependence on the density (Fig. 12). A
similar result can be deduced from the experimental
data obtained in[156].

Let us examine the p-V-T diagrams investigated in
greatest detail at the present time for mercury (Fig. 13)
and cesium (Fig. 14).

No reliable interpretation of the electric conductivity
is possible without a notion concerning the structural
changes occurring in the region of the critical param-
eters. We start from available information on the equa-
tion of state. The trans-critical state can be subdivided
conditionally into three regions, which can have signifi-
cantly different structures[165,167]. In the first region
the predominant structure is that characteristic of
liquid metals having normal parameters. The electric
conductivity in this region obeys the laws governing
liquid metals. In the next structure region, the local
fluctuations of the density increase to such an extent
that the ions falling in the rarefaction zone produce
local centers that capture the conduction electrons.
The result is an appreciable decrease of the conduction-
electron concentration. The metallic conductivity van-
ishes at the upper limit of this region. The third region
is that with electric conductivity characteristic of dense
ionized gases.

To understand the structural changes occurring when
the density of a metal is decreased, we can attempt to
use as a first approximation an obviously simplified
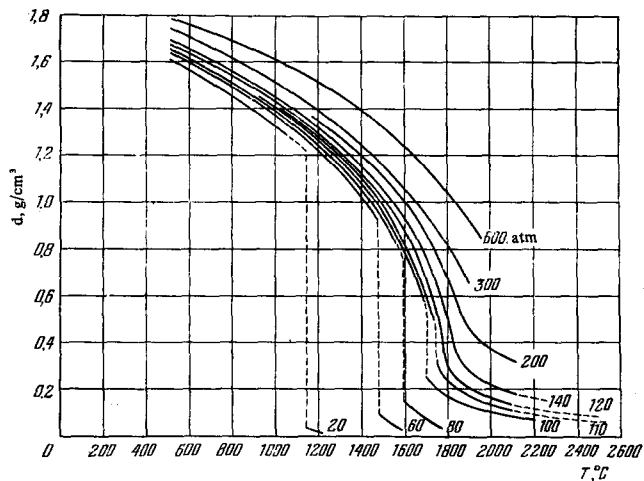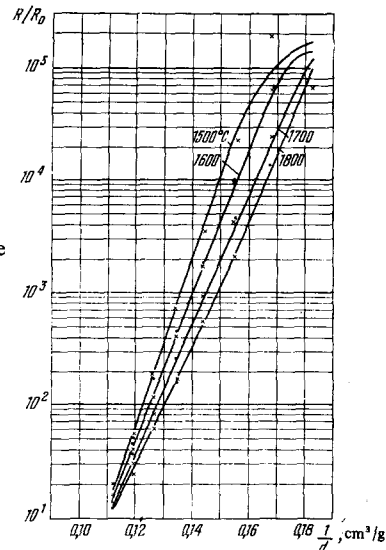mechanical model[165,167]. The gist of this model con-

sists of replacing the real atoms or ions by metallic
spheres, and replacing the atomic thermal motion by
mechanical vibrations of these spheres in three dimen-
sions. Lowering of the density was simulated by de-
creasing the number of spheres in a specified volume.
At the same time, measurements were made of the elec-
tric resistance R of a system of spheres containing in
an insulated tube with electrodes on its ends. The R(d)
dependence obtained in this manner as a result of form-
ation of conducting chains is represented by the formula

$$R = R_0 \exp\left(\frac{A}{d} - \frac{B}{T^{5/2}} + \frac{C}{dT^{5/2}}\right). \tag{17}$$

Figure 15 shows a plot of the relative electric resis-
tance of mercury against the reciprocal density for
mercury at different temperatures. The same figure
shows the theoretical curves based on formula (17).
The constant coefficients A, B, and C are parameters
used to reconcile the results. The plot corresponds to a
region of the p-V-T diagram defined as intermediate be-
tween the metallic and gaseous regions.

Naturally, the model of metallic spheres cannot be
used at low densities. The electric conductivity can be
qualitatively analyzed in this case by methods developed

for a dense plasma. Vedenov has proposed that the log $\sigma(1/T)$ dependence may be due to interactions between "free" electrons and neutral atoms[168]. The average energy of the "free" electrons can be reduced by their large polarization interaction with the neutral atoms by an amount $u_1 = n\hbar^2\sqrt{\pi q/m}$, where q is the total cross section for the elastic scattering of the slow electrons by the gas atom. The lowering of the energy of the ion in the gas is due to polarization of the neighboring neutral atoms by an amount $u_2 = 4n\pi e^2 a/r_0^2$[170,171]. Lowering of the ionization potential I by an amount $u_1 + u_2$ can lead to an exponential dependence of the electron concentration on the gas density[169]

$$n_e \backsim \exp\left(-I + u_1 + u_2\right)/2T.$$

In the density region $0 < d < d_C$, the formula for the electric conductivity can be written in the form

$$\sigma \backsim \exp\left(-I/2T\right) + (n/n^*),$$
$$1/n^* \approx \left(2mT/\sqrt{\pi q}\,\hbar^2\right)^{-1} + (Tr_0/2\pi e^2 a)^{-1};$$

the first and second terms describe the electron-atom and ion-atom interactions, respectively ($q \sim 10^{-13}$ cm², a = 400 at. un., $r_0 = 2.3$ Å). The obtained value of the electric conductivity, assuming a weak dependence of the mobility on the density, agrees satisfactorily with the experimental values of the electric conductivity of cesium[156,165]. In[172], a "plasma" approach was likewise used to explain the phenomena occurring in the trans-critical state, assuming a decreasing of the ionization potential with decreasing gas density. This interpretation was applied also to the transition region. Assuming that the formalization considered above for the conductivity in this region is correct, the contribution to the conductivity of the plasma electrons should become significant mainly at the end of the transition region. The plasma approach was considered in[173,175]. The influence of density fluctuations on the degree of ionization of the plasma was pointed out in[175]. An attempt to describe the metal-dielectric transition in the case of metals was made in[123], but at densities below the critical region the proposed model contradicts the experimental data on the electric resistivity and on the equation of state of the metal, since no account is taken in this model of the influence of the strong Coulomb interaction between the plasma particles on the liquid-gas coexistence curve of metals. As a result, the statement made in[123], that the liquid phase is non-conducting at densities above critical in a certain density interval, is in error. The transition to metallic conductivity takes place in the vicinity of the critical point, so that at densities below critical there exists in the plasma a noticeable degree of ionization.

The behavior of a plasma at temperatures above critical under conditions of strong Coulomb interaction is of interest, as predicted in a number of papers[184-189], in view of the possible violation of thermodynamic stability. It is not clear as yet whether this agrees with the observed phenomena. A critical review of this question is given in[174].

Hensel and Franck[162] relate the activation energy obtained from the temperature dependence of the electric conductivity with formation of a gap in the energy spectrum of the electrons. This *semiconducting scheme was first considered by Mott in*[71]. *According to Mott,*
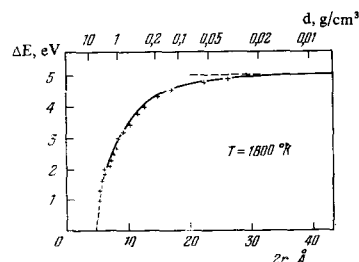

FIG. 16. Energy dependence of the s and p states on the average internuclear interaction [176].

all the phenomena in mercury at high temperatures can be described on the basis of the model of non-interacting electrons. The energy gap in the electron spectrum must be replaced in this case by a quasigap whose depth can be determined by starting from the assumption that localization sets in if the electron wavelength and the mean free path become comparable. When the states become localized in the quasigap, the substance begins to behave like a semiconductor in which electron transport is realized by jumps from one localized state to another, with a certain activation energy. Sechenkov also holds with such an interpretation[196].

In light of the investigation of the mechanism of conductivity in the gaseous region, particular interest attaches to work performed by Hensel[176] on the optical absorption of mercury in the transcritical state. He observed a shift of the red boundary of the optical absorption in gaseous mercury when the density of the mercury increased up to critical; the interval between the ground state 6s and the first excited state 6p for isolated non-interacting mercury atoms, which equals 4.9 eV (2537 Å), drops to 1.3 eV at a density 3.5 g/cm³. The absorption edge vanishes at mercury density 5.0—5.5 g/cm³, corresponding to the region of the critical point (Fig. 16). This value agrees with the increase of the electric conductivity in this region, from 10^{-4} to 10^2 ohm⁻¹cm⁻¹, when the density is increased to 6 g/cm³. We note that the activation energy determined from log σ (1/T) in the gaseous phase, at the densities close to critical, does not agree with the results of optical investigations.

* The aggregate of the measurement data on the electric properties of metals when the density is continuously decreased makes it possible to answer a question raised back in 1943 by Zel'dovich and Landau[177] concerning the relation between the liquid-gas phase transition and the metal-dielectric phase transition. In the subcritical region the liquid-vapor phase transition coincides with the metal-dielectric phase transition[148,152,162,178,179,180,169]. In the transcritical region, the metal-dielectric transition is not accompanied by a first-order phase transition. This transition becomes smeared out at temperatures above T_c, and the average line of equal electric conductivities shifts with increasing temperature into the region of values lower than the values lying on the critical isobar[181].

The second fundamental question not solved at the present stage is the degree to which the metal-dielectric transition in the transcritical region can be identified with a transition of the Mott type. On the one hand, experiments with simulation of the real situation by metallic spheres seems to show that the smooth variation
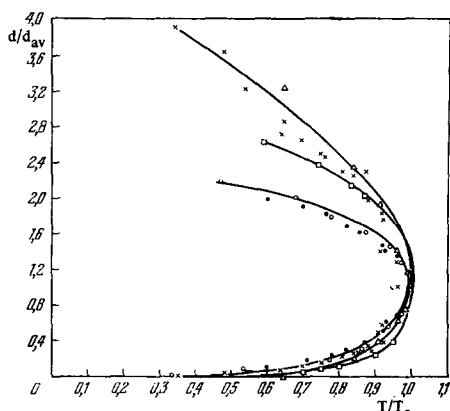
FIG. 17. V-T diagram for mercury, cesium, inert gases, and carbon dioxide. Mercury: O—[150], ●—[151], cesium: X—[154], Δ—[157]; inert gases and carbon dioxide—□.

of the electric conductivity can be explained without making use of the collective effect of interelectron correlation. On the other hand, it is likewise impossible to reject fully the interpretation given in[162,182] on the basis of the Mott transition, since the abrupt Mott transition can be obscured by density fluctuations in the system, which are quite considerable in the transition region. The author of the present chapter regards the first point of view as preferable.

Unfortunately, there are not enough completed measurements of the electric resistance of binary systems. Individual measurements of the electric resistance of the systems mercury-cesium[162] and sodium-chlorine[181], performed in 1968, revealed a decrease of the electric resistance in a mixture of dense gases. These data, however, are only preliminary. In[181], thermal decomposition of the salt NaCl at high pressures and temperatures was used. Reactions of this type can be important in the new field of plasma chemistry, which can be called the plasma chemistry of a dense (non-ideal) plasma. Experimental and theoretical papers on the thermoelectric power of cesium have recently been published[174,183].

In conclusion, let us mention some questions concerning the thermodynamic equation of state of mercury and cesium. An analysis of the p-V-T diagrams of mercury and cesium shows that the law of corresponding states is violated for both mercury and cesium[160,165,169].

In the gaseous phase, all substances have approximately equal compressibility. In the liquid phase, cesium had the largest compressibility and mercury the smallest, while other conducting substances occupy intermediate positions[165]. This can be easily seen on the V-T diagrams shown in Fig. 17 for cesium[150,151], mercury[154,157], inert gases, and carbon dioxide.

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