

Semiconductor-metal transition in liquid semiconductors

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1. INTRODUCTION

Investigations of electron transport processes in structurally disordered systems (amorphous and liquid semiconductors, and also metals) have grown into an independent and rapidly growing branch of the physics of condensed matter.

The range of physical phenomena which occur in disordered systems is at least as wide as the range in crystalline solids, and the practical importance of these systems is increasing year by year. Among disordered structures there are good metals as well as typical semiconductors and insulators. As usual, their properties are governed mainly by the structure of the electron energy spectrum. When external parameters are altered or when the system changes, this structure may be modified giving rise to changes in the various electronic properties, in particular, to semiconductor-metal or metal-semiconductor transitions. The special nature of this effect in disordered systems is associated primarily with the dominant role of disorder, which gives rise to new transition mechanisms not applicable to crystalline solids. From this point of view, investigations of the semiconductor-metal transition in liquids are particularly illuminating because they provide an opportunity to alter the structure of the system within a very wide range and thus study the role of structural changes in the formation of the electron spectrum. Accumulation of data on this topic is par-

ticularly desirable because the state of theoretical ideas on disordered systems is far from that degree of completeness which is characteristic of the theory of crystalline solids. On the other hand, investigations of this kind deal with the states of matter over a very wide range of external parameters (such as pressure and temperature) covering practically the whole range accessible at present under laboratory conditions; this extends greatly our ideas on the physics of condensed matter. The founder of investigations of noncrystalline materials and specifically of the electronic phenomena—conduction mechanisms and structure of the energy spectrum—is Abram Fedorovich Ioffe. His leading role in the establishment of this branch of physics is generally recognized and one is left to wonder at the foresight of the scientist who in the forties and fifties of the present century was able not only to formulate the fundamental problems in a new branch of physics but also to forecast (albeit in a qualitative form) the solutions of the most important problems.¹

One of Ioffe's predictions, based on profound scientific intuition, is the hypothesis of the dominant role of the short-range structural order in the formation of the energy spectrum of electrons in noncrystalline materials and the idea of localization of electron states as the structural disorder factor increases.

Further development of the ideas of A. F. Ioffe and establishment of an electron theory of disordered systems owes much to the more recent contributions of

At present the research on the topic of interest to us is being pursued on a very wide front, including not only investigations of the semiconductor-metal (SM) transition in such noncrystalline materials as amorphous and liquid semiconductors, but also studies of impurity subsystems in crystalline matrices. Work of the latter kind is largely an independent subject and for this reason will not be considered in the present review. We shall confine ourselves mainly to investigations of electronic conduction in liquid semiconductors over a wide range of temperatures, including the transcritical state. Experimental studies, carried out mainly in the last decade owing to the development of techniques for measuring electrical properties at high pressures and temperatures² (4000 atm and 2000°C), have shown that liquid semiconductors generally undergo two transformations of the electron spectrum at high temperatures: the SM transition occurs at lower temperatures and is preceded by enhancement of the interaction between electron shells of the atoms (this is a delocalization factor, operating in opposition to the structural disordering factor), and the metal-insulator (or metal-dense plasma) transition occurs at higher temperatures, in the range of critical temperatures and pressures, and is associated with a reduction in the density of the material and with an opposite relationship between the interatomic interaction and structural disordering factors. The two transitions obviously have common criteria.

Apart from the intrinsic physical interest, the subject discussed in the present paper is also of considerable importance in geophysics because it makes it possible to understand a large number of fundamental phenomena which occur in the interior of the earth. Many molten rocks are typical semiconductors, they exhibit the semiconductor-type temperature dependence of the electrical conductivity, and have high values of the thermoelectric power whose sign may vary with temperature. We can expect SM transitions at high temperatures and pressures in the earth's interior. The results of an analysis of these phenomena may be decisive in support of the hypothesis of metallization of molten matter in the earth's core and the high value of the thermoelectric power can be a powerful source of heating of certain parts of the crust and mantle.¹⁾

In the present review we shall be concerned with the current status of the theory (Sec. 2) and we shall compare the theoretical and experimental results (Secs. 3-5). One should also mention that understanding of the mechanism of the SM transition requires general knowledge of the structure of the electron energy spectrum and of the special features of the electron transport phenomena in disordered systems. Consequently, we shall consider briefly these topics in Sec. 2 by way of introduction to the main theoretical and experimental data.

2. THEORETICAL MODELS OF THE SEMICONDUCTOR-METAL TRANSITION IN DISORDERED SYSTEMS

A theory of the SM transition in disordered systems should, in principle, follow the corresponding theory for crystalline solids. First of all, one should determine the structure of the electron energy spectrum of disordered systems and the changes in this structure under the action of external parameters. The ideas obtained in this way can then be used to go over to the next stage which is a description of the electron kinetics and classification of the investigated systems into metals, semiconductors, and insulators. The knowledge of possible changes in the electron spectrum should make it possible to compare directly these changes with the transitions observed experimentally. This approach is fundamentally clear, but its realization meets with considerable difficulties.

In spite of much work of theoreticians and in spite of the availability of extensive experimental data, a self-consistent theory of electrons in disordered structures is in practice still lacking. However, there are many models and ideas of a qualitative nature which make it possible to interpret the observed effects. A detailed presentation of these ideas can be found in the well-known books of Mott and Davis³ and Mott⁴, as well as in several reviews.⁵⁻⁹ We shall consider briefly the main theoretical results relevant to the subject of the present review.

The main difficulty in the theory is the absence of translational symmetry because such symmetry leads to very great simplification in the case of ideal solids, in an analysis of the electronic properties associated with the Bloch theorem and with the results of the band theory. As is known, classification of solids into metals, semiconductors, and insulators is usually associated with the energy band structure. A considerable simplification of the theory arises also from the fact that it is usually possible to reduce the real many-body problem to an effective weak interaction between quasiparticles, i.e., it is possible to reduce the problem to the one- or two-particle level. In the case of disordered systems neither the former nor the latter simplification is possible. Strictly speaking, in the absence of translational symmetry we cannot introduce the concept of the band electron spectrum or the idea of effective quasiparticles. In view of the random nature of disordered systems one has to employ characteristics which are statistical averages over ensembles describing the structure of a system of one or another kind. It is then found that although usually it is not possible to specify the dispersion law for electrons in the form of a well-defined dependence of the energy on the quasimomentum $E(p)$, it is nevertheless possible to describe the electron spectrum by the density of the electron states $N(E)$ averaged over the ensemble of random configurations.⁸ The work on the theory of imperfect crystals, particularly doped semiconductors and alloys, giving rise to the concept of density-of-states tails in the band gap¹⁰⁻¹³ and the ideal of localization of electrons in such tails have been important in

¹⁾Some of these problems are discussed in Ref. 221.

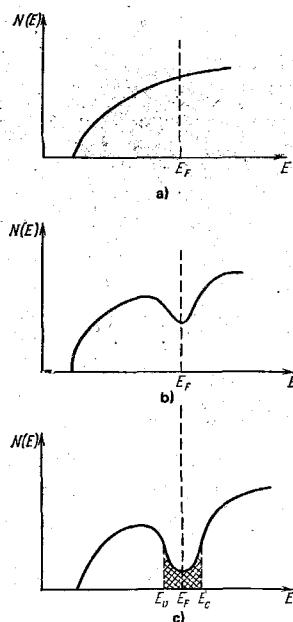


FIG. 1. Density of electron states in liquids: a) liquid metals; b) quasimetallic liquids; c) liquid semiconductors (the localized-state region is shaded).

the development of suitable representations. Mott^{3,4} proposed several possible variants of transformation of the energy band spectrum of solids as a result of loss of order (for example, at the melting point). Figure 1 shows the various densities of electron states in the order of increasing importance of the short-range order or the degree of binding of electrons to the potential field of the atomic structure. The case shown in Fig. 1a corresponds to the total disappearance of the band gap and then $N(E)$ is analogous to that for free electrons and it describes, for example, liquid metals. In the case shown in Fig. 1b there is a dip in the density of states in the range of energies corresponding to the band gap in the crystalline state. This range of energies is usually called the pseudogap. The depth of this pseudogap is usually described by the ratio $g = N(E_F)/N_0(E_F)$, i.e., by the ratio of the true density of states at the Fermi level to that calculated in the free-electron approximation.

Since the pseudogap region can be regarded as the range of energies where the density-of-states tails of the "valence" and "conduction" bands overlap, the idea of localization of electrons at the band edges mentioned earlier is applied to the two-band case in Fig. 1c when the pseudogap is sufficiently pronounced.

In general, we have $N(E) \neq 0$, but we cannot exclude the possibility of a situation in which there is a true band gap, i.e., when there is a range of energies where $N(E) = 0$. However, in spite of the fact that $N(E_F) \neq 0$, in the case shown in Fig. 1c when the Fermi level lies within the region of localized states in the pseudogap, we effectively have a model of a liquid or amorphous semiconductor. Since the electron mobility at localized states bounded by the mobility thresholds E_v and E_c is much less than the mobility of electrons of energy exceeding E_c or less than E_v , at sufficiently high tem-

peratures T the conduction process is dominated by carriers in delocalized states. The range of energies $E_c - E_v$ acts as a mobility gap³⁻⁵ and it is responsible for the semiconductor behavior of the system in the absence of a true band gap. The conductivity then obeys a typical semiconductor equation:

$$\sigma = \sigma_0 \exp \left(-\frac{E_c - E_F}{kT} \right), \quad (1)$$

where E_F is the Fermi energy of electrons, i.e., it is governed by the thermal excitation of carriers across the pseudogap. The presence of this pseudogap gives rise to a number of special features of the transport phenomena (compared with the case of free electrons), even when there are no localized states inside the pseudogap.

The "two-band" scheme of the density of states of the type shown in Fig. 1c is a natural consequence of the approach postulating a pattern of a "faulty" crystal which has initially an energy band structure on which a random field is then superimposed. However, there is also the fundamental problem of postulating an analog of the band structure (of the type shown in Fig. 1c) for an intrinsically disordered system, such as a liquid or an amorphous body, without making any assumptions about the initial periodicity. Attempts to find the energy spectrum of disordered systems should start from two limiting cases considered in the theory of solids:¹⁴ the tight-binding approximation or the model of almost-free electrons.

In the former case we have electrons whose wave functions are localized near individual atoms. As the atoms approach one another, their levels spread into energy bands because of the overlap of the wave functions and in general this is not related to any long-range order. Therefore, it would seem natural that in this situation there should be some kind of "band" structure governed only by the short-range order and by the overlap of the wave functions of the nearest neighbors. One would then expect to retain even the true band gap. Theoretical papers implementing these ideas in mathematical form have been published recently.¹⁵⁻¹⁹ Weaire and Thorpe¹⁵ considered a model Hamiltonian of a disordered system comprising germanium-type atoms (with covalent bonds) and electrons regarded as localized at atoms and bonds. They were able to demonstrate rigorously that, in spite of the structural disorder, a system of this kind should have a band structure with a true band gap. The valence and conduction bands are formed by electron states of the bonding and antibonding type. It is probable that this model will apply to the properties of systems such as amorphous germanium and silicon.

The Ziman group used machine calculations to show¹⁶⁻¹⁹ that the density of states in amorphous Ge and Si structures is governed by the scattering of electrons by relatively small clusters (~ 10 atoms) with a specific geometry of the distribution of atoms, and the density of states is found to be relatively insensitive to the distribution of the clusters themselves. The density of states has a typical pseudogap which is in full agreement with the available experimental results.

All these investigations confirm the idea first put forward by A. F. Ioffe²⁰ that the "band" structure of amorphous and liquid systems is governed primarily by the short-range order.

A special difficulty arises in the derivation of the density of electron states with a pseudogap using the language of almost-free electrons scattered by a weak pseudopotential of ions²¹ distributed in a correlated manner in a liquid. The first attempts in this direction were made by Edwards.²¹ The subsequent calculations carried out using real structure factors of liquids and model pseudopotentials of ions gave a density of states very close to that for free electrons.^{22,23} Ziman²⁴ showed that under certain (fairly rigorous) assumptions about the higher correlation functions of ions (in particular, the four-ion function) it is possible to obtain a semiconductor-type density of states. However, there are at present no theoretical or experimental methods which would make it possible to find the higher correlation functions for a liquid.

Sadovskii^{25,26} showed that the use of a characteristic binary structure factor of a liquid and the assumption of a strong nonlocality of the ion pseudopotential corresponding to predominance of the backscattering makes it possible to construct a model of the electron spectrum of a liquid with a pronounced pseudogap in the energy range corresponding to the band gap of a crystal. This model is equivalent to an ensemble of ideal semiconductors whose energy gap in the spectrum varies in a random manner from one semiconductor to another.

We can summarize the current situation by saying that the evolution of the structure of the energy spectra (densities of electron states) on transition from crystalline solids to liquids and amorphous structures is now qualitatively understood but the representations employed cannot be regarded as having the same reliability as in the case of crystals and, moreover, they cannot be used to calculate the spectra of real systems.

A theoretical understanding of the kinetics of electrons in disordered systems and particularly of possible mechanisms of the SM transition, which is the subject of the present review, is in an even earlier stage of development. Before discussing the current ideas, we shall deal first with the concept of localization of electrons in a random field which is one of the main mechanisms for the transition from metallic to semiconducting type of conduction in disordered systems.

The first and still the fundamental results on localization were obtained in the well-known work of Anderson.²⁷ We shall consider briefly the Anderson model without attempting to be rigorous. The reader interested in details should turn to the original papers²⁷⁻³⁶ and to reviews.^{6,9}

We shall consider a three-dimensional lattice of sites distributed regularly or randomly. An electron at a site j has an energy E_j which is regarded as a stochastic variable distributed in a band of energies of

width W with a certain distribution density $P\{E_j\}$. The overlap of the wave functions at neighboring sites gives rise to an interaction V_{ij} describing the transfer of an electron from one site to another. In an irregular lattice the interaction V_{ij} is also generally a stochastic quantity, but it is usual to consider the case of an ideal lattice with an energy disorder of levels at the different sites.

We shall assume that initially (at $t=0$) an electron is located at some specific site i and we shall consider the time dependence of its wave function. The main result of Anderson is that for V_{ij} which decreases with distance between the sites $|R_{ij}|$ faster than $|R_{ij}|^{-3}$ and has an average value smaller than a certain critical potential $V_c \sim W$, an electron remains localized in the vicinity of the site i in the sense that even as $t \rightarrow \infty$ the amplitude of the wave function at the site i is finite and decreases rapidly with distance. The physical meaning of this result is related to the circumstance that an electron can tunnel only to a site of energy which is identical with the level E_i determined by the initial conditions. However, under the above conditions the probability of finding, in the vicinity of a given site, another site with the same energy increases with distance away from this site at a rather much slower than the rate of reduction of the interaction V_{ij} with the same distance. Therefore, the probability of electron jumps is zero and there is no electron transport in the system as long as we consider the case of zero temperature.

We shall now consider a very much simplified version of the proof given by Anderson. The Hamiltonian of the Anderson model has the form

$$H = \sum_j E_j a_j^\dagger a_j + \sum_{ij} V_{ij} a_i^\dagger a_j, \quad (2)$$

where a_j^\dagger and a_j are the electron creation and annihilation operators at sites j and i ; V_{ij} is assumed to be equal to the constant V which differs from zero only for transitions between the nearest neighbors.

It is assumed that initially an electron is at a site i whose wave function is $|i\rangle$. Subsequently $t > 0$ the wave function has the form

$$\psi(t) = \sum_i c_i(t) |i\rangle. \quad (3)$$

The quantity $p_{ii} = \lim_{t \rightarrow \infty} c_i(t)^2$ represents the probability of finding a particle in a state $|i\rangle$ at the moment $t = \infty$. The probability p_{ii} naturally depends on the set $\{E_j\}$. If $p_{ii} \neq 0$, there are electron states localized near the site i . The nature of the electron states is governed by the one-electron Green function

$$G_{ij}(E) = \left\langle i \left| \frac{1}{E - H} \right| j \right\rangle, \quad (4)$$

representing the amplitude of the probability of a transition of an electron of energy E from a site j to a site i . In particular, p_{ii} can be expressed in terms of $G_{ii}(E)$ (Ref. 30). A renormalized series in the theory of perturbations with respect to V is obtained for this Green function. Anderson showed that the problem of

²¹In the case of crystalline semiconductors such a description has now reached a highly advanced state.¹⁴

localization reduces to a study of the convergence of this series and, in view of the random nature of the quantity E_j , the convergence is understood to be in the sense of probability.²⁷⁻³⁰ Simplifying the treatment in Ref. 31, we can say that it reduces to whether the diagonal element (4) has an isolated pole:

$$G_{ii}(E) = \frac{A_i}{E - \mathcal{E}_i(E)}, \quad (5)$$

which can be interpreted as the eigenenergy of an electron localized at the i -th site. The quantity \mathcal{E}_i should be real because otherwise such a state decays with time, i.e., an electron becomes delocalized in the limit $t \rightarrow \infty$. The eigenvalue \mathcal{E}_i is given by the Brillouin-Wigner perturbation theory:

$$\mathcal{E}_i = E_i + \sum_j V \frac{1}{E - E_j} V + \sum_{jj'} V \frac{1}{E - E_j} V \frac{1}{E - E_{j'}} V + \dots \quad (6)$$

If the series (6) (or, more precisely, a renormalized series in which the repeated sites are eliminated in the sums) converges near the real axis of E (apart from the point \mathcal{E}_i), a sequence of real terms converging to the real value of \mathcal{E}_i is obtained along the real axis. The localization condition reduces to the requirement of convergence of a series of the type given by Eq. (6).³¹

Since E_j are random variables, the convergence of the series (6) should be considered, as mentioned above, in the statistical sense and this requires a complex analysis.^{27,30} However, a simplified estimate of the convergence condition can be obtained as follows.³¹ We shall consider various contributions of the order of V^{L+1} , where $L \gg 1$. Since each lattice site has Z nearest neighbors, there are in all Z^L contributions and each of them is a product of L factors of the type

$$T_i(E) = \frac{V}{E - E_i}. \quad (7)$$

If we assume that the quantities E_i in these cofactors are independent, we can find the value of the product in question by taking the average of its logarithm over the distribution of E_i :

$$\langle \ln |T_i T_{i'} \dots T_i| \rangle = L \langle \ln |T| \rangle. \quad (8)$$

Then, the series (6) behaves, on the average, as a geometric progression and converges if

$$Z \exp \langle \ln |T(E)| \rangle < 1. \quad (9)$$

This condition (the equation for E) defines the range of energies where electrons are localized. Anderson²⁷ used the following distribution of E_i :

$$P\{E_i\} = \begin{cases} \frac{1}{W} & \text{for } |E_i| < \frac{1}{2}W, \\ 0 & \text{for } |E_i| > \frac{1}{2}W. \end{cases} \quad (10)$$

Then,

$$\begin{aligned} \langle \ln |T(E)| \rangle &= \frac{1}{W} \int_{-W/2}^{W/2} dE_i \ln \left| \frac{V}{E - E_i} \right| \\ &= 1 - \frac{1}{2} \left[\left(1 + \frac{2E}{W} \right) \ln \left| \frac{W}{2V} + \frac{E}{V} \right| + \left(1 - \frac{2E}{W} \right) \ln \left| \frac{W}{2V} - \frac{E}{V} \right| \right]. \end{aligned} \quad (11)$$

³¹We shall, in fact, ignore a number of finer aspects which are discussed in detail in Refs. 6, 27-30, and 32.

The scatter of the energy at sites W required for localization clearly depends on the energy E of the state of interest to us. We shall consider the state at the center of the band where $E = 0$ (such states are most difficult to localize). Then, the condition (9) simplifies and reduces to the inequality³¹

$$\frac{W}{V} > 2eZ. \quad (12)$$

For a simple cubic lattice of Eq. (8), we can introduce the band width $B = 2ZV$ and obtain $W/B > e$.

Thus, if the random scatter of the energy at lattice sites is sufficiently large in the sense of the condition (12), all the electron states in a band are localized. A system is then an insulator of special type in which electron transport can take place only as a result of thermally activated jumps between local states. The metal-insulator transition caused by localization in a random field is usually called the Anderson transition. The criterion of total localization given by Eqs. (9) and (12) has been refined by many authors.^{6,30,32-34} Different values for the critical scatter of the energy levels W_c are obtained depending on the approximations used in analyzing the convergence of a series of the type of (6). In order-of-magnitude estimates we can use Eq. (12) or the best numerical estimate of Anderson.²⁷ The fundamental point is the existence of such a critical ratio.

For a fixed value of W the localization condition can be analyzed as a function of E , which is the energy of a band electron.^{30,31,35} The qualitative situation is illustrated in Fig. 2 (the localization region is shaded). The most important is the appearance of critical fields E_c and $E_{c'}$ separating the regions of localized and delocalized states. These energies are usually called the mobility thresholds. Naturally, location begins at band edges and on increase in the amplitude of the random fields W the mobility thresholds tend to move toward the center of the band, so that the localized states cover increasing parts of the spectrum.

A description of the behavior of electron states and their kinetics near the mobility thresholds is the fundamental problem in the theory of disordered systems. Anderson²⁹ showed that in the range of energies corresponding to localized states the electron wave functions decrease exponentially with distance over a length equal to the localization radius and as the energy of the state E tends to the localization threshold, the radius

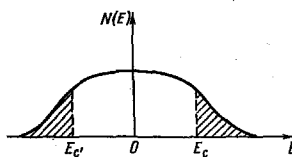


FIG. 2. Density of electron states in the Anderson model for a given ratio W/V . Here, E_c and $E_{c'}$ are the mobility thresholds.

diverges:

$$R_{loc} \sim a \left| \frac{E - E_c}{E_c} \right|^{-\nu} \quad (13)$$

where a is a length of the order of the interatomic distance. This behavior resembles the divergence of the correlation radius of fluctuations at a second-order phase transition point and suggests that the behavior of electron states in the critical region near the mobility threshold may be governed by scaling dependences (typical of phase transitions) with critical indices governed only by the dimensionality of space.³⁷ Some results on this point are obtained in Ref. 36, where it is shown that the index ν in Eq. (13) is the index of the correlation length in a specific problem of a second-order phase transition with a null-component order parameter.^{38,39} The index ν is calculated there by the Wilson ϵ expansion method.³⁷ It is found that for a three-dimensional space the index is $\nu \approx 0.6$, in full agreement with the Anderson result²⁹ obtained by numerical analysis of the statistics of nonintersecting paths on a lattice, which governs the structure of the perturbation theory series for the Green's function (4) [see comments after Eq. (6)]. It is shown in Ref. 36 that the spatial behavior of this Green's function is identical with the corresponding behavior of the correlation function of the phase transition mentioned above. The behavior of the Green's function in question at the localization threshold demonstrates³⁶ that a power-law localization of wave functions in the Anderson model assumed by Thouless⁴⁰ is impossible. It should be stressed that the results of Ref. 36 apply to the *most probable* Green's function of an electron found using the Anderson approach. However, the majority of the measured physical quantities are governed by the *average* Green's functions. Attempts to apply an analogous treatment to the average correlation functions (relating to the density of states or the conductivity) have met with serious difficulties.⁴¹⁻⁴⁵ It has been found that the problem reduces to an analysis of an unstable field-theoretic problem and the application of perturbation theory gives nonphysical singularities reflecting probably a smooth transition from weak to strong binding.⁴¹ The size of the transition region on the energy scale is identical with the size of the critical region in the theory of phase transitions,^{41,44} but the scaling behavior of the correlation functions is not observed. Similar results are obtained in Refs. 42 and 43. An analogy between localization and a transition to a spin glass state is suggested in Ref. 45 but once again scaling behavior is not observed. The whole problem is considerably more complex than that of critical phenomena in second-order phase transitions.⁵¹

The above analysis of localization is directly applicable to systems with energy disorder of which the only

examples are probably disordered alloys. Real disordered systems usually have structural disorder (liquids, amorphous bodies). It is usual to assume that structural disorder always results in energy disorder because of unavoidable (due to the irregular distribution of atoms) fluctuations of the potential field acting on electrons. The above analogy with phase transitions suggests universality of the localization effect. Attempts to generalize the theory of Anderson have already been made.⁴⁶ With this in mind, detailed investigations have been made of electrons in a system of randomly distributed scattering centers⁴⁷⁻⁵¹ and fairly rigorous results have been obtained, particularly those on the behavior of the localization radius of the type described by Eq. (13). It may be that further development of methods not based directly on perturbation theory (quasiclassical approach) will help to solve the above problem of the behavior of the average correlation functions.

It is of fundamental interest to estimate the minimal metallic conductivity, which is typical of the Anderson model in the case when a system is at the threshold of localization of all the states in a band.⁶¹ Estimates of this conductivity were obtained by Mott.^{3,4,52} We shall use the Kubo-Greenwood formula for the static conductivity at absolute zero:^{3,4}

$$\sigma = \frac{2\pi e^2 \hbar^3 \Omega}{m^3} |D_{EF}|^2 N^2(E_F), \quad (14)$$

where e is the electron charge, m is the electron mass, Ω is the volume of the system, and D_{EF} is the matrix element of the momentum operator averaged over the states on the Fermi surface. The Fermi level E_F is at the midpoint of the band. It is assumed that the phases of the wave functions of electrons at neighboring localization centers (atoms) are not correlated. Then,

$$D_{EF} \approx \sqrt{N} \delta, \quad (15)$$

where $N = \Omega/a^3$ is the number of sites (atoms) in a volume Ω , and the quantity δ has been estimated in various ways.^{3,52} In particular, Mott³ assumed

$$\delta \sim \frac{m}{m^*} \left(\frac{a^3}{\Omega} \right) \frac{\pi}{a}, \quad (16)$$

where m^* is the effective electron mass in a periodic lattice. Then,

$$\sigma \approx \frac{2\pi^3 e^2 \hbar^3 a}{m^{*3}} [N(E_F)]^2, \quad (17)$$

so that introducing an overlap integral $V \sim \hbar^2/2m^*a^2$ and also assuming approximately that $N(E_F) \approx 1/a^3 W$ (the notation is the same as in the above discussion of the Anderson model), we obtain

$$\sigma \approx \frac{8\pi^3 e^2}{\hbar a} \left(\frac{V}{W} \right)^2. \quad (18)$$

It follows from the best estimate of Anderson²⁷ that the localization of electrons in the band occurs for $(W/V_e) \approx 60$ when the lattice is characterized by $Z = 6$. Therefore, for a system with the Fermi level lying at the

⁴¹In the case of a transition at the center of a band we have

$R_{loc} \propto a |(W - W_c)/W_c|^{-\nu}$ for $W \geq W_c$.

⁵¹The scaling theory of localization has been developed further in recent papers²¹⁶⁻²²⁰ but the problem is far from finally solved and the results obtained by different authors are quite contradictory.

⁶¹At absolute zero.

midpoint of the band the minimal metallic conductivity is

$$\sigma_{\min} \approx 0.06 \frac{e^2}{h a}. \quad (19)$$

For $a = 4 \text{ \AA}$, Eq. (19) gives $\sigma_{\min} \approx 350 \Omega^{-1} \cdot \text{cm}^{-1}$.

Mott modified the estimates given by Eqs. (16)–(19) on several subsequent occasions.^{4,52} In view of the scatter in the values of $(W/V)_c$ and the fairly large indeterminacy of the estimate given by Eq. (16), one should not treat the specific values too seriously. However, Eq. (19) can be expected to give the correct order of magnitude: $\sigma_{\min} \approx 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$. Estimates obtained using the elementary Drude formula^{3,4} for the case when the mean free path is $l \sim a$ give values $\sigma \approx 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$.

A rigorous justification of the concept of minimal metallic conductivity is one of the main tasks of the theory. Recently, Thouless and Licciardello⁵³ were able to demonstrate the existence of a universal metallic conductivity minimum for two-dimensional systems. Their analysis is in fact based on the above analogy between localization and phase transitions, and on application to the two-dimensional Anderson model of an analog of the Kadanoff procedure used earlier to describe the critical region in the problem of phase transitions.³⁷ In the Anderson lattice a unit cell of side a is replaced with a new cell of side L containing N sites of the original lattice (Fig. 3). Periodic continuation of such a large cell in space has the effect that in the new lattice each of the N levels spreads into a band of width $2\Delta E$. The initial Anderson lattice can obviously be described as consisting of new cells of side L in each of which there are N random levels. Then, the effective binding of electrons at two levels in neighboring cells (an analog of the overlap integral V for the system of new cells) is evidently of the order of $V_N \approx (1/Z)\Delta E$ (Z is the number of the nearest neighbors) because this type of binding ensures a band of width $2\Delta E$ when the new cell is continued periodically in space. The separation between the energy levels in neighboring cells is of the order of $W_N \approx L^{-d}N^{-1}(E)$, where $N(E)$ is the density of states per unit volume (d is the number of dimensions of space) of the original lattice. If one of the N bands is considered in the new lattice, then W_N can be regarded as an analog of the statistical scatter of levels W in the original lattice. We thus have a procedure for going over from the original Anderson model characterized by the ratio W/V to a new (scale-transformed) model of the same type with an effective Hamiltonian characterized by a new ratio W_N/V_N , which is an exact analog of the scaling transformations in the theory of phase transitions.³⁷ The process of scale transformations can be continued along the chain:

$$\begin{aligned} V_N &\rightarrow V_{N^2} \rightarrow V_{N^3} \rightarrow \dots, \\ W_N &\rightarrow W_{N^2} \rightarrow W_{N^3} \rightarrow \dots \end{aligned}$$

⁷⁾Recent results relating to this scaling description of the mobility threshold can be found in Refs. 219 and 220, where it is shown that the problem of existence of the minimal metallic conductivity is not clear even for $d=2$.

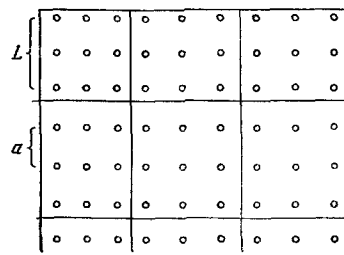


FIG. 3. Thouless and Licciardello construction. Each cell with the side L is regarded as a site in a new lattice.

by considering cells containing N^2, N^3 , etc. of the original lattice sites, i.e., by increasing the sides of each new cell by the factor L . If the states of energy E are localized, then each transformation to a new scale causes V_N to decrease as $\exp(-L)$, whereas W_N decreases as $L^{-d} \propto N^{-1}$, so that V_N/W_N decreases as $\propto N \exp(-N^{1/d})$. Since for some value V/W there is a mobility threshold for any E in the original band,^{30,31} there must be a maximum ratio $(V_N/W_N)_c$ for which exponential decrease of this kind still occurs. We can show^{33,54} that in the case of delocalized states, we have

$$V_N \approx \hbar D(E) L^{-2}, \quad (20)$$

where $D(E)$ is the diffusion coefficient of an electron of energy E . This relationship can be interpreted as follows. A delocalized electron in a system of cells of length L may diffuse in a time τ_N from one cell to another. The coefficient of such diffusion is $D \propto L^2/\tau_N$. Clearly, the indeterminacy of the electron energy is $V_N \propto \hbar/\tau_N$, which leads to Eq. (20). Then, $V_N/W_N \approx \hbar D(E)L^{d-2}$ and, application of the Einstein relationship between the diffusion coefficient and the conductivity

$$\sigma(E) = 2e^2 D(E) N(E), \quad (21)$$

gives

$$\sigma_{\min} = \frac{2e^2}{h} L^{d-2} \left(\frac{V_N}{W_N} \right)_c. \quad (22)$$

This formula demonstrates the universality of the minimal metallic conductivity for $d=2$ if $(V_N/W_N)_c$ is in this case a constant under scale transformations. Numerical analysis of this model^{53,54} shows that for $d=2$ we have $(V_N/W_N)_c = 0.12 \pm 0.003$, so that $\sigma_{\min} \approx 3 \times 10^5 \Omega^{-1} \cdot \text{cm}^{-1}$, irrespective of the nature of the original lattice, confirming universality of the localization effect, similar to the universality of critical phenomena. An analogous result is not obtained for $d=3$. In this case the minimal metallic conductivity depends on the scaling length. The Mott formula (19) follows from Eq. (22) if $(V_N/W_N) \propto N^{1/3}$, but detailed numerical calculations confirming this behavior have not yet been carried out.

It nevertheless seems natural to assume that in the region of delocalized states we have $V_N \propto L^{-2} \propto N^{-2d}$ and $W_N \propto N^{-1}$ (Ref. 33). This scaling approach is clearly not rigorous and requires special justification.⁷⁾

Wegner⁵⁵ attempted to construct an analytical renormalization group scheme realizing the Thouless and Licciardello procedure. The framework of two alternative hypotheses on the behavior of the renormalization group transformations made it possible to obtain scaling behavior of the physical quantities near the mobility threshold. However, it should be stressed that explicit justification of these hypotheses (calculation of indices, etc.) may—as mentioned above—meet with difficulties associated with the inapplicability of perturbation theory. Therefore, the question of scaling at the mobility threshold remains open.

In a recent paper⁵⁶ Mott gave qualitative reasons in support of the dependence of the existence of a minimal metallic conductivity on the critical index ν of the localization radius [see Eq. (13)], because it is not possible to ensure that the phases of wave functions at neighboring sites [see Eq. (15)] are random for sufficiently small values of ν . According to these estimates, there is a minimal metallic conductivity if $\nu \geq 2/d$, where d is the dimensionality of space. The index $\nu \approx 0.6$ obtained for $d=3$ ($d=4-\epsilon$) in Refs. 29 and 36 does not satisfy this condition, whereas $\nu=2/3$ obtained in Ref. 51 does satisfy it. For $d=2$ a numerical analysis⁵⁷ of a model considered in Refs. 53 and 54 is shown to give $\nu \approx 1$, which satisfies the condition of existence of a minimal conductivity. These results stress the need for a correct analysis of the critical behavior near the mobility threshold. For $d=3$ the difference between the values 0.6 and $2/3$ may be important but the existing theory (and experimental results!) are not sufficiently sensitive to be affected by this difference.

Assuming that the localization effect is universal, we can apply the results obtained in the Anderson model in constructing a qualitative picture of electronic phenomena in disordered systems, particularly in liquids.^{3,4} It is assumed that, as in the Anderson model, regions of localized states appear near the band edges (Fig. 2) and that mobility thresholds E_v and E_c (Fig. 1c) occur if the pseudogap in the density of states of a liquid is sufficiently deep, which corresponds to a transition from a quasimetallic to a semiconducting liquid. It should be stressed that there is as yet no self-consistent theory of the transport phenomena in quasimetallic liquids. Typical conductivities of these liquids are such that the mean free path of electrons is clearly less than the interatomic distance. Then, electrons exhibit an analog of diffuse (Brownian) motion.^{58,59} Mott suggested for this case the following heuristic generalization of the usual formula for the conductivity of a liquid metal:^{3,4}

$$\sigma = \frac{e^2 S_F l}{12\pi^3 \hbar} g^2, \quad (23)$$

where $g = N(E_F)/N_0(E_F)$, $S_F = 4\pi p_F^2/\hbar^2$ is the area of the

Fermi surface in the reciprocal space, l is a characteristic length resembling the mean free path or, more likely, the phase coherence length.⁵⁹ The arguments put forward by Mott³ in support of Eq. (23) are very qualitative and are based on generalization of the Ziman formula in the theory of liquid metals by introduction of the dependence $\propto N^2(E_F)$, typical of the Kubo–Greenwood formula (14). It is assumed that this dependence appears in a situation when $p_F l/\hbar \sim 1$ because of strong scattering. On the other hand, it is known²¹ that in the case of weak scattering (liquid metals, $p_F l/\hbar \gg 1$) this dependence disappears completely. The result $\sigma \propto g^2$ was obtained by Friedman⁶⁰ in the random phase model when the phase coherent length is less than the interatomic distance. The Hall coefficient is then given by

$$R \approx \frac{C}{g} R_0, \quad (24)$$

where R_0 is the Hall coefficient in the free-electron approximation and $C \approx 0.7$. If $l \sim a$ (a is the interatomic distance) in Eq. (23), then for one electron per atom, we obtain

$$\sigma \approx \frac{e^2}{3a\hbar} g^2. \quad (25)$$

For $a=3 \text{ \AA}$ and $g=1$, we have $\sigma \approx 1500 \Omega^{-1} \cdot \text{cm}^{-1}$. In the case of a divalent metal, multiplication of this value by $2^{2/3}$ gives $2500 \Omega^{-1} \cdot \text{cm}^{-1}$. We have seen above [Eq. (19)] that the transition from the scheme in Fig. 1b to the one in Fig. 1c occurs at the localization threshold for $\sigma_{\min} \approx 0.06e^2/\hbar a$.⁶¹ Therefore, a reasonable estimate of the depth of the pseudo gap at which localization begins and a liquid metal changes to a liquid semiconductor is $g^2 \approx 0.2$, i.e., $g_c \approx 0.45$. It should be stressed that this estimate varies depending on the estimated minimal metallic conductivity within the limits^{3,4}

$$g_c \approx 0.2-0.5. \quad (26)$$

It should be noted that these ideas on the diffusive nature of the conduction process hold for microscopically homogeneous systems when the phases of the electron wave functions are uncorrelated over distances shorter than the interatomic spacing. However, real systems may contain microscopic inhomogeneities⁶¹⁻⁶⁶ caused, for example, by fluctuations of the density near the critical point, formation of regions with specific short-range order,⁶⁷ etc. Then, bearing in mind the ideas on the dominant role of the short-range order in the formation of the electron energy spectrum, we can imagine the appearance of regions having semiconducting and metallic spectra with the size of, for example, semiconducting regions governed by the corresponding short-range correlation radius $R_c > a$.

If the coherence length of the wave function phase is $l \ll R_c$, the electron structure of such regions can be discussed quasiclassically and it is governed by the local atomic structure. Similarly, the electron response to an external perturbation is now local. In the first approximation we can assume that the semiconducting regions are forbidden for the conduction electrons and

⁶¹ It would be more correct to assume^{3,4} that the estimate of σ_{\min} includes here not the interatomic distance a but a_{E_F} , which is the distance between states with a given $\sim E_F$ and which can be greater than a .

we can introduce $C(E)$ representing the fraction of the volume of the system consisting of the regions which are allowed for electrons of energy E . We can then define $C(E)$ by⁶⁵

$$N(E) = N_0(E) C(E), \quad (27)$$

where $N(E)$ is the average density of states per unit volume of the system and $N_0(E)$ is the density of states per unit volume in a metallic region, which is usually identical with the density of states in the free-electron model. We shall now consider an electron at the Fermi level E_F . Clearly, $C(E_F) = g$ is the Mott factor. The Fermi level usually lies in the range of energies corresponding to the semiconductor gap (pseudogap) and an electron with $E \sim E_F$ experiences Bragg reflection at the boundary between metallic and semiconducting regions, its wave function decreasing rapidly within the latter region. If we ignore the tunneling across the forbidden regions, we find that the kinetics of this inhomogeneous case can be described by applying the percolation theory.^{65,68-71} Then, if $C(E) < C^*$, where C^* is the critical value in the percolation theory, the system does not have a continuous path for an electron of energy E , which would pass through the metallic regions, and electrons of energy E are locked in metallic islands which are separated in space. When $C(E) = C^*$, the first path passing continuously through the whole sample appears in the system. Correspondingly, if $g < C^*$ the system is in the semiconducting state and conductivity exists only to the extent of tunneling across the forbidden regions (the conductivity vanishes in the classical percolation theory), for $g = C^*$ an infinite metallic cluster appears in the system, and for $g > C^*$ this cluster grows occupying increasingly greater portion of the system (the whole volume is occupied in the limit $g \rightarrow 1$). Thus, if $g > C^*$, we observe a continuous (percolation) semiconductor-metal (SM) transition. The critical value C^* for this type of percolation in a continuous medium lies, depending on the estimate, within the range $0.15 < C < 0.3$ (Refs. 72 and 73). The most reliable value is $C \approx 0.17$ for a Gaussian random potential.⁷³ Therefore, the criterion for the pseudogap depth obtained from the percolation theory and corresponding to the SM transition does not differ very greatly from the Mott criterion (26), but is not identical with the latter. Cohen and Jortner⁶⁵ proposed a description of the transport properties of an inhomogeneous system of this kind on the basis of the theory of an effective medium generalizing the treatment of Kirkpatrick⁷⁰ for lattices (networks) of random resistances. They provided a quantitative description of the SM transition for a large number of disordered systems in which one would expect microscopic inhomogeneities. The behavior of the electrical conductivity in the effective medium theory is shown by the curves in Fig. 4 taken from Ref. 65. It should be pointed out that the behavior of the transport characteristics of an inhomogeneous

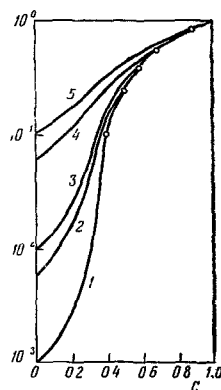


FIG. 4. Electrical conductivity of a microscopically inhomogeneous system in the effective medium theory.⁶⁵ Here, C is the fraction of the volume occupied by the allowed regions; $X = \sigma_1/\sigma_0$, where σ_0 is the conductivity of the allowed regions and σ_1 is the conductivity of the forbidden regions. 1) $X = 10^{-3}$; 2) $X = 6 \times 10^{-3}$; 3) $X = 10^{-2}$; 4) $X = 6 \times 10^{-2}$; 5) $X = 10^{-1}$.

system might not be described by the simple scheme of the effective medium theory, particularly near the percolation transition itself where a special treatment is needed.^{70,71,74} In a series of papers,^{4,75} Mott criticized the ideas of Cohen and Jortner on inhomogeneous transport. However, his criticism is effectively based on a discussion of the Anderson model which does not allow for the appearance of strong inhomogeneities of metallic and insulating types because of the absence of correlation between energies at neighboring sites assumed in this model.⁹⁾ In fact, real systems may exhibit correlation producing a behavior of the type described above. It should be pointed out that this concept of forbidden and allowed regions may be too approximate. For example, the model of the spectrum of liquid semiconductors is considered in Ref. 26 and the theory automatically predicts an ensemble of metallic and semiconducting regions with a certain distribution of gaps in the spectrum. A description of the kinetics in terms of the percolation theory and the effective medium theory should be regarded only as the first approximation to the true situation in such a complex ensemble. The percolation SM transition is a manifestation of a specific second-order phase transition associated with the percolation phenomenon itself.^{71,76} A full description of the critical percolation region in terms of the scaling pattern of this phase transition has been obtained recently.^{77,78} The question arises of the relationship between the percolation and Anderson transitions. The percolation mechanism ignores the quantum-mechanical tunneling effects.^{65,68}

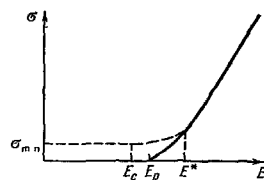


FIG. 5. Relationship between the percolation and quantum conductivities. Here, E_p is the percolation threshold, E_c is the mobility (localization) threshold, and E^* is the energy of the transition from the percolation to the tunneling mechanism.

⁹⁾ Moreover, Mott criticizes mainly the idea of the existence of insulating regions in the classical theory of percolation. The effective medium theory deals with regions characterized by different but finite conductivities.

Classical motion of an electron in a random field is possible in the energy range $E > E_p$, where E_p is governed by the condition $C(E_p) = C^*$. Quantum-mechanical tunneling is possible in the energy range $E_0 < E < E_p$, where E_0 is the mobility threshold in the random field under consideration. The corresponding qualitative behavior of the conductivity as a function of the electron energy is of the kind shown in Fig. 5 (Ref. 4). At the energy $E^* = E_p + \Delta E^*$ a transition takes place from the percolation (quasiclassical) conduction mechanism to the quantum process. If ΔE^* is sufficiently small, the percolation theory can give a satisfactory description. The first attempts to estimate ΔE^* were made by Toulouse and Friedel (Refs. 79 and 80).¹⁰⁾

We shall conclude this discussion by describing a transition from a liquid semiconductor to a metal in the way it can occur in a real system as temperature is increased from the melting point T_{mp} by identifying the conduction regimes which occur in the course of this transition.

1. Temperature range $T \geq T_{mp}$. A typical liquid semiconductor has an energy spectrum of the type shown in Fig. 1c. Its Mott factor is $g < 0.15-0.2$. The conductivity is described by a formula of the type^{3,4}

$$\sigma = \sigma_0 \exp \left(-\frac{E_0 - E_F}{kT} \right) = \sigma_0 \exp \left(-\frac{E_0 - E_v}{2kT} \right) \quad (28)$$

if the Fermi level is in the middle of the pseudogap, and it is found that $\sigma_0 \sim \sigma_{min} \sim 10^2 \Omega^{-1} \cdot \text{cm}^{-1}$. The thermoelectric power may also exhibit typical semiconductor behavior⁴

$$|\alpha| = \frac{k}{e} \left(\frac{E_0 - E_v}{2kT} + A \right), \quad (29)$$

where $A = \text{const}$. The behavior of the Hall effect usually differs considerably from that expected for semiconductors.⁸²

2. $T > T_{mp}$. As temperature rises, it is most likely that the short-range order governing the energy spectrum of a liquid semiconductor is destroyed. The pseudogap fills gradually^{4,65,26} and the spectrum changes to the type shown in Fig. 1c and the Mott factor becomes $0.2 < g < 1$. Then, as the factor g increases, electrons become delocalized in the pseudogap, we find that $E_0 - E_v \rightarrow 0$ in the limit $g \rightarrow g_c$ [Eq. (26)] and a transition from a liquid semiconductor to a quasimetallic state takes place.^{3,4} Up to the point of this transition electron transport is governed by formulas of semiconducting type with a temperature-dependent gap $E_0 - E_v$. The transition point may be governed by the Mott-Anderson or by the percolation mechanism in the case of systems with pronounced structure fluctuations (spatial inhomogeneities).^{4,65} If $g > g_c$, the quasi-

metallic state is characterized either by the homogeneous (diffusion) conduction mechanism [Eqs. (23) and (24)].^{4,60}

$$\sigma \propto g^2 \propto R^{-2}, \quad R \propto g^{-1}, \quad (30)$$

and the thermoelectric power obeys the formula for metals^{4,82,83}

$$\alpha = \frac{\pi^2}{3} \frac{k^2 T}{e} \frac{d \ln \sigma(E)}{dE} \Big|_{E=E_F}, \quad (31)$$

or by the percolation regime for an inhomogeneous system described by the formulas of the effective medium theory^{65,70} and by the results of Levinstein *et al.*⁷⁴ near the percolation threshold. In the quasimetallic range we typically have $(2-3) \times 10^2 \Omega^{-1} \cdot \text{cm}^{-1} < \sigma < 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$. The selection between these two alternative (homogeneous and percolation) descriptions of the quasimetallic region of a melt can only be made experimentally.

3. Further increase in the temperature may transform the conductivity and other transport properties to the metallic regime with $\sigma \geq 3 \times 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$. The conductivity should then be described by the Ziman theory and the Hall effect by the model of free electrons.^{7,83} The energy spectrum is then of the type shown in Fig. 1a.

4. A further increase in temperature and/or reduction in the density of the system enhances the importance of random scattering of electrons which now has the one-band spectrum of the type shown in Fig. 2. Consequently, the Anderson transition occurs when the disorder in the system becomes sufficiently strong.^{4,6,27-30} The conductivity decreases to a value of the order of σ_{min} and then the conduction process changes (after localization of all the states in the band) to the hopping mechanism: $\sigma \ll \sigma_{min}$, $\ln \sigma \propto -T^{-x}$, where $x = 1/4 - 1$ (Refs. 4, 84, and 85).

Naturally, the proposed semiconductor-metal-semiconductor transition scheme for liquids is fairly approximate, in accordance with the qualitative nature of the current theory. In particular, a real system may not exhibit some of the conduction regimes described above (for example, pure metallic conduction), when an increase in importance of the random scattering causes the system to reach the maximum values of the conductivity characteristic of the diffusion regime and this is followed directly by the Anderson transition.

The most serious shortcoming of our analysis is the total neglect of possible effects of the electron-electron interaction. The dominant role of this interaction in many metal-insulator transitions in crystalline solids is well known.⁴ We have not considered these effects because of the almost total lack of investigations of the role of the electron-electron interaction in disordered systems. In particular, the problem of the influence of this interaction on the Anderson localization has not been studied at all and this is also true of the influence of disorder on the mechanisms of the metal-insulator transition induced by this interaction in crystalline solids. These problems are expected to be tackled

¹⁰⁾It should be noted that the percolation transition and localization depend in different ways on the number of spatial dimensions. The critical number of dimensions which can be used to describe a transition (i.e., the number of critical indices) considered in the self-consistent field approximations is $d_c = 4$ for the localization,³⁶ whereas it is $d_c = 6$ for the percolation theory.⁸¹

soon by theoreticians.¹¹⁾

The following sections of this review will describe the results of experimental investigations of the SM transition in liquid semiconductors and metals near the critical point and will show how they compare with the theoretical ideas. We shall attempt to demonstrate to what extent these results agree or disagree with the proposed qualitative description of the transition governed by the role of disorder as given above. Naturally, any real material differs considerably from the corresponding theoretical idealizations but in discussing the experimental results we shall be forced to turn to ideas and theoretical results which have not been mentioned above. One should bear in mind that the qualitative nature of our ideas means that attempts to interpret the experimental results are also essentially qualitative, which frequently makes it difficult to select the appropriate theoretical model.

3. SEMICONDUCTOR-METAL TRANSITION IN MOLTEN SEMICONDUCTORS AT HIGH TEMPERATURES

Experimental investigations of the electrical conductivity and some other properties of liquid semiconductors confirm, on the whole, the description of the transition to the metallic conduction on increase in temperature given in the preceding section. In the very first work of A. F. Ioffe and A. R. Regel¹ on liquid semiconductors it was shown that those materials which retain the short-range structure after melting retain also semiconducting properties in the liquid phase; the electrical conductivity of such melts increases exponentially with increase in temperature. It is clear from general considerations that the process of rise of the electrical conductivity cannot continue without any restrictions. In fact, subsequent investigations⁸⁶⁻⁹⁰ carried out at higher temperatures have shown that the conductivity of molten semiconductors tends to saturation at a level typical of metals. However, systematic and reliable investigations at high temperatures have become possible only when the experimental methods have been developed sufficiently and techniques have become available for carrying out measurements at high neutral gas pressures in order to suppress boiling of the melts.² This technique has been used to investigate a wide range of melts of chalcogenide semiconductors and also of elemental materials (tellurium and selenium)⁸⁹⁻⁹⁷ at temperatures from T_{mp} to 2000°C.¹²⁾ Alloys belonging to the Se-Te system have been studied by the same technique also in Ref. 98.¹³⁾

The results obtained are summarized partly in Figs. 6-10. An analysis of these results (see also Refs. 99-101) shows that at $T > T_{mp}$ the conductivity increases to a level where $\sigma(T)$ reaches a plateau. The conductivity

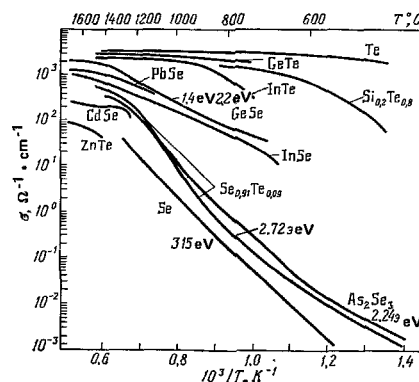


FIG. 6. Temperature dependences of the electrical conductivity of semiconductor melts.⁸⁹

at the plateau is $(1-3) \times 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$. This typical metallic conductivity and the absence of a significant temperature dependence shows that the melts have now become metallized. This demonstrates that the SM transition has occurred. We can easily see that, in the first approximation, the experimental results are in agreement with the theoretical expectations (see preceding section). In fact, in the case of those semiconductors whose short-range order does not change drastically as a result of melting (selenium, selenium alloys, selenides, etc.) and which remain semiconducting in the liquid phase, we can identify (in accordance with Sec. 2) three regions in the functional form of $\log \sigma(1/T)$: the first corresponds to essentially semiconducting behavior with the electrical conductivity obeying an exponential law; the second (intermediate) region is characterized by a variable activation energy of conduction which eventually decreases strongly; the third region, described above, is typical of metallic conduction. We shall now analyze the experimental data in greater detail. We shall begin by considering the third region of the curves of $\sigma(T)$, i.e., the metallic state on the plateau.

The most characteristic feature of the electrical conductivity of molten semiconductors in the plateau region is that the absolute value of σ_{sat} of all the investigated tellurides and partly of selenides is within the range 2500-3000 $\Omega^{-1} \cdot \text{cm}^{-1}$ (see Table I taken from Ref. 89). This conductivity corresponds to the theoretical estimates made using the model of almost-free electrons on the assumption that only two valence electrons per atom take part in the conduction process:

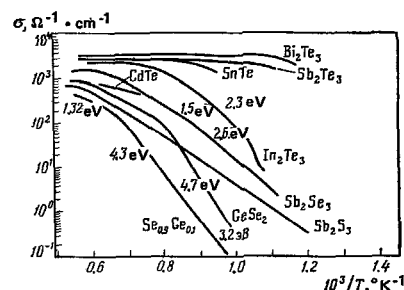


FIG. 7. Same as in Fig. 6 but taken from Ref. 90.

¹¹⁾For lack of space we shall not discuss the first investigations on this subject, which have appeared very recently.²²²⁻²²⁶

¹²⁾Liquid tellurium has been investigated close to the melting point T_{mp} at high pressures.²²⁷

¹³⁾In a recent investigation²²⁸ the Se-Te and other systems were studied at even high pressures.

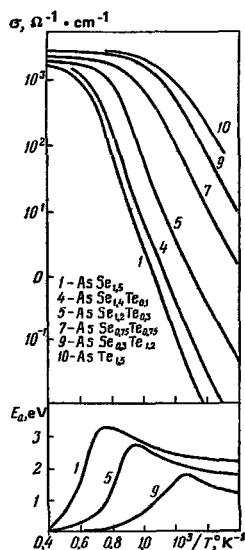


FIG. 8. Temperature dependences of the electrical conductivity and activation energy of electrical conduction of melts of glassy semiconductors.⁹⁷

$\sigma = e^2/3\hbar a \approx 2700 \Omega^{-1} \cdot \text{cm}^{-1}$ when the average interatomic distance is $a = 3 \times 10^{-8} \text{ cm}$.¹⁴⁾ This agreement cannot be accidental and it suggests that the upper valence subbands are destroyed by fluctuations of the potential. The electrons in these subbands form a Fermi sphere whose radius p_F is limited by the value of π/a . The Hall coefficient calculated for $p_F = \pi/a$ is approximately three times greater than the estimate obtained from the structure of the valence shells of atoms on the assumption that all the valence electrons participate in the conduction process. These ideas on the Hall coefficient are supported directly by the experimental results (see Table II for the telluride group). Thus, the available experimental data allows us to conclude that the chemical binding remains quite strong in the melts even at very high temperatures. In spite of the metallic nature of conduction, the telluride melts clearly cannot be regarded as systems of atoms with totally ionized valence shells and the free-electron model in the form applied to liquid metals does not hold for molten semiconductors even in the region of saturation of the temperature dependence of the electrical conductivity. At lower temperatures characterized by a positive temperature coefficient of the conductivity the rise in the conductivity is associated with the formation of a Fermi sphere, i.e., with an increase in the density of states at the Fermi level to values corresponding to the limiting wave vector approximately equal to π/a , i.e., $N(E_F) \leq 1 \times 10^{22} \text{ electrons} \cdot \text{V}^{-1} \cdot \text{cm}^{-3}$. The temperature dependences of the magnetic susceptibility and estimates of the paramagnetic contribution made by free carriers show (Fig. 11) that the increase in the electrical conductivity is correlated with the increase in the paramagnetic component of the magnetic susceptibility obey-

¹⁴⁾The formula is based on the assumption of diffusion of electrons, i.e., that the mean free path does not exceed the interatomic distance.

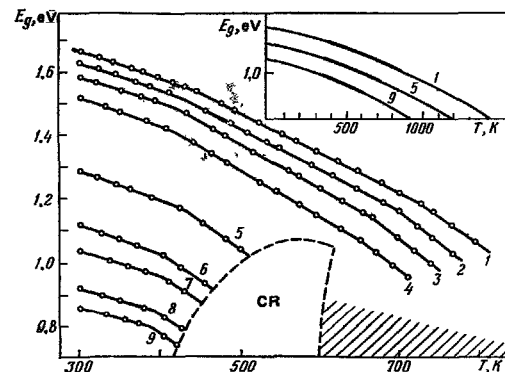


FIG. 9. Temperature dependence of the energy gap of liquid semiconductors in the As-Se-Te system over a wide range of temperatures. The thin curves in the inset are plotted using the dependence $\log \sigma = f(1/T)$. The thick curves and those with points are the results of direct optical measurements of the shift of the fundamental absorption edge with temperature (Ref. 97): 1) $\text{AsSe}_{1.5}$; 2) $\text{AsSe}_{1.45}\text{Te}_{0.05}$; 3) $\text{AsSe}_{1.45}\text{Te}_{0.05}$; 4) $\text{AsSe}_{1.4}\text{Te}_{0.1}$; 5) $\text{AsSe}_{1.2}\text{Te}_{0.3}$; 6) $\text{AsSe}_{0.9}\text{Te}_{0.6}$; 7) $\text{AsSe}_{0.75}\text{Te}_{0.75}$; 8) $\text{AsSe}_{0.45}\text{Te}_{1.05}$; 9) $\text{AsSe}_{0.3}\text{Te}_{1.2}$. The shaded region is opaque; CR is the crystallization region.

ing the relationship $\sqrt{\sigma} \propto \chi_{\text{para}}$. Since $\chi_{\text{para}} \propto N(E_F)$, it follows that $\sigma \propto N^2(E_F)$. This last result is in full agreement with the relationship $\sigma \propto g^2$ discussed in Sec. 2.

In the case of selenides whose conductivity in the saturation region is less than that of tellurides (Table I) we can simply put forward the hypothesis that the valence shell of the chalcogen is even more stable and only a small proportion to electrons in the outer valence shell of the metal participates in the conduction process. These qualitative ideas suggest that the saturation conductivity should be between 1500 and $1000 \Omega^{-1} \cdot \text{cm}^{-1}$, which is in agreement with the experimental values for many selenides.

We shall now consider the behavior of the curves of $\sigma(T)$ from T_{mp} to the temperature of the SM transition

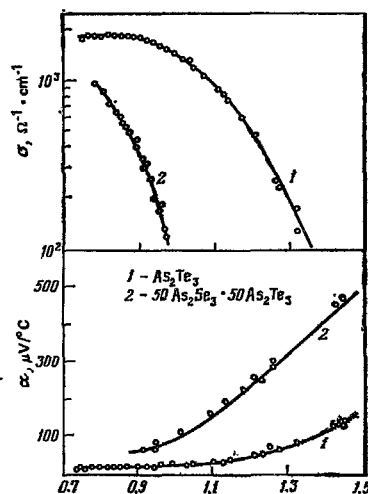


FIG. 10. Electrical conductivity and thermoelectric power of liquid As_2Te_3 (curves denoted by 1) and $\text{As}_2\text{Te}_3 \cdot \text{As}_2\text{Se}_3$ (curves 2) plotted as a function of $10^3/T$ ($^\circ\text{K}^{-1}$) on the basis of Ref. 107.

TABLE I.

Substance	Temperature range, °K	σ_{sat} , $\Omega^{-1} \cdot \text{cm}^{-1}$	Substance	Temperature range, °K	σ_{sat} , $\Omega^{-1} \cdot \text{cm}^{-1}$
Te	1000–1700	3300	Sb ₂ Te ₃	1360–1700	2800
PbTe	1500–1850	2700	GeSe	1780–2000	2000
SnTe	1430–1740	2800	InSe	1850–2000	1000
CeTe	1430–1780	3000	Sb ₂ Se ₃	1800–2000	1450
In ₂ Te ³	1540–1750	2500	Sb ₂ S ₃	1880–2000	800
InTe	1450–1750	2500	PbSe	1830–2000	1300
Bi ₂ Te ₃	950–1780	3300			

in the melts with the highest resistivity, such as selenium, alloys of selenium with tellurium, arsenic selenide, and similar melts. A characteristic feature in the graph of $\ln \sigma = f(1/T)$ observed in this range is a smooth increase in the activation energy of conduction on approach to the SM transition temperature (Fig. 8). Since the activation energy at a given temperature represents extrapolation of the temperature dependence $E_g(T)$ of the pseudogap E_g to absolute zero, we can plot this temperature dependence $E_g(T)$ (Ref. 100). We plotted the temperature dependences of the pseudogap of selenium,^{89,99} arsenic selenide,⁹² and $\text{Ge}_{0.1}\text{Se}_{0.9}$ (Ref. 94) using reference data on the optical width of the gap at low temperatures. The results obtained for melts

TABLE II. Electrical properties of semiconductor melts.

Semiconductor melt	σ , $\Omega^{-1} \cdot \text{cm}^{-1}$, (1)	Sign of $d\sigma/dT$	R , cm^2/C	R/R_0	α , $\mu\text{V}/\text{deg}$	L/L_0 3)	References
Metallic melts of semiconductors							
Ge	15 200	—	$-3.6 \cdot 10^{-5}$	1.06	-1.0	0.86	1, 87, 124
Si	12 880	—	—	—	—	0.8	87
InSb	9 350	—	$-6.9 \cdot 10^{-5}$	1.4	—	0.94	1, 87, 124
InAs	7 000	—	—	—	—	—	—
Metal-like melts 3)							
CdSb	5 200	+	$-8.3 \cdot 10^{-5}$	1.5	0	0.95	111
ZnSb	4 200	+	$-5.3 \cdot 10^{-5}$	1.2	+2.6	—	111
As ₂ Te ₃	3 460	+	$-8.3 \cdot 10^{-5}$	2.1	—	—	112
Bi ₂ Te ₃	2 800	+	$-8.7 \cdot 10^{-5}$	2.2	+1.0	0.84	1, 87
GeTe	2 600	+	$-15 \cdot 10^{-5}$	3.6	+20	0.82	97, 113
CuTe	1 900	+	$-16 \cdot 10^{-5}$	4.0	—	—	113
Sb ₂ Te ₃	1 850	+	$-17 \cdot 10^{-5}$	3.9	+10	1.03	97, 111, 125
SnTe	1 870	+	$-12 \cdot 10^{-5}$	2.3	+42	0.86	97, 113, 126
PbTe	1 510	+	$-14 \cdot 10^{-5}$	—	-3.7	1.1	97, 113
Te	1 700	+	$-12 \cdot 10^{-5}$	3.0	+26	0.97	112, 124, 127
Te _{0.9} Se _{0.1}	1 250	+	$-17 \cdot 10^{-5}$	—	+50	—	86, 128
AgTe	600	+	$-3.2 \cdot 10^{-4}$	—	—	—	117
Tl ₂ Te ₃	500	+	$-7.4 \cdot 10^{-4}$	15	—	1.0	120
InTe	500	+	$-5.0 \cdot 10^{-4}$	—	—	—	126
In ₂ Te ₃	250	+	$-(5-7) \cdot 10^{-4}$	—	+10	1.2	126, 131, 132, 135
TlTe	290	+	$-13.8 \cdot 10^{-4}$	25	—	1.6	130
GaTe	250	+	$-3.2 \cdot 10^{-3}$	—	—	—	117
Ag ₂ S	120	+	$-2.8 \cdot 10^{-3}$	—	+190	—	117
Liquid semiconductors 4)							
Tl ₂ Te	67	+	$-1.6 \cdot 10^{-3}$ 5)	-150	2.8	—	112, 133
GeSe	51	+	$-3.6 \cdot 10^{-2}$ 5)	+50	—	—	139, 137
As ₂ Te ₃	25	+	$-5 \cdot 10^{-2}$	+200	—	—	88, 128
CuSbSe ₃	16	+	$-7.3 \cdot 10^{-3}$	+180	7.7	—	139
Tl ₂ Se	10	+	$-2.5 \cdot 10^{-2}$ 5)	+240	17	—	120, 121, 136
Tl ₂ Se + 0.8 at% In	40	+	$-2.5 \cdot 10^{-3}$	—	—	—	122
Te _{0.9} Se _{0.1}	27	+	$-2.6 \cdot 10^{-3}$	—	290	—	86, 99, 128
Te _{0.9} Se _{0.1} 5)	1.0	+	$-3.0 \cdot 10^{-2}$	+630	—	—	86, 99, 128
InSe	3.0	+	$-1.0 \cdot 10^{-4}$	-220	45	—	138
Sb ₂ Se ₃	2.4	+	$-1.5 \cdot 10^{-3}$ 5)	+3	3.6	—	130, 139
Sb ₂ Se ₃ + 2.5 at% Sb	3.1	+	$-2.1 \cdot 10^{-2}$	-20	—	—	120, 139
Sb ₂ Se ₃ + 5 at% Te	3.0	+	$-2.2 \cdot 10^{-2}$	+36	—	—	130, 139
Sb ₂ Se ₃ 5)	1.10 ⁻¹	+	$-3.5 \cdot 10^{-1}$ 5)	-100	—	—	114
60As ₂ Te ₃ ·40As ₂ Se ₃	7.10 ⁻¹	+	-1.0	—	—	—	128, 140
V ₂ O ₅	7.10 ⁻¹	+	$-3.0 \cdot 10^{-1}$	—	—	—	134
As ₂ Te ₃	1.10 ⁻³	+	-10^{-2}	—	—	—	140

Notes. 1) For explanations of symbols see text. 2) All the results are given for temperatures 20–50°C above the melting point. 3) Data on the Lorenz number are given in accordance with Ref. 115. 4) The selected boundaries dividing these melts into groups should be regarded as nominal. 5) Considerable changes in properties occur on deviation from the stoichiometric composition or on addition of a third element as an impurity.

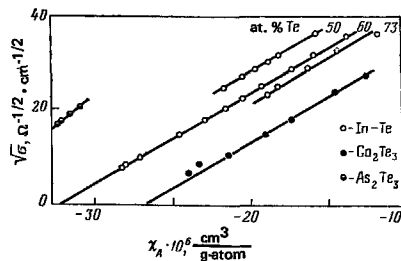


FIG. 11. Correlation between the behavior of the electrical conductivity and the paramagnetic susceptibility of In-Te and $\text{Ga}_2\text{-Te}_3$ alloys and of As_2Te_3 (Ref. 108).

of the As-Se-Te system are represented by thin lines in Fig. 9. The thick lines, as well as the curves with points in Fig. 9, are the results of direct optical measurements of the shift of the fundamental absorption edge with temperature.^{97,102} Similar optical measurements carried out on liquid selenium and on glassy and liquid As_2Se_3 are reported in Refs. 99, 88, and 103–106. We can easily see from Fig. 9 that the pseudogap degrades at high temperatures and this process occurs at an increasing rate. It is important to note also that the gap disappears at those temperatures at which the conductivity reaches values close to σ_{min} . Some support for the proposed explanation of the disappearance of the pseudogap is provided also by the thermoelectric power data.¹⁰² Figure 10 (based on Ref. 107) gives the temperature dependences of the thermoelectric power and electrical conductivity for molten chalcogenides As_2Te_3 and $\text{As}_2\text{Te}_3 \cdot \text{As}_2\text{Se}_3$. We can easily see that the thermoelectric power has values typical of semiconductors at temperatures $T \geq T_{\text{mp}}$ and that it decreases on increase in temperature. It is important to note that the thermo-emf falls to a value of the order of $k/e \approx 80 \mu\text{V}$ at temperatures corresponding to $\sigma = \sigma_{\text{min}}$. According to Ref. 3, the thermoelectric power of amorphous or liquid semiconductors can be described by

$$\alpha = \frac{k}{e} \left(\frac{E_V - E_F}{kT} + A \right),$$

where E_V is the valence band edge (in the case under consideration the dominant carriers are holes) and A is a constant. It is assumed in Ref. 3 that in the case of amorphous materials we have $A = 1$ for carriers moving in the allowed-energy band. Thus, $\alpha \approx k/e$ applies in the case when the energy gap vanishes. It should be noted that the correlation between the thermoelectric power and electrical conductivity data is far from being as reliable or as self-evident for other materials.

The proposed explanation of the phenomena occurring in the region of the SM transition is far from unambiguous, as already pointed out in Sec. 2. It is very likely that in some materials, whose structure admits with equal probability the formation of clusters with different local structures, the SM transition is described by the formulas of the effective medium theory. An attempt to give a quantitative interpretation of the SM transition on this basis is made in Ref. 103 for melts in the In-Te system. Satisfactory agreement is

obtained there with the experimental results but the critical values of the parameter representing the ratio of the metallic and semiconducting phases calculated on the basis of these data is higher than the theoretically permissible limit. Thus, the treatment of the SM transition on the basis of a heterogeneous model of the melt using the effective medium theory also fails to give rigorous quantitative conclusions. The problem of competition between two possible SM transition schemes based on the homogeneous and heterogeneous models of a liquid semiconductor is discussed in detail in Sec. 2. We have shown that both models predict quite similar characteristic parameters of the transition. For this reason an analysis of the electrical conductivity data, usually carried out making a number of assumptions, does not make it possible to draw definite conclusions. Convincing proof in support of the heterogeneous model and percolation nature of the transition can be obtained only as a result of careful structural investigations of melts in the intermediate region, but direct studies confirming the coexistence of two structural phases with higher and lower electrical conductivity have not yet been made.

It seems most reasonable to assume that both (homogeneous as proposed by Mott and percolation) mechanisms may coexist or predominate in different materials, depending on the characteristic structural and crystallochemical properties of a material. The percolation mechanism of conduction in the region of the metal-nonmetal transition will be discussed again in Sec. 5.

The experimental data discussed in the present section are summarized in a diagram (Fig. 12) whose theoretical description is given at the end of Sec. 2. The metal-insulator transition shown in the transcritical region will be discussed in detail in Sec. 5.

4. SEMICONDUCTOR-METAL TRANSITION AND CRITERION FOR MINIMAL METALLIC CONDUCTIVITY OF MELTS AT $T \geq T_{mp}$

In the preceding section we have discussed the features of the transition to metallic conduction in a liquid semiconductor on increase in temperature. Equally interesting is the transformation of the properties of molten semiconductors not on the temperature scale but on the scale of substances considered slightly above the melting point and arranged in accordance with increasing electrical conductivity. Melts of electronic semiconductors are unique objects in the sense that they include both metallic and essentially semiconducting compositions, as well as materials with intermediate properties. This makes it possible to analyze the conditions and criteria for the transition from the semiconducting to metallic conduction process. An important feature of this analysis is the fact that the degree of stability of the short-range order structure at $T \geq T_{mp}$ is relatively high; consequently, the level of fluctuations of the atomic potential is still low and we

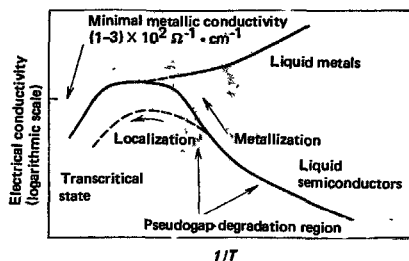


FIG. 12. Generalized temperature dependence of the electrical conductivity of molten semiconductors showing the main tendencies in changes in the properties over a wide temperature range. The dashed curve represents the probable Anderson transition.

can assume approximately that this level is the same for a large group of melts. It follows that the variable parameter, which governs the process of localization of electron states at the Fermi level in the liquid metal-liquid semiconductor series if the interaction potential in Eq. (12), which governs the Anderson localization of electron states at the Fermi level.

The published experimental data for electronic melts are summarized in Table II, which gives a full list of the materials on which the Hall effect measurements have been carried out in the liquid phase. The data on the Hall effect, together with those on the electrical conductivity, thermoelectric power, and thermal conductivity make it possible to establish the main relationships governing liquid semiconductors. In the present section we shall consider the consequences which follow from Table II.

The melts in Table II are arranged in decreasing order of the absolute value of their electrical conductivity. Moreover, the melts are divided into three groups: 1) metallic; 2) metal-like; 3) semiconducting.¹⁵⁾

It follows from this division that the first group consists of the melts of those semiconductors which lose their semiconducting properties at the melting point and exhibit behavior typical of liquid metals: the electrical conductivity is $(5 - 10) \times 10^3 \Omega^{-1} \cdot \text{cm}^{-1}$ and the temperature coefficient of the electrical conductivity is negative; the Hall coefficient R is also negative and it agrees well with the value of R_0 predicted by the theory of free electrons. It is shown in Refs. 1 and 87 that metallization caused by melting of semiconductors of the first group is due to the change in the short-range structure.

The second group of metal-like melts consists of those materials whose properties are highly contradictory: measurements of the Hall coefficient and of the thermoelectric power, an analysis of the electron component of the thermal conductivity, and the absence of any significant effect of doping with a third component all suggest that these are also metallic melts, i.e., that there is no gap at the Fermi level in the energy spectrum of these materials. On the other hand, the same melts are characterized by a positive temperature coefficient of the electrical conductivity, i.e., by semiconducting behavior. The reasons for this com-

¹⁵⁾ Similar in content but different in terminology classification of semiconductor melts has been proposed earlier.^{3,82,87,108,110}

plex combination of properties are discussed in Refs. 109–115. It is usual to assume at present that a positive temperature coefficient of the electrical conductivity is related not to the typical (for semiconductors) thermal-generation of carriers across a gap but to a minimum of the density-of-states function at the Fermi level (Fig. 1c) and to degradation of this minimum on increase in temperature. In other words, the Mott relationship $\sigma \propto g^2$ applies. Attempts to show this experimentally by measuring the Knight shift were reported in Ref. 116. Indirect data in support of this interpretation follow from an analysis of the Hall effect in Ref. 117. We can thus see that melts of the second group are also metals but they have certain special properties associated with a minimum of the density of states at the Fermi level. These special properties are reflected also in the adopted terminology: they are called metal-like melts.

Melts of the third group [$\sigma \approx (1-2) \times 10^2 \Omega^{-1} \cdot \text{cm}^{-1}$] have a set of properties which largely resemble those of semiconductors. The temperature dependence of the electrical conductivities is clearly exponential, the thermoelectric power may reach hundreds of more of microvolts per degree, the Hall coefficient is considerably greater than the values predicted by the theory of free electrons, the electron component of the thermal conductivity is anomalously high for a degenerate electron gas, and in some cases the experimental results have to be interpreted invoking the ambipolar mechanism of heat transport.^{115,118} Moreover, the doping effects are significant for some of the melts (Sb_2Se_3 , GeSe , TeSe). Addition of a third element makes it possible to control the sign of the thermoelectric power, as well as the values of the electrical conductivity and Hall coefficient.^{114,119-123} All these properties can be explained only if we assume that the energy spectrum of the investigated semiconductor melts has an energy (mobility) gap. However, it should be pointed out that semiconducting properties of liquid semiconductors can be described only quantitatively by the standard theory. There are certain special properties, the most striking of which is the so-called $p-n$ anomaly. It is found that the signs of the thermoelectric power and the Hall coefficient do not agree: the Hall effect is usually negative whereas the thermoelectric power is positive.¹²⁰⁻¹²² The unusual properties of liquid semiconductors can be understood qualitatively if we assume that the energy gap in the spectrum of these materials is more likely a region of localized states and not the gap in the sense used in the case of crystalline materials. The region of localized states is the mobility gap and, therefore, it acts as an activation gap in the conduction mechanism (Fig. 1c).

Our analysis of the experimental data on molten semiconductors arranged in the order of decreasing electrical conductivity thus yields an important conclusion: variation of the absolute value of the conductivity of the melts is correlated with changes in their properties. A reduction in the conductivity enhances the semiconducting properties. It follows from the data obtained that the conductivity separating melts with metallic and semiconducting properties is approximate-

ly $(1-3) \times 10^2 \Omega^{-1} \cdot \text{cm}^{-1}$. It is worth mentioning that in analyzing the SM transition in Sec. 3 as a function of temperature we have found that a conductivity of the order of $(1-3) \times 10^2 \Omega^{-1} \cdot \text{cm}^{-1}$ also corresponds to the point of transition from the semiconducting to the metallic mechanism.

The fact that different and independent experimental data indicate that the conductivity of $(1-3) \times 10^2 \Omega^{-1} \cdot \text{cm}^{-1}$ separates the semiconducting and metallic states is the most important conclusion of our analysis of the experimental data in Secs. 3 and 4. Since $\sigma = (1-3) \times 10^2 \Omega^{-1} \cdot \text{cm}^{-1}$ corresponds to σ_{min} , which is the minimal metallic conductivity predicted for disordered systems by the Anderson-Mott criterion, we can assume that the theoretical model of the SM transition presented in Sec. 2 describes reality and that, in the first approximation, it is correct. In the next section we shall discuss a third set of experimental data showing that the concept of minimal metallic conductivity applies to the behavior of liquid metals and semiconductors at transcritical temperatures and pressures.

5. METAL-SEMICONDUCTOR TRANSITION NEAR CRITICAL POINTS OF METALS AND SEMICONDUCTORS

A. Results of experimental investigations of cesium and mercury

In the present section we shall consider the behavior of metallic and semiconducting melts at still higher temperatures at which considerable changes take place in the density of the melts and these result in weakening of the overlap of the electron shells. In the case of a metallized semiconductor we may observe localization of electron states, which is analogous to the corresponding localization in liquid metals, so that it is possible to compare such materials with the usual liquid semiconductors discussed in Sec. 4 (see Fig. 12). Continuous changes in the density of liquids can be produced at temperatures and pressures exceeding the critical values. The majority of metals and some semiconductors have far too high critical temperatures (see the reviews in Refs. 141 and 142) and calculations of the parameters of critical points and state equations for sixteen metals¹⁴³ have given values which are not accessible in steady-state experiments when a high stability of temperature and pressure is required. Recent experience has shown that the transition from the metallic to the nonmetallic state in metals and semiconductors is accompanied by effects which occur in a very narrow temperature range (10–15°C according to Refs. 144–147) so that the attention of most investigators is currently concentrated on an increase in the precision of experimental studies of substances with critical temperatures lying below 2100°C. Work of this kind started in the Soviet Union in the middle sixties under the leadership of Kikoin (studies of mercury) and Velikhov (studies of cesium); in the Federal German Republic similar work was performed by the group of Franck.

Among the elements of various groups in the Mendeleev periodic system the most suitable for experimental studies of this kind are cesium, rubidium, potassium,

sodium, mercury, arsenic, selenium, and possibly tellurium. Transitions from the metallic to the nonmetallic state are exhibited by mercury,¹⁴⁸⁻¹⁵¹ cesium,^{152,153} and arsenic,¹⁵⁴ whereas semiconductor-metal-semiconductor transitions occur in selenium (Refs. 96, 155-158).¹⁶¹ All these elements exhibit a transition from the metallic to the nonmetallic state on continuous reduction in the density in the vicinity of the critical point at high temperatures and pressures.

We shall now consider the behavior of liquid metals during continuous reduction in the density in the critical temperature range. The metal-nonmetal transition in mercury and cesium has been investigated most thoroughly: the PVT dependences have been obtained for mercury^{149-151,159-161} and cesium,¹⁶²⁻¹⁶⁵ studies have been made of the acoustic properties of mercury,¹⁶⁶ specific heat of cesium,¹⁶⁷ and thermal conductivity of mercury (Ref. 168);¹⁷¹ studies have also been made of the viscosity of mercury and cesium,¹⁶³⁻¹⁷¹ electrical conductivity of mercury^{146,148-151,160,172,173,174} and cesium,^{144,145,152,153,175} Hall effect in mercury¹⁷⁶ and cesium,¹⁷⁷ thermoelectric properties of cesium (Refs. 144, 145, 175, and 178)¹⁸¹ and mercury,^{145-147,179-181} optical properties of mercury,¹⁸²⁻¹⁸⁴ and the Knight shift in mercury has been investigated.¹⁸⁵ These studies have given fairly comprehensive experimental data and can be used as the current illustration of the well-known work of Zel'dovich and Landau,¹⁸⁶ who were the first to consider various metal-nonmetal transitions and liquid-gas phase transitions.

Clearly, the nature of the metal-insulator transition and its position relative to the critical point in the liquid-vapor phase diagram can be determined if we know the equation of state of the metals and semiconductors in the region of the metal-insulator transition and have sufficiently accurate parameters of their critical points. Unfortunately, the thermodynamic properties of metals and semiconductors have not yet been studied sufficiently thoroughly near the critical points. A good agreement on the critical parameters is available only in the case of cesium. We shall use the equation of state and the critical parameters given in Ref. 163. The critical parameters of cesium are $T_{cr}=1760 \pm 20^\circ\text{C}$, $P_{cr}=116 \pm 5$ bar, and $\rho_{cr}=0.40 \pm 0.02$ g/cm³.

In the case of mercury the scatter in the critical parameters is considerably greater than the limits of the experimental errors. By way of example, we shall

¹⁶¹The first data on the semiconductor-metal transition in liquid selenium were given in Refs. 96 and 158.

¹⁷¹The thermal properties of mercury and cesium were determined^{167,168} before the metal-nonmetal transition.

¹⁸¹The first study¹⁷⁸ involving measurements and theoretical analysis of the behavior of the thermoelectric power in the region of the metal-nonmetal transition was carried out to determine the possibility of obtaining higher values of this power for the purpose of conversion of thermal energy.

¹⁹¹In a recent paper¹⁴⁷ a report was given of a determination of the critical pressure and temperature ($P_{cr}=1675 \pm 25$ bar and $T_{cr}=1495 \pm 5^\circ\text{C}$). The critical temperature reported in this study agreed well with the published values, whereas the critical pressure was close to the value given in Ref. 159 but very different from the values reported in Refs. 150 and 151.

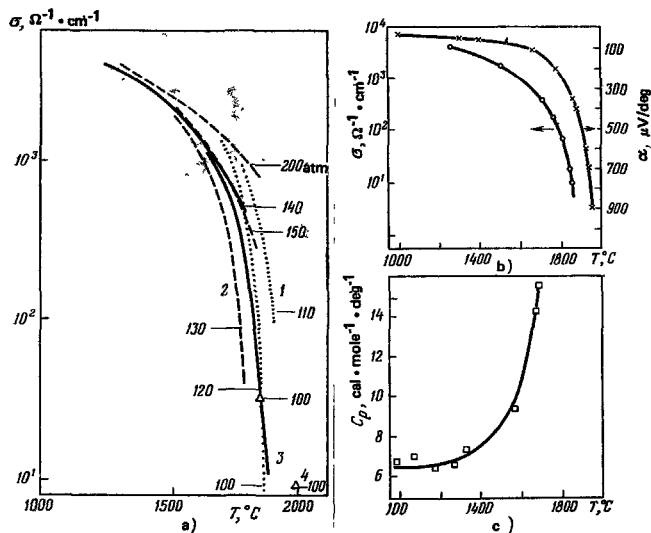


FIG. 13. Electronic and thermal properties of cesium in the region of the metal-nonmetal transition at various temperatures. a) Temperature dependences of the electrical conductivity of cesium obtained at various pressures in the region of the metal-nonmetal transition: 1) Ref. 152 (an error in the graph in Ref. 152 is corrected so that the order of the electrical conductivity agrees with the text of the paper); 2) Ref. 175; 3) Refs. 144 and 145; 4) Ref. 204. b) Temperature dependences of the electrical conductivity and thermoelectric power ($P=120$ atm) (Ref. 145). c) Specific heat at $P=120$ atm (Ref. 167).

quote here the results of two different investigations: $P_{cr}=1510 \pm 20$ bar, $T_{cr}=1490 \pm 15^\circ\text{C}$, $\rho_{cr}=4.2 \pm 0.4$ g/cm³ (Ref. 151), and $P_{cr}=1730 \pm 30$ bar, $T_{cr}=1510 \pm 15^\circ\text{C}$, $\rho_{cr}=5.9 \pm 0.2$ g/cm³ (Ref. 159).¹⁹¹ We shall use the equation of state found in Ref. 159, because this investigation was clearly carried out most carefully.

We shall quote the experimental data on the main electrical properties of cesium (Figs. 13 and 14) and mercury (Fig. 15) at high pressures and temperatures when the density decreases continuously. In the case of mercury we shall also give the values of the Knight shift (Fig. 15e) and the velocity of sound in the region of the metal-nonmetal transition (Fig. 15f); in the case of cesium we shall discuss the specific heat data (Fig. 13c).

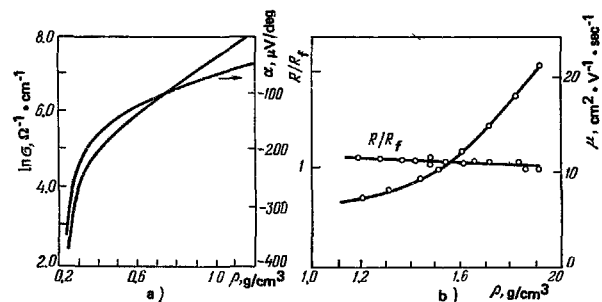


FIG. 14. Electronic properties of cesium as a function of continuous variation of the density. The Hall mobility of cesium and the ratio of the Hall coefficient to the free-electron value R/R_f are taken from Ref. 163 (b) and electrical conductivity and thermoelectric power are taken from Refs. 144, 145, and 152 (a).

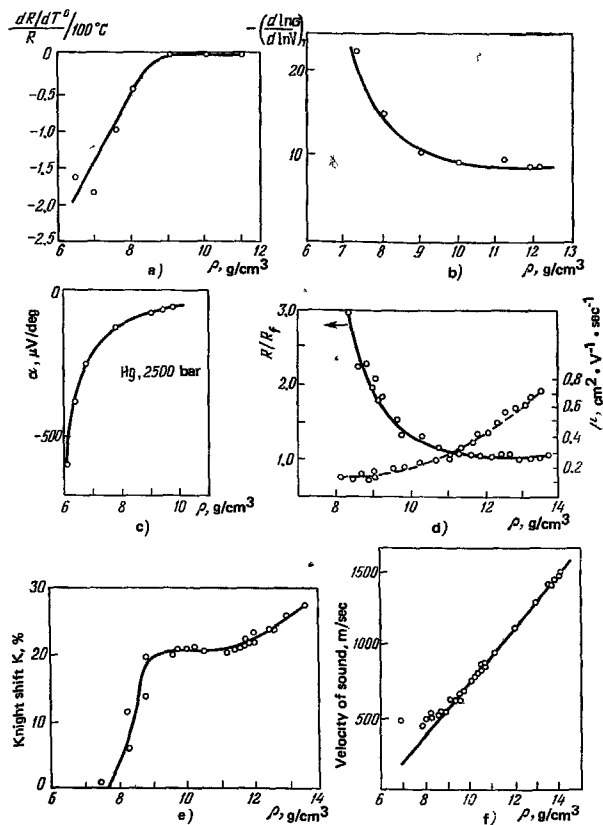


FIG. 15. Electrical and acoustic properties, and Knight shift of mercury plotted as a function of continuous reduction in the density: a) Temperature coefficient of the electrical resistance;¹⁵⁰ b) volume coefficient of the conductivity¹⁷³; c) thermoelectric power¹⁴⁵; d) Hall mobility and ratio of the Hall coefficient to the free-electron value¹⁷⁶; e) Knight shift;¹⁸⁵ f) velocity of sound.¹⁶⁶

The curves representing the electrical conductivity and thermoelectric power of univalent cesium and divalent mercury exhibit the following ranges characteristic of the metal-insulator transition whose theoretical aspects are considered in Sec. 2: 1) liquid metal range; 2) transition range; 3) range with properties resembling liquid semiconductors; 4) range of dense ionized gases.²⁰⁾

1) *Liquid metal range.* In this range the conduction is metallic [Sec. 2.3, after Eq. (29)]. Both cesium and mercury have electrical conductivities in the range $\sigma \geq 2500\text{--}3000\ \Omega^{-1}\cdot\text{cm}^{-1}$ and thermoelectric powers $\alpha < -50\ \mu\text{V}/^\circ\text{C}$. The mean free path is $L > a$. The Hall coefficient has the free-electron value $R = (nec)^{-1}$ (Figs. 13a–15d). It is clear from the figures that in the case of cesium and mercury (Figs. 14b and 15d) the Hall coefficient is a linear function of the density throughout this

²⁰⁾ This last region was not considered in Sec. 2.

²¹⁾ In principle, such a dependence should be retained by cesium up to the critical region, but there are no experimental data on the range of densities from $1\ \text{g}/\text{cm}^3$ to the critical value ($0.42\ \text{g}/\text{cm}^3$).

²²⁾ The minimum density was not determined for cesium. The lowest density for which calculations were made amounted to $\approx 1.14\ \text{g}/\text{cm}^3$ (Ref. 188).

range and this is typical of liquid metals. In the case of cesium this is true up to $\approx 1\ \text{g}/\text{cm}^3$ (Ref. 177),²¹⁾ whereas in the case of mercury the linear dependence ends at $\approx 11\ \text{g}/\text{cm}^3$ (Ref. 176).

The rapid variation in the mobility observed in this range for mercury and cesium is a consequence of a change in the mean free path of electrons. For example, in the case of cesium it is estimated in Ref. 177 using the equation of state from Ref. 163 that the mean free path should be $L = 80\ \text{\AA}$ when the density is $\rho = 1.92\ \text{g}/\text{cm}^3$ and $L = 10\ \text{\AA}$ when the density is $\rho = 1.1\ \text{g}/\text{cm}^3$. We recall that the average interatomic distance is $a = 7\ \text{\AA}$.

In the metallic range we can justifiably use the Ziman theory⁸³, as shown already in Sec. 2. The electrical resistivity of mercury and cesium, whose liquid structure factor was based on the hard-sphere model, were calculated in the low density range.^{187–188} It would be interesting to find the maximum reduction in the density of a metal at which the Ziman electrical resistivity formula still holds well. According to calculations on the reduction in the density of mercury, the lowest density is $\approx 11\ \text{g}/\text{cm}^3$ (Ref. 187).²²⁾

At lower densities a good agreement between the theories and experimental results is obtained if allowance is made for the structural properties of a liquid of reduced density, which weakens screening and facilitates changes in the form factor of the pseudopotential. Several models of the pseudopotential were checked in Ref. 188 for liquid mercury with densities in the range $11.15 > \rho > 9.71\ \text{g}/\text{cm}^3$ at a pressure of 2000 atm assuming a reduction in the screening. Figure 16 shows the results of calculations carried out using the Ziman formula and the Harrison pseudopotential¹⁸⁹ and also allowing for the screening. We can see from this figure that the agreement between calculations and experiment improves considerably when the reduction in the screening is allowed for.

2) *Transition range.* This range is characterized by destruction of the metallic conduction and it corresponds to a situation described in Sec. 2. The electrical conductivity can then vary in the range $\sim 2500\ \Omega^{-1}\cdot\text{cm}^{-1} \geq \sigma \geq 200\ \Omega^{-1}\cdot\text{cm}^{-1}$, the thermoelectric power is $\alpha < -80\ \mu\text{V}/^\circ\text{C}$, the mean free path L is of the order of the interatomic distance $L \sim a$, and the Mott factor is $g < 1$. In this range the Hall coefficient of mercury rises

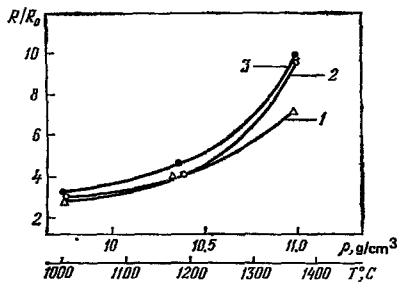


FIG. 16. Resistance of mercury at various densities and temperatures calculated and found experimentally under a pressure of 2000 atm: 1) calculation carried out using the Ziman formula and the Harrison pseudopotential;¹⁸⁹ 2) calculation with variable screening conditions;¹⁸⁸ 3) experimental results.¹⁵⁰

rapidly on reduction in the density to $\sim 9 \text{ g/cm}^3$. A strong reduction in the temperature coefficient of the electrical resistivity of mercury also occurs at this density.^{150,173} An increase in the Hall coefficient is usually attributed to a reduction in the mean free path to a distance of the order of the interatomic value and it corresponds to the onset of the Mott-Anderson localization. According to one of the hypotheses, this may occur on formation of a pseudogap between the S and P bands.¹⁹¹

In contrast to divalent mercury, the level corresponding to the minimum metallic conductivity of cesium lies in the critical density region where probably separation between two Hubbard bands begins.

A special feature of this region is that the onset of localization is complicated by inhomogeneities, particularly in the vicinity of the critical point where the conductivity may be governed by closed regions with a higher electrical conductivity. This possibility was first pointed out in Refs. 61-64. Thus, in accordance with Sec. 2, we are speaking here of the relationship between the Mott-Anderson and percolation transitions.

Evidence that the transition is of the percolation type can be provided by the relationship between the thermoelectric power and electrical conductivity. A comparison of these properties for mercury made using the coordinates of pressure and temperature,¹⁴⁵ and of density and pressure, reveals a fundamental property of the metal-nonmetal transition, namely that the thermoelectric power reaches a value corresponding to the minimum of the metallic conductivity before that minimum is reached on the conductivity scale.

By way of example, we shall consider the dependences of the thermoelectric power and conductivity of mercury at a constant pressure but at different temperatures (Fig. 17). We may assume that the thermoelectric power of this system is shunted by the more highly conducting through channels, whose number decreases on increase in the density.¹⁴⁵

The acoustic properties of mercury in the region of the metal-nonmetal transition are also of interest (Fig.

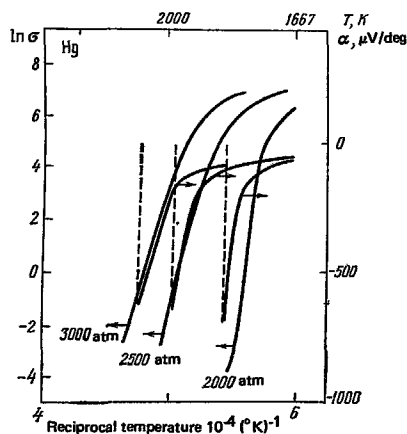


FIG. 17. Electrical and thermoelectric properties of mercury at various temperatures in the region of the metal-nonmetal transitions.¹⁴⁵ (Electrical conductivity data taken from Ref. 149.)

15f); here, there is a slight deviation from the linear dependence of the velocity of sound on the density. It is at present not clear how such deviations are related to the metal-nonmetal transition.

In the case of cesium information is available on the specific heat at various pressures near the metal-nonmetal transition.¹⁶⁷ The specific heat rises strongly on approach to the critical point (Fig. 13c). However, in contrast to nonconducting substances (for example, argon) the interval of rapid rise of C_p and C_v for cesium is wider on the T/T_{cr} scale. This may be due to the fact that the compressibility of cesium is greater than the compressibility of nonconducting substances (in particular, that of argon).

3) *Range with some properties of liquid semiconductors.* The reduction in the density beginning from the near-critical region in the case of cesium and in the range of densities below 9 g/cm^3 in the case of mercury (see Figs. 13 and 15) demonstrates the existence of a range with properties resembling those of semiconductors.

In this range the relationship between the electrical conductivity and thermoelectric power is of the type

$$\ln \sigma \sim \alpha, \quad (32)$$

which is obtained from Eqs. (28) and (29). This dependence is illustrated clearly in Fig. 18. There is an important difference in the positions of this dependence in the phase diagrams of cesium and mercury: in the case of cesium this dependence lies in the critical density region and extends to the gas densities, whereas in the case of mercury this region corresponds to densities of the liquid phase. In the case of cesium we have a transition from the metallic state to a dense plasma whose properties are briefly described in the next subsection; therefore, we shall confine our attention to the properties of mercury. The relationship (32) is valid up to the critical density region. In this region the value of the thermoelectric power falls abruptly to zero on all the isobars.^{145-147,179,181} Figure 17 shows this by dashed lines. The maximum absolute values of the thermoelectric power from which it begins to fall rapidly increase on increase in the pressure.¹⁴⁵ The positions of the resultant "zero" values of the thermoelectric power are shown in the P - T diagram in Fig. 19. No experimental investigations have yet been made of the subsequent fate of the thermoelectric power in the plasma state.

One of the possible interpretations can be given on the basis of allowance for the contributions made to the kin-

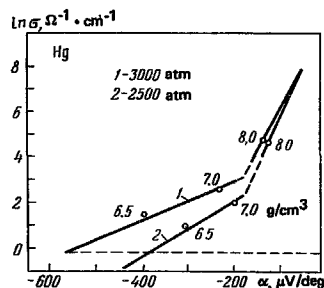


FIG. 18. Dependences of the electrical conductivity on the absolute thermoelectric power of mercury at two pressures.¹⁴⁵

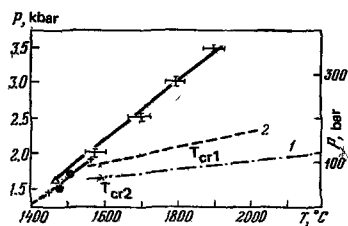


FIG. 19. Positions of points with zero thermoelectric power of mercury plotted in the P - T diagram: o) results from Refs. 145 and 179; Δ) Ref. 174; +) Ref. 181. T_{cr1} represents the critical point of mercury according to Ref. 159; T_{cr2} is taken from Ref. 151. Curve 1 gives the calculated positions of the minima of the thermoelectric power in a mercury plasma and curve 2 gives the corresponding positions for a cesium plasma.¹⁷⁸

etic properties of mercury by, on the one hand, fluctuations of the density resulting in an increase in the depth of the potential wells and, on the other, by an increase in the Fermi level of the electron gas because of increase in temperature.¹⁷⁹ This possibility is supported also by the calculations made in Ref. 192. The experimental data on the electrical conductivity and thermoelectric power suggest that a pseudogap does indeed appear on expansion in mercury.¹⁸¹ This is demonstrated also by the data on the Hall effect,¹⁷⁶ while the recent measurements of the optical reflection coefficient in the frequency range $0.3\text{ eV} \leq \hbar\omega \leq 3\text{ eV}$ and of reduction in the density of mercury indicate (Fig. 20) that small reflection coefficients (0.2) correspond to densities below 8 g/cm^3 (Ref. 184), i.e., they lie in the same region.

Direct calculations of the electron spectrum of mercury in various hypothetical structures carried out in Ref. 193 for varying lattice constants also show that the energy gap in different structures should appear when the density becomes 8.5 g/cm^3 . This value is in good agreement with the experimental data; however, further calculations¹⁹⁴⁻¹⁹⁷ indicate that the densities at which the energy gap opens differ from structure to structure and the transition region may lie between 9.3 and 4 g/cm^3 .

The uncertainty about the possible formation of a pseudogap on expansion of mercury has increased after recent measurements of the Knight shift (see Fig. 15e).¹⁸⁵ These results indicate the possibility that a pseudogap exists in mercury at densities $\rho > 9\text{ g/cm}^3$. The reasons for this disagreement between the experimental results are not clear.

4. Range of dense ionized gases. In the range of densities below the critical value a metal may undergo a transition to a dense plasma state. Calculations of the thermoelectric power and electrical conductivity have been made for this range using an ionized gas model and allowing for the reduction in the ionization potential on increase in the density because of the interaction between charged and neutral particles:^{198,199,200} see also the reviews in Refs. 200 and 201. This interaction results in an exponential dependence of the electrical con-

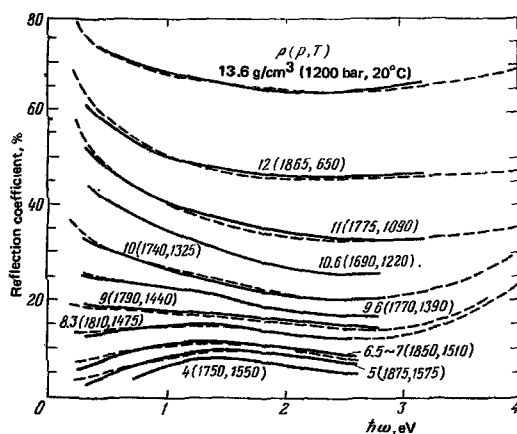


FIG. 20. Frequency dependence of the optical reflection coefficient on reduction in the density of mercury.¹⁸⁴

ductivity on the density, as demonstrated in the first paper by Vedenov¹⁹⁸ and in his subsequent work (Refs. 199 and 209-211).^{23, 24} Moreover, allowance for this interaction may give rise to new effects in the plasma. In fact, an expression for the thermoelectric power of a dense plasma is obtained in Ref. 199:

$$\alpha \sim \frac{\Delta E}{kT}, \quad (32')$$

where $\Delta E \sim (I_0/2)(1 - a\rho/\rho_{cr})$; $a \sim 1$; I_0 is the atomic ionization potential; ρ_{cr} is the critical density of the metal. Here, ΔE represents the change in I_0 on reduction in the density because of the interaction between charged and neutral particles. We can then expect an increase in the absolute value of the thermoelectric power since the plasma density decreases. It is clear from Eq. (32) that the thermoelectric power should exhibit a minimum at values of ΔE equal to the ionization potential of a metal atom. Lines of such minima for cesium and mercury at various pressures were predicted in Refs. 178 and 179 and were detected experimentally for cesium in Ref. 144 (Fig. 21).

The relationship between the thermoelectric power and electrical conductivity in the ionized gas range is

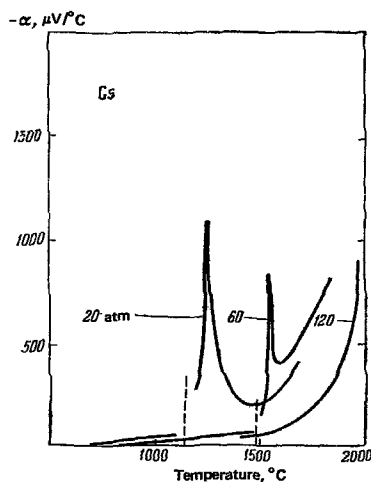


FIG. 21. Temperature dependences of the thermoelectric power of cesium at pressures below the critical point (20 and 60 atm) and above this point (120 atm), based on Ref. 144.

²³) The results of Ref. 202 suggest that the attraction of ions via a neutral gas should induce the ionization potential.

²⁴) This interaction was also partly considered in Ref. 229.

obtained in Ref. 203:

$$\alpha \sim \frac{d \ln \sigma T}{dT}. \quad (33)$$

This dependence is analogous to Eq. (32) applicable to liquid semiconductors. One of the interesting results in this range is an electrical conductivity minimum reported in Ref. 144 (Fig. 22).²⁵⁾ This effect has been considered in many papers using a variety of models: allowing for the formation of ion complexes,²⁰⁶ employing the fluctuation model,²⁰⁷ etc.²⁶⁾ The results obtained using some of these models are shown in Fig. 22. The ranges of existence of a nonideal cesium plasma were determined in Ref. 212.

A variant of the Ziman theory for the electrical properties of a dense cesium vapor was considered in Ref. 203, where a pseudopotential describing the interaction of an electron with neutral atoms was suggested. A semiconductor model, analogous to the theory of an extrinsic semiconductor with partial ionization of donor centers, was applied by Faber to cesium vapor⁸³ but without allowance for the reduction in the ionization potential due to the interaction between charges and neutral ions. In this range there may be a considerable contribution to the conduction process from clusters. This subject is being pursued actively²⁰⁰ employing variants of the cluster model.²⁷⁾

B. Results of experimental investigations of selenium and arsenic. Se-Te system

1) *Selenium and arsenic.* It should be pointed out that, in contrast to metals, very little is known about liquid semiconductors near their critical temperatures and pressures. Information on the electrical conductivity obtained in two laboratories is available.¹⁵⁵⁻¹⁵⁸ Figure 23 shows the temperature dependences of the electrical conductivity of selenium obtained at various pressures. It is clear from this figure that below 500 atm the temperature dependences exhibit a steep fall when a certain temperature (which varies with the pressure) is reached on the saturation line.²⁸⁾ The 500 and 1000 atm isobars lie well above the critical point of selenium and, therefore, the results obtained apply to the region of continuous reduction in the density of selenium.²⁹⁾

Measurements of the electrical conductivity demonstrate another interesting feature, namely conductivity of

²⁵⁾ Moreover, it was reported in Ref. 208 that the electrical conductivity minimum occurred at much higher temperatures than in Ref. 144, but interpretation of this minimum encounters considerable difficulties.

²⁶⁾ In one of the models it is pointed out that charged drops can appear under these conditions because of the strong attraction of atoms to ions.²⁰⁸

²⁷⁾ This topic will not be considered because a recent review²³⁰ has been devoted to the subject.

²⁸⁾ The critical temperature and pressure of selenium are $T_{cr} = 1766^\circ\text{K}$ and $P_{cr} = 268$ atm (Ref. 215). The critical parameters reported in Ref. 157 are $T_{cr} = 1590^\circ\text{C}$ and $P_{cr} = 380$ atm, which can be seen to be different from those given in Ref. 215.

²⁹⁾ The experimental data reported in Ref. 155 are in good agreement with those of Ref. 231, whereas a higher saturation value of the electrical conductivity is given in Ref. 157.

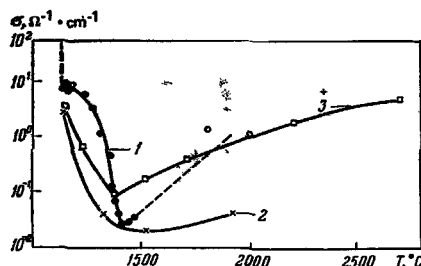


FIG. 22. Temperature dependences of the electrical conductivity of a dense cesium plasma at a pressure of 20 atm: 1) Ref. 144; o) experimental points from Ref. 204; +) point taken from Ref. 205; 2) calculated curve from Ref. 206; 3) calculated curve from Ref. 207.

the exponential dependence of the electrical conductivity at temperatures 1700–2000 °K and conductivities of the order of $200 \Omega^{-1}\text{cm}^{-1}$, i.e., at values corresponding to the minimal metallic conductivity.

It is clear from Fig. 23 that the experimental curves demonstrate a reduction in the activation energy on increase in temperature.^{83, 96} This reduction in the activation energy of conduction has been interpreted as a consequence of a progressive (with temperature) reduction in the pseudogap. It is estimated that the pseudogap disappears at 1500 °K. According to the experimental data,⁹⁶ metallization occurs at $T \sim 1700^\circ\text{K}$. In view of the approximate nature of the extrapolation, the agreement between these metallization temperatures of selenium should be regarded as satisfactory.

The saturation region is followed by a range where the electrical conductivity falls steeply from a level corresponding to the minimum conductivity. If we assume that in this range of temperatures and pressures the selenium represents a homogeneous system, we can interpret this transition to the insulating state as an Anderson transition associated with the electron localization (Sec. 2); the electrical conductivity then changes abruptly (under experimental conditions the transition is nonabrupt because of finite temperatures) from the metallic to the hopping conduction mechanism. It would be interesting to determine the electrical conductivity corresponding to the onset of the hopping mechanism,

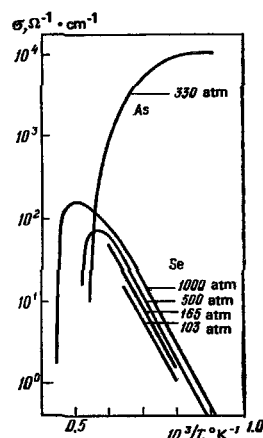


FIG. 23. Relative changes in the electrical conductivity of selenium and arsenic above the critical points.¹⁶⁶

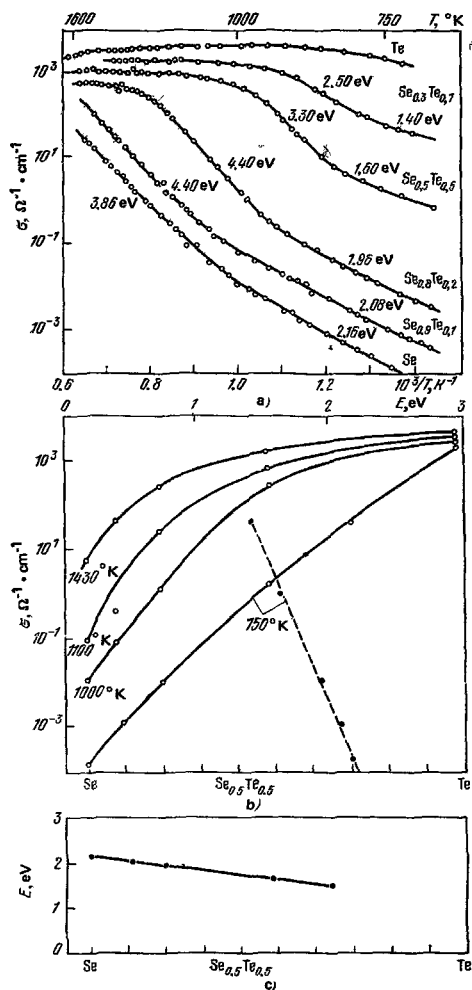


FIG. 24. Changes in the electrical conductivity of the Se-Te system with different selenium concentrations plotted as a function of temperature and composition ($P = 180$ atm).⁹¹ a) Temperature dependences of the electrical conductivity of various compositions in the selenium-tellurium system. b) Composition dependences at a constant temperature (the dashed line shows the ratio of the energy gap to the conductivity). c) Dependence of the energy gap on the composition of the selenium-tellurium system at $T = 750^\circ \text{K}$.

since this would make it possible to check the correctness of theoretical estimates.^{155, 156}

It is interesting to compare the electrical conductivity of selenium in the electron localization region with the value for the metal which is the closest analog of selenium and which has approximately similar critical parameters. This metal is arsenic, whose electrical conductivity has been measured at pressures exceeding the critical value of 330 atm (Ref. 154).

Figure 23 shows the temperature dependences of the electrical conductivity not only of selenium but also of arsenic.¹⁵⁶ The steep fall of the conductivity of selenium beyond the plateau has already been explained by the Anderson localization. We can see from this figure that in the case of arsenic the steepest fall of the electrical conductivity begins from $200 \Omega^{-1} \cdot \text{cm}^{-1}$. Up to this value the localization effect may be shunted by regions whose

conductivity is equal to or greater than the minimum metallic value.

2) Se-Te system. We shall compare the transition from the metallic to the nonmetallic state in metals and to the metallic state in semiconductors and in ordinary semiconductor melts by considering the results of an experimental study of the electrical conductivity of the selenium-tellurium system at various temperatures and for various tellurium concentrations.⁹¹ This investigation was carried out at a pressure of 180 atm. The results are given in Fig. 24. The metallic component here is tellurium (it has metallic conduction)⁸⁹ whose amount is reduced continuously. The system then goes over into a typically semiconducting state. The curves in Fig. 24 show some characteristic features considered above for mercury and cesium, and also for selenium at transcritical temperatures. This may be regarded as an indication of the identity of the nature of the corresponding phenomena occurring in these systems.

We can summarize by concluding that in the case of metal-nonmetal transitions under transcritical conditions the processes of electron localization begin in the vicinity of the electrical conductivity values corresponding to the minimum metallic conductivity and in this sense the results of these investigations are in agreement with the results reported earlier (Secs. 3 and 4) for liquid semiconductors.

6. CONCLUSIONS

We have attempted to summarize all those theoretical and experimental investigations of low-density liquid semiconductors and metals which are of direct relevance to the phenomena of localization (or delocalization) of electron states. The experimental results reviewed in the last three sections demonstrate the common features of the semiconductor-metal transition observed in independent experiments and they show that the existing experimental data largely support the qualitative description of this transition as due to the influence of disorder. In particular, it is clear that such a theoretical concept as the minimal metallic conductivity is undoubtedly a feature of the experimental results if only as a characteristic scale and it has universal meaning as the conductivity separating a metal from a semiconductor. We shall stress only this fundamental aspect and note that accurate quantitative relationships governing the minimal metallic conductivity cannot be as yet obtained theoretically or experimentally.

The general quite unsatisfactory state of the theory and experiment is manifested by the fact that selection cannot be made between the existing theoretical models. As a rule, we cannot say definitely whether in a given specific case the microscopic inhomogeneities are important (giving rise to an inhomogeneous percolation conduction regime), what is the role of the electron-electron correlations, whether the minimal metallic conductivity has any deeper meaning than a simple characteristic conductivity scale, etc. These problems can only be solved by further efforts of theoreticians and experimentalists.

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