

The electron-hole liquid in a semiconductor

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Usp. Fiz. Nauk 145, 3-50 (January 1985)*

Research on the electron-hole liquid in a semiconductor is reviewed. The basic properties of the liquid, their theoretical description, and methods for studying them experimentally are discussed. The behavior of an electron-hole liquid in external electromagnetic and stress fields, the motion of droplets of the liquid, and the interaction of the liquid with nonequilibrium phonons (the phonon wind) are described.

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INTRODUCTION

The discovery of the electron-hole liquid (EHL) in semiconductors is one of the most interesting events in solid state physics over the past 15 years. In 1968, Keldysh¹ pointed out that electrons and holes might condense into a metallic liquid at low temperatures. In 1969 an EHL was discovered experimentally in germanium: by Pokrovskii and Svistunova,² from the appearance of a new line in the recombination spectrum; by Asnin and Rogachev,³ from structural features in optical absorption; by Vavilov, Zayats, and Murzin,⁴ from absorption in the far-IR range; and by Bagaev, Galkina, Gogolin, and Keldysh,⁵ from the behavior of a new line in the recombination spectrum upon deformation of the crystal.¹⁾ The discovery triggered a program of active research on the EHL. It was discovered in silicon and later in many semiconducting compounds. Some truly elegant experimental techniques were developed for studying its properties: the properties of the ground state, the phase diagram, the formation kinetics, and the responses to external agents. It turned out that the EHL is an ideal entity for a comparison of theory and experiment and for testing and refining the methods of many-body theory. Research on the EHL has also proved beneficial to the physics of semiconductors, revealing the variety of phenomena at high excitation levels. Theoretical methods developed in various fields of physics have been called upon to interpret these phenomena. The EHL, which is formed not by "genuine" particles, but by quasiparticles or quantum excitations of a semiconductor, behaves at a macroscopic level in a manner analogous in many ways to that of

¹⁾Certain manifestations of an EHL had been observed even earlier,^{6,7} but they were not interpreted correctly.

an ordinary atomic liquid. Several features of the EHL (its pronounced quantum nature and the finite lifetimes of its constituent particles) give rise to some new effects, which are clearly of general physical interest.

The number of publications on EHLs is now approaching 10^3 . Reviews have been published.⁸⁻¹³ The present state of the problem is outlined most comprehensively in Ref. 14. Our purpose in the present review is to give a general picture of the EHL and of the clear understanding of its properties which has now been achieved. In Section 2 we describe the basic properties of nonequilibrium current carriers: electrons, holes, and their possible bound states (excitons, biexcitons, and the EHL). We also discuss the relationship between the condensation of excitons and the metal-insulator transition. Section 3 deals with the properties of the EHL: the characteristics of its ground state, its surface properties, its phase diagram, and its condensation and decay kinetics. Section 4 reviews the basic methods for experimentally studying the EHL and its behavior in external electromagnetic and stress fields. Section 5 deals with the motion of electron-hole droplets, and section 6 describes phenomena associated with the interaction between an EHL and nonequilibrium phonons (the phonon wind).

2. EXCITONS, BIEXCITONS, AND THE ELECTRON-HOLE LIQUID (EHL)

The excited state of the electron system of a semiconductor reduces to a set of one-particle excitations: *electrons* (*e*) and *holes* (*h*), which are free charge carriers. An electron occupying a state in the unfilled lower band (the conduction band) carries a negative charge, while a hole with a free state

in the filled upper band (the valence band) carries a positive charge. Electrons and holes have effective masses m_e and m_h , and the interaction between them is a Coulomb interaction (in accordance with the magnitudes of the charges that they are carrying), weakened by the static dielectric permittivity of the semiconductor, ϵ_0 .

At equilibrium at low temperatures, $k_B T \ll E_g$ (E_g is the width of the gap between the valence band and the conduction band), there are essentially no excitations in an intrinsic semiconductor. In a nonequilibrium state, e.g., in a semiconductor subjected to electromagnetic radiation with $\hbar\omega > E_g$, electrons and holes appear. The Coulomb attraction between them may result in their binding in a hydrogen-like state: a Wannier-Mott exciton (see Ref. 15, for example). The binding energy²⁾ and the dimensions of an exciton can be estimated from the Bohr formula and from the values $\epsilon_0 \sim 10$ and $m_{e,h} \sim (0.1-0.3)m_0$, which are typical values for germanium, silicon, and other semiconductors (m_0 is the mass of a free electron):

$$E_{ex} = \frac{e^4 m_r}{2\epsilon_0^2 \hbar^2} \sim 10^{-2} - 10^{-3} \text{ Ry}, \quad a_{ex} = \frac{\epsilon_0 \hbar^2}{m_r e^2} \sim 10 - 100 \text{ \AA}, \quad (2.1)$$

where $m_r^{-1} = m_e^{-1} + m_h^{-1}$. The binding energy of an exciton is thus considerably lower than the characteristic atomic energies, and its radius is considerably larger than atomic dimensions. The exciton thus causes a negligible perturbation of the semiconductor lattice and is a macroscopic formation which "senses" the lattice only on the average, through parameters such as ϵ_0 and $m_{e,h}$. By analogy with the atomic world we would expect the scale values of the energies E_{ex} and of the distances a_{ex} also to be characteristic of all the many-particle states which arise in an e-h system.

At temperatures $k_B T \ll E_{ex}$ most of the carriers which form in a semiconductor become bound in excitons. At extremely low temperatures, *biexcitons*, excitonic molecules,^{16,17} and also three-particle charged complexes ("trions"¹⁷⁻¹⁹: eeh and ehh) may form. With increasing excitation level, the density of excitons and biexcitons increases, and they may condense into an *electron-hole liquid*.¹ The equilibrium density of an EHL can be expected to be $n_l^0 \sim a_{ex}^{-3}$ and its binding energy $E_l^0 \sim E_{ex}$. In the theory of an electron gas the density of the system is customarily represented by the dimensionless parameter $r_s \equiv (3/4\pi n)^{1/3} a_{ex}^{-1}$, where n is the density of electrons. In the case of EHL we would thus have $r_s \sim 1$.

The detailed picture of phase transitions which occur in a given semiconductor depends on the relations among the binding energies E_{ex} , E_b and E_l^0 [$E_b = E_{ex} + (E_D/2)$ is the binding energy of a biexciton, and E_D is the dissociation energy of a biexciton]. The various possibilities are analyzed in Ref. 20; here we simply note that an EHL can form only if $E_l^0 > E_{ex}$, E_b . In certain cases, e.g., in germanium and silicon, the binding energy of the EHL is quite high: $E_l^0 \sim 1.5E_{ex}$. The dissociation energy of a biexciton is very low because it has no heavy particles. Theoretical^{21,22} and experimental²³⁻²⁷ research have revealed $E_D \sim (10^{-2}-$

²⁾Here and below, the binding energy (of an exciton, a biexciton, etc.) is a positive quantity, equal to minus the energy of the ground state (of the exciton, the biexciton, etc.) reckoned from the lowest energy of a noninteracting e-h pair, per e-h pair.

$10^{-1})E_{ex}$; i.e., the dissociation energy is about an order of magnitude smaller than (at the corresponding scale) that of the hydrogen molecule ($E_D = 0.348\text{Ry}$). For this reason, biexcitons can be observed experimentally in such semiconductors as germanium and silicon only under special conditions such that the formation of an EHL is suppressed.

An EHL exhibits many of the familiar properties of liquids. Its density n_l^0 , for example, is maintained constant by internal forces. The condensation of excitons, like an ordinary gas-liquid transition, is a first-order phase transition: It occurs when the exciton gas becomes supersaturated, and it is accompanied by a stratification of the gas into two phases, one with a high density (the liquid) and the other with a low density (the gas). There are critical values of the density (n^c) and of the temperatures (T^c): Stratification does not occur at $T > T^c$. The interface has a positive surface energy at $T < T^c$: The EHL has a surface tension. If there are not enough excited carriers in a semiconductor to fill the entire sample with the liquid, the EHL exists in the form of *electron-hole droplets* (EHDs), whose shape is approximately spherical because of the surface tension and whose dimensions are definitely macroscopic: of the order of a few microns. An EHL can flow through a crystal: The droplets are easily accelerated by external agents (e.g., by a nonuniform deformation of the semiconductor; see Subsection 4b2).

Two circumstances distinguish the EHL in a fundamental way from ordinary liquids: the absence of heavy particles and the finite lifetime of the electrons and holes. Since there are no heavy particles, the zero-point vibrations in an EHL have a large amplitude (incidentally, this is also true of all bound states of the e-h system)—of the order of the distance between the particles. The large zero-point vibrations have the consequence that the EHL does not crystallize even at $T = 0$. An EHL can crystallize only²⁰ if the electron and hole masses differ by a factor greater than 10^2 , but this situation is unlikely for a semiconductor.

Other consequences of the large zero-point vibrations are a collective behavior of the electrons and holes in the liquid and a metallic nature of the spectrum of excitations of the liquid. Even if the binding energy of a biexciton in a low-density system exceeds the binding energy of the EHL, with increasing density (certainly at $r_s \sim 1$) the exchange repulsion between biexcitons²⁸ must work against the existence of a molecular phase. Furthermore, at $r_s \sim 1$ there is no exciton bound state (more on this below). Only under certain conditions, e.g., in a semiconductor with isotropic bands, can the coherent pairing of electrons and holes give rise to a gap in the spectrum of one-particle excitations and cause the EHL to become an insulator [by analogy with the semimetal-(excitonic insulator) transition²⁹⁻³¹].³⁾

³⁾The isotropic model with $m_e = m_h$ is the least suitable for the formation of a metallic EHL; see Subsection 3b1. Strictly speaking, at $T = 0$ the spectrum of one-particle excitations of the EHL always has a gap; at low densities, this gap coincides with E_{ex} , while at high densities it is exponentially small.²⁹⁻³² At small but nonzero temperatures, $k_B T \ll E_{ex}$, the gap disappears with increasing n , and a metal-insulator transition occurs in the system (more on this below). An insulating EHL of low density [$r_s = 4$ (Refs. 33 and 34) or 3 (Ref. 35)] and with a low binding energy [$E_{l,d} = (1.07 - 1.1)E_{ex}$] may form in such a system, but it would be more favorable than a gas of biexcitons ($E_b = 1.03E_{ex}$; Ref. 22).

The Fermi energy of the electrons and holes in an EHL is

$$E_F^{(e, h)} = \frac{\hbar^2 (3\pi^2 n_i^0)^{2/3}}{2m_{e, h}} \sim E_{ex}. \quad (2.2)$$

Since $k_B T^c \sim 0.1 E_F^0$ (Ref. 36) and $E_F^0 \sim E_{ex}$, the EHL is always a degenerate Fermi liquid; in contrast with the situation in a metal, both the negatively and positively charged particles are degenerate.

The finite lifetime is a consequence of the circumstance that the electrons and holes are excitations of the semiconductor which tend to recombine (annihilate). An important point to note, however, is that the carriers have time to become thermalized before they annihilate (at $\hbar\omega > E_g$ the carriers are "hot," i.e., far from the extrema of the corresponding bands, when they appear), and they then become bound in excitons and an EHL. In semiconductors the thermalization time is usually $\sim 10^{-9}$ s; the binding times depend on the carrier density and may be of the same order of magnitude. The lifetime is determined by the probabilities for various recombination processes. If an electron and a hole can undergo a radiative recombination, emitting a photon, the lifetime is $\sim 10^{-9}$ s. In so-called indirect semiconductors, however, in which the extrema of the conduction and valence bands are at different points in the Brillouin zone, direct radiative recombination is forbidden by quasimomentum conservation. Recombination is accompanied by the emission of phonons (quanta of the lattice vibrations), which gives rise to long lifetimes, up to 10^{-4} – 10^{-5} s. Germanium and silicon, in which the EHL has been studied most thoroughly, are in fact indirect semiconductors. As is always the case when a large number of nonequilibrium processes are occurring simultaneously, the sequence (and variety) of events depends on the hierarchy of their scale times. Research on the EHL presents some exceedingly rich opportunities. It becomes possible, for example, to study the formation of a two-component liquid in deformed germanium and silicon (Subsection 4b1).

The finite lifetime has some important consequences. First, two possibilities arise for an experimental study of the EHL: with static or pulsed excitation. While a quasiequilibrium EHL is observed in the case of continuous excitation (the carriers which annihilate are replaced by newly produced carriers), the EHL appears and disappears in the case of pulsed excitation. Second, the emission which accompanies the recombination embodies extensive information about the properties of the EHL (Subsection 4a). Third, there are some unusual phenomena associated with the recombination: a recombination magnetism of electron-hole droplets (Subsection 4d), the absence at extremely low temperatures of the hysteresis effects which are usually characteristic of first-order phase transitions (Subsection 3e), and the excitation of nonequilibrium phonons (the phonon wind), which influence the spatial distribution of the EHL (Section 6). The recombination of carriers in the liquid and the action of the phonon wind have the effect that the EHL is usually observed as a cloud of small droplets (Subsection 3e and Section 6). Only in external force fields, e.g., in nonuniformly compressed germanium samples, can a single large electron-

hole droplet form with a radius as large as 0.5 mm (Subsection 4b3).

We will conclude the review with a discussion of some interesting possibilities associated with the behavior of a system of nonequilibrium current carriers.

a) Superfluidity and superconductivity of an EHL

The collective interaction among carriers can give rise to a gap at the Fermi surface of an EHL, as mentioned above. The scattering of current carriers by phonons is then suppressed,³⁷ and there can be a relaxation-free transfer of the excitation energy concentrated in the EHL. We wish to stress that, in contrast with a superfluid flow in helium, we are dealing here with a transfer of energy but not mass³⁸ (Subsection 5c). Superconducting pairing—an alternative event—is also possible in principle in an EHL.^{8,39}

b) Bose condensation of biexcitons

While a gas of biexcitons is preferred to an EHL from the energy standpoint at low temperatures and densities, this gas can in principle undergo a Bose condensation.^{40,20} (Bose condensation of excitons is prevented by their attraction to each other.^{20,41}) In order to achieve a high condensation temperature, however, we need a high density of biexcitons, and we do not know whether the biexcitons will first turn metallic. Certain recent discoveries indicate that a Bose condensation of biexcitons may occur at $T < 0.5$ K in germanium which is compressed nearly along a $\langle 001 \rangle$ axis.²⁷ Such a deep cooling of an excited electronic system would be extremely difficult to arrange, however, and it might be an experimental impossibility.⁴²

c) Metal-insulator transition

One of the most important directions in solid state physics is research on the metal-insulator transition (see Ref. 43, for example). A system of nonequilibrium carriers in a semiconductor is a very convenient system for the experimental study of such transitions, since the density of the system can be varied over a broad range by varying the excitation intensity. At low temperatures and at sufficiently low densities, the system is an insulator because of the formation of excitons. As the density is increased, at $r_s < r_s^m$, an exciton gas should become metallic because of the screening of the Coulomb interaction. A modification of the Mott criterion⁴³ yields $r_s^m = 6$ – 10 (Refs. 43–45) or isotropic bands with $m_e = m_h$. Another criterion, which is more justified⁴⁶ at $r_s > 1$ —the vanishing of the gap in the spectrum of one-particle excitations of the exciton system with increasing density—yields values $r_s^m = 2$ (Ref. 47) and 1.8 (Ref. 46). The latter estimate has been confirmed by experiments in uniaxially compressed germanium and silicon.^{48,49} We thus see that the metal-insulator transition should occur in the same density range as the transition from an exciton gas to an EHL. Just how the two transitions are related is not clear either experimentally or theoretically. There are two possibilities here. First, the metal-insulator transition is also a gas-liquid transition.^{50–52} Second, two phase transitions occur, each with its own critical points and with a triple point

at which three phases coexist: an insulating gas, an insulating liquid, and a metallic liquid.^{47,53} This possibility in the case of mercury was first pointed out by Zel'dovich and Landau.⁵⁴ There is some evidence for this situation for the EHL in germanium and silicon: It has been established experimentally that while the EHL coexists with an exciton gas at low temperatures, $T \ll T^c$, at $T \sim T^c$ the EHL coexists with a nondegenerate e-h plasma.^{55,56} It is not clear, however, whether this transition is a sharp one⁵⁷ or a gradual one,^{58,48} because of thermal ionization of excitons. The discovery of two distinct transitions, with $T_m^c = 7$ K and $T_i^c = 4.5 \pm 0.5$ K, and of a triple point at ~ 4 K in deformed germanium has recently been reported.⁵⁹ In general, this interesting topic requires further research, both experimental and theoretical.

d) Equilibrium EHL

If a semiconductor has a narrow band gap, the spontaneous generation of e-h pairs followed by their binding in an EHL may be preferred from the energy standpoint⁶⁰ ($E_i^0 > E_g$). In its ground state, such a medium should be a metal with a carrier density equal to that of the EHL, n_i^0 . The possibility of this situation in layered dichalcogenides (TiS₂ and TiSe₂) is supported by calculations⁶¹ based on the model of a semiconductor with a highly anisotropic spectrum (Subsection 3b2).

3. BASIC PROPERTIES OF AN EHL

The most important characteristics of an EHL are its equilibrium density n_i^0 , the binding energy per e-h pair (E_i^0), the work function of the EHL with respect to the escape of an exciton ($\varphi = E_i^0 - E_{ex}$), the Fermi energy $E_F = E_F^{(e)} + E_F^{(h)}$, the surface tension σ , the critical density n^c , the critical temperature T^c , the lifetime τ_i , and the radius (R) of the electron-hole droplets. Table I shows values of these characteristics for the EHLs in germanium and silicon. Electron-hole liquids are also observed in several semiconducting compounds, but they have not been studied to the same extent as in germanium and silicon; some data on compounds are shown in Table II. In the semiconductors in the lower part of this table, the EHLs have short lifetimes, $\sim 10^{-9}$ s. All these are direct-band semiconductors.

a) Spectrum of a semiconductor in the presence of an EHL

To see the meaning of the quantities φ , E_i^0 , and E_F , we consider the changes in the spectrum of a semiconductor upon the formation of a metallic EHL in it. Figure 1a shows a schematic spectrum (double lines) of an indirect semiconductor: the parts of the curves of the electron and hole energy as functions of the quasimomenta, $\varepsilon^{(e,h)}(\mathbf{k}^{(e,h)})$, near the extrema of the corresponding bands [at the points $\mathbf{k}_0^{(e)}$ and $\mathbf{k}_0^{(h)}$ with $\mathbf{k}_0^{(e)} \neq \mathbf{k}_0^{(h)}$]. For isotropic and parabolic bands we would have $\varepsilon^{(j)}(\mathbf{k}^{(j)}) = (\mathbf{k}_0^{(j)} - \mathbf{k}^{(j)})^2/2m_j$, $j = e, h$.

The interaction between nonequilibrium carriers results in a change in the spectrum. Let us find the quantity of greatest importance to the discussion below: $E(n)$, the energy of the ground state (at $T = 0$) of the metallic phase of N e-h pairs in a volume V , per pair, reckoned from the bottom of

the bands ($n = N/V$). The equilibrium density of the EHL, n_i^0 , and the binding energy E_i^0 are found by minimizing $E(n)$:

$$\left. \frac{dE}{dn} \right|_{n=n_i^0} = 0, \quad E_i^0 = -E(n_i^0). \quad (3.1)$$

The chemical potential of the EHL at $T = 0$ is

$$\mu = d \frac{d}{dN} \left[NE \left(\frac{N}{V} \right) \right]_{n=n_i^0} = -E_i^0. \quad (3.2)$$

It follows⁴⁾ that when an EHL is preferred from the energy standpoint ($E_i^0 > 0$) the electron and hole Fermi levels lie in the band gap of the unexcited semiconductor, and the interaction between carriers in the EHL causes shifts of the electron and hole bands as shown by the solid lines in Fig. 1a. The hatched regions show states which are filled up to the corresponding Fermi levels: $E'_g = E_g - E_i^0 - E_F$ is the renormalized gap width. The band curvature changes slightly during the shift (the masses are renormalized by $\sim 10\%$; Ref. 119).

The changes in the spectrum of a semiconductor upon the appearance of electron-hole droplets in some regions in the semiconductor are illustrated by Fig. 1b, which shows the energy of an e-h pair as a function of the spatial coordinates. The hatched region is the region filled by a droplet. The dashed line shows the ground state of an exciton outside the droplet.

The bands of a real semiconductor are usually far more complicated than as shown in Fig. 1a. Germanium and silicon, for example, are multivalley semiconductors. The germanium conduction band has four energy-degenerate absolute minima (valleys) at the boundary of the Brillouin zone along $\langle 111 \rangle$ directions (Fig. 2a). Silicon has six electron valleys along $\langle 100 \rangle$ directions. The hole band of germanium or silicon has an absolute maximum at the center of the Brillouin zone, is fourfold degenerate at this point, and splits into nonparabolic light- and heavy-hole bands in the case⁵⁾ $\mathbf{k} \neq 0$. As we will see below, these complications of the electron spectrum make the metallic EHL more stable.

b) Binding energy and equilibrium density

The most important theoretical problem in research on the EHL in a specific semiconductor is to calculate $E(n)$, the ground-state energy of the metallic phase of the electrons and holes which are undergoing a Coulomb interaction. Knowing $E(n)$, we can determine [see Eq. (3.1)] the equilibrium density n_i^0 and the equilibrium binding energy E_i^0 of the EHL; and by comparing E_i^0 with E_{ex} and E_b , we can determine whether it is possible for a metallic liquid to form in the given semiconductor. Calculations of $E(n)$ in various semiconductors have been carried out in many papers, which are discussed in detail in the reviews in Refs. 40, 11, and 14.

Three basic problems arise in a calculation of $E(n)$. First, it is necessary to take into account the complicated band structure of the specific semiconductor. Second—and this is a complication of fundamental importance—there is

⁴⁾As was shown by L. V. Keldysh.⁶³

⁵⁾Detailed data on the band structures of germanium and silicon are given in Ref. 40.

TABLE I. Basic characteristics of the electron-hole droplets in germanium and silicon. 28,42,55-57,62-95

	Ge	Reference	Si	Reference
n_i^0 , 10^{17} cm^{-3}	1,8 2,0 2,2 2,3±0,1	62, 28 T 63 T 64 T 42 *) 76	34 31 32 33±1 33,5±0,5 35±0,5 33 36±1 0,9	62, 28 T 68 T 64 T 42 *) 56 77 78, 79 66 28 62-65 T
r_s	0,6	28 62-65 T		62-65 T
E_i^0 [φ], meV	5,3 [1,45] 6,1 [1,95] 5,9 [1,75] 6,2 [2,05] 6,0±0,2 [1,8±0,2] [1,9±0,3]	62, 28 T 68 T 64 T 65 T 42 *) 42 *) 76	20,3 [5,7] 21 [6,3] 22 [7,3] 22,9 [8,2] 22,1 [7,4] 22,9±0,5 [8,2] 24,0 [9,3] 24,2 [9,5] 24,0±0,2 [9,3±0,2] 14,7	62, 28 T 68 T 64 T 65 T 66 T 42 *) 77 78 66
E_{ex} , meV	1,9±0,2 4,15	85 80		94 T 95
E_F [E_F^c , E_F^h], meV	6,1 [2,4; 3,7] 6,4±0,4	64 T 42 *)	21,2 [7,5; 13,7] 22,2±0,2 [7,9; 14,6] [7,6; 14,0]	64 T 42 *) 56 77 78
T^c , K	6,26±0,12 5,9 8 7,2 5 7,91 6,5±0,1 6,7±0,2 7,0±0,1	76 64 T 67 T 68 T 69 T 70 T 81 82 55	20,8 28 21,6 29,1 28±2 27±1 23±1	64 T 67 T 69 T 70 T 56 57 66
n^c , 10^{17} cm^{-3}	0,93 0,7 0,6 0,845 0,436 0,8±0,2 0,89±0,05	64 T 67 T 68 T 69 T 70 T 81 55	12 8 10,4 4,22 12±2	64 T 67 T 69 T 70 T 56, 66
σ , 10^{-4} erg/cm^2	0,83 3,5 2,5 1,84 3,7 2,3 1,8 1,8-2,6 2,6±0,3 2±0,5 2,3-2,6	71 T 72 T 73 T 74 T 75 T **) 83 84 85 86 87 74 88	32 87,4 35,0 50 125±60 < 110 20 28±5	74 T 75 T 66 T **) 91 92 93 66
Sign of charge of EHD	1 3 — +	71, 73 75 T 73 T 89, 90	—	75 T
τ_i , μs	40	42 *)	0,15	42 *)
R , μm	2-20	43 *)	≤ 1	43 *)

T) Theoretical paper

*Data averaged over many experimental studies.

**Calculated from the Langmuir formula, (3.13).

no small parameter in the problem: We have $r_s \sim 1$ for the EHL. Finally, in semiconducting compounds with a high degree of polarity (and with a pronounced dispersion of the dielectric permittivity) we cannot use a statically screened Coulomb interaction. We will begin with the case in which the dispersion of the dielectric permittivity can be ignored.

1) Isotropic model; germanium and silicon

It is customary to write $E(n)$ as the sum of kinetic, exchange, and correlation energies:

$$E(n) = E_{kin}(n) + E_{exc}(n) + E_{cor}(n). \quad (3.3)$$

The component E_{kin} , which is the energy of the degenerate ideal Fermi gas, and the component E_{exc} , which is the change in the energy caused by the exchange repulsion of like carriers by each other, can be calculated exactly for any complicated spectrum of a semiconductor.⁶³ In the simplest case of a semiconductor with isotropic bands [$p_F = \hbar(3\pi^2n)^{1/3}$ is the Fermi momentum] we would have

$$E_{kin}(n) = \frac{3}{5} \frac{p_F^2}{2m_r} = \frac{2,21}{r_s^2} E_{ex}, \quad (3.4)$$

TABLE II. Characteristics of the electron-hole liquids in semiconducting compounds.^{65,96-118}

Compound	$n_i^0, 10^{17} \text{cm}^{-3}$	ϕ, meV	τ_i, ns	$n^c, 10^{17} \text{cm}^{-3}$	T^c, K	Reference (T = theo.)
AgBr	100	30				⁶⁵ T
SiC	80	55	15		> 100	⁹⁶
	110	19				⁹⁷ T
$\text{Ge}_{0.85}\text{Si}_{0.15}$	78	19.5 ± 4	57 ± 3		41	⁹⁸
	8,5	3,8		3,5	7,7	⁹⁹ T
GaP	5	3	4400			100
	70	6				101 T
	71	11,9				⁶⁵ T
	157	8-11	30		> 50	101
	74	15,5	30		> 70	102
GaS	86	17.5 ± 3			45	103
	120 ± 20	$15-21$	30 ± 3		50 ± 5	118
AlAs	4500	9				104
Ga _{0.98} Al _{0.02} As	125	14,5				⁶⁵ T
	160	16			52 ± 3	106
PbI ₂	14	4,1		4	52	117
CdS	55	14		7,8	64	105 T
	39	1				⁶⁵ T
	20	13	1		55	107
	10	12 ± 1			< 77	108, 109
CdSe	8				> 77	110
	8,3	5		1,2	30	111
	5,4	-4				105 T
ZnS		2				⁶⁵ T
	8,3	12		14	79	107
ZnO	49	-5				105 T
	200	-21				⁶⁵ T
CdTe	9,8	22			70	112
	33	26		4	80	113
ZnSe	2,9	0,9		0,44	18	105 T
	2,4	0				⁶⁵ T
ZnTe	32	5				⁶⁵ T
	10	4-7				114
GaAs	6,6	3				⁶⁵ T
	2,5	2-3				115
	0,34	1,8		0,043	6,5	105 T
	0,37	0,28				⁶⁵ T
	0,1	1				116

$$E_{\text{exc}}(n) = -\frac{3e^2 p_F}{2\pi \hbar \epsilon_0} = -\frac{1,83}{r_s} E_{\text{ex}}. \quad (3.5)$$

The basic complexity is in determining E_{cor} , which takes into account the correlation between carriers. Various methods of the theory of an electron gas modified for a multicomponent e-h system have been used to calculate this component. Hubbard's modification¹²¹ of the random phase approximation¹²⁰ (RPA) was used in Refs. 62, 28, and 65; the Nosières-Pines interpolation¹²² was used in Ref. 63; and the self-consistent scheme of Singwi *et al.*¹²⁴ was used in Refs. 64

and 123. All these methods lack a rigorous basis. Historically, they have been used in the theory of metals. Ions play a major role in metals, however; their effects are difficult to take into account and become an independent problem. For this reason, experiments do not provide a direct test of the merits of these methods. In the case of an EHL there is no such complication; the spectra of many semiconductors have been studied thoroughly, and the theoretical methods can be tested directly.

These studies can be summarized by saying that in a

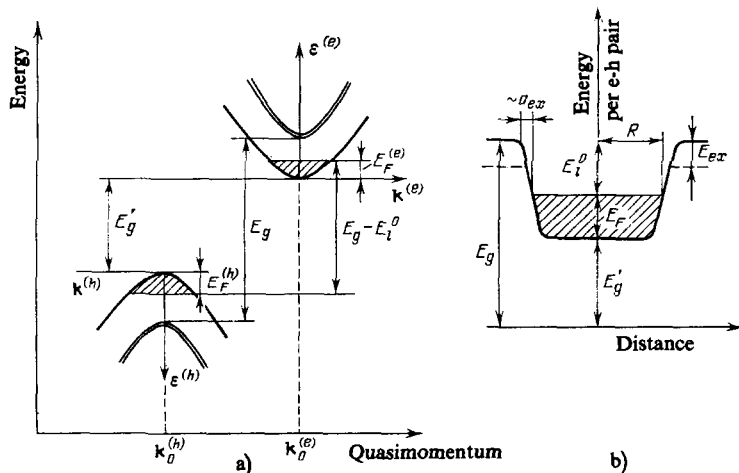


FIG. 1. Change in the electron spectrum of a semiconductor upon the formation of electron-hole droplets (see the text proper for an explanation).

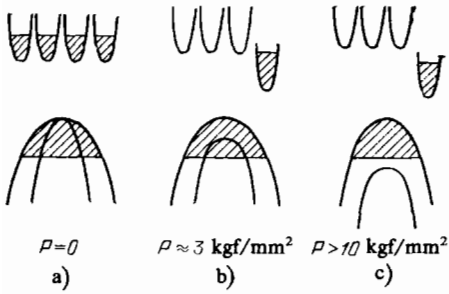


FIG. 2. a—Valence band and conduction band of germanium; b, c—their changes during uniaxial compression along a (111) direction (schematic). The hatched regions are filled with carriers in the EHL state.

model semiconductor with isotropic bands and $m_e = m_h$ a metallic EHL is apparently not preferred from the energy standpoint [$E_i^0 = 0.86E_{ex}$ (Ref. 62) or $0.99E_{ex}$ (Ref. 123)]. Calculations carried out for germanium and silicon yield similar results, which are in excellent agreement with experiment (Table I). The multivalley nature, the anisotropy, and the complexity of the bands all promote a metallic phase (as was first pointed out in Refs. 5 and 125). For example, if there are ν_e electron valleys, the energy component E_{kin} , which makes a positive contribution to $E(n)$, decreases by a factor of $\nu_e^{2/3}$. As for the dependence of E_{exc} and E_{cor} on the details of the band structure, we note that in the range $0.2 < r_s < 3$ the dependence of one of these energy components balances that of the other,¹²⁶ at least in the random phase approximation, Hubbard's approximation, and the self-consistent scheme. The sum of E_{exc} and E_{cor} , expressed in units of E_{ex} , is essentially independent of the band structure and can be approximated well by the expression¹²⁶

$$E_{Coul} \equiv E_{exc} + E_{cor} = -\frac{5.0879r_s + 4.8316}{r_s^2 + 3.0426r_s + 0.0152} E_{ex}. \quad (3.6)$$

The use of (3.6) substantially simplifies calculations of n_i^0 and E_i^0 . All the structural features of the electron spectrum are incorporated in E_{kin} , which is given by the following expression for a semiconductor with ν_e ellipsoidal electron valleys (with longitudinal and transverse masses $m_{e,\parallel}$ and $m_{e,\perp}$) and two spherical bands of light holes (with a mass $m_{h,L}$) and heavy holes ($m_{h,H}$):

$$E_{kin}(n) = \frac{3}{10} \hbar^2 (3\pi^2 n)^{2/3} \left(\frac{1}{\nu_e^{2/3} m_{d,e}} + \frac{1}{m_{d,h}} \right), \quad (3.7)$$

where

$$m_{d,e} = (m_{e,\parallel} m_{e,\perp}^2)^{1/3}, \quad m_{d,h} = m_{h,H} \left[1 + \left(\frac{m_{h,L}}{m_{h,H}} \right)^{3/2} \right]^{2/3}$$

Quantities which depend directly on electron-hole correlations (the binary correlation function, for example, turn out to be quite different when calculated by these methods; the differences are attributed to the different extent to which correlations are taken into account.

2) Semiconductors with a highly anisotropic electron spectrum

Expression (3.6) does not hold for systems with an extremely pronounced anisotropy (e.g., multivalley semiconductors and semimetals with $\nu_{e,h} > 1$, quasi-one-dimensional systems in which the distance between filaments is small in comparison with a_{ex} , and quasi-two-dimensional systems

with closely spaced layers). The energies $E(n)$ of such systems can be calculated asymptotically exactly,¹²⁷ as was first pointed out in Ref. 128 for the case of an electron liquid in an ultrastrong magnetic field. The qualitative conclusion that the anisotropy promotes the formation of a metallic phase remains in force here: An EHL in such a system should be dense, with $r_s \ll 1$, and should have a large binding energy $E_i^0 > E_{ex}$. In this case E_{ex} turns out to be negligibly small in comparison with E_{cor} , which is given by

$$E_{cor} = -\frac{A}{r_s^{3/4}} E_{ex}, \quad (3.8)$$

where the coefficient $A \sim 1$ depends on the mass ratio of the electrons and holes, their anisotropy, and other details of the electron spectrum. A formal criterion for a strong anisotropy is that the following inequalities be satisfied in some density range:

$$r_s^{3/4} \ll \frac{\hbar}{a_{ex} p_F} \ll 1. \quad (3.9)$$

For multivalley semiconductors, for example, we would have $\hbar/a_{ex} p_F \sim \nu^{1/3} r_s$, and with $\nu > 1$ and $r_s \ll 1$ inequalities (3.9) can be satisfied. We then have¹²⁷

$$n_i^0 = B a_{ex}^{-3} \nu^{8/5}, \quad E_i^0 = C E_{ex} \nu^{2/5}, \quad (3.10)$$

where B and C are determined by the characteristics of the bands. It would be interesting to see an experimental test of the predictions of this model. To some extent, such a test has already been carried out (for an EHL in an ultrastrong magnetic field; Subsection 4d). We note in this connection that an empirical dependence for E_{Coul} which literally corresponds to (3.8) and which differs from (3.6) has been proposed in Refs. 129:

$$E_{Coul}(n) = -B n^p E_{ex}. \quad (3.11)$$

The best agreement with the calculated results is obtained with $b = 3.5$ and $p = 0.24$ (in the model of a highly anisotropic system we would have $p = 0.25$).

3) Uniaxially deformed germanium and silicon

That a metallic EHL becomes more stable with increasing complexity of the electron spectrum is illustrated nicely by the situation in uniaxially deformed germanium and silicon. A uniaxial deformation disrupts the equivalence of electron valleys and lifts the degeneracy of the valence band at $k = 0$. For example, when germanium is compressed along the [111] axis one of the electron valleys drops to a lower point on the energy scale, while the three others rise (Fig. 2, b and c). If the sample contains carriers, the intervalley scattering of electrons and the transitions between the bands of light and heavy holes will cause electrons to flow to a lower valley, and holes to a higher valley. As a result, the state density at the Fermi level decreases; E_{kin} increases; the binding energy of the EHL decreases; and its density decreases. These effects were first seen experimentally in Ref. 5. At a pressure $P \gtrsim 3$ kgf/mm², the splitting of the electron valleys exceeds $E_F^{(e)}$, and all the electrons populate the [111] valley. At $P \gtrsim 10$ kgf/mm² the hole splitting exceeds $E_F^{(h)}$. As $P \rightarrow \infty$, germanium becomes a single-valley semiconductor

with simple ellipsoidal bands. Corresponding changes in the spectrum in silicon are caused by compression along the [001] axis (two valleys become lower: [001] and [00 $\bar{1}$]). The behavior of the EHL in uniaxially deformed germanium and silicon has been studied in detail experimentally (Subsection 4a and Section 2). The observed decrease in the stability of the EHL is described satisfactorily by the calculation methods listed above (the calculations have been carried out for^{28,123,64} $P \rightarrow \infty$ and also for finite pressures, with allowance for the nonparabolic shape of the valence band¹³⁰⁻¹³²). The agreement between the results of the different studies, however, is significantly worse than for undeformed germanium and silicon.

4) Polar semiconductors

In a polar semiconductor the retardation of the ions in an alternating electric field gives rise to a pronounced dispersion of the dielectric permittivity at frequencies corresponding to a longitudinal optical (LO) phonon,¹³³ ω_L :

$$\epsilon(\omega) = \epsilon_\infty \epsilon_0 \frac{\omega_L^2 - \omega^2}{\epsilon_\infty \omega_L^2 - \epsilon_0 \omega^2}, \quad (3.12)$$

where $\epsilon_{(0\infty)}$ is the static (high-frequency) dielectric permittivity. The optical activity of LO phonons gives rise to a strong interaction of these phonons [the interaction is proportional to $(\epsilon_\infty^{-1} - \epsilon_0^{-1})^{1/2}$] with the electron subsystem, which in turn causes a polaron shift and a renormalization of the masses (see Ref. 134, for example). This interaction is also important to the behavior of nonequilibrium carriers. If the typical electron frequencies (E_i^0/\hbar , E_F/\hbar , E_{ex}/\hbar) were much greater than ω_L (if the ions were not able to "keep up with" the carriers), there would be a smaller dielectric permittivity ϵ_∞ in expression (2.1) for E_{ex} and in Coulomb's law, $e^2/\epsilon r$. In a polar semiconductor, however, the electron frequencies are typically comparable to ω_L , so that the interaction with LO phonons weakens the interaction between carriers and leads to a decrease in the binding energies E_{ex} and E_i^0 . The characteristics of the ground state of the EHL in polar semiconductors have been calculated in Refs. 65, 97, and 135 (for CdS, CdSe, ZnS, ZnO, AgBr, GaP, AlAs, CdTe, CnSe, ZnTe, GaAs, GaSb, InSb, InP, SiC, lead chalcogenides, and thallium halides) and in Ref. 105 (for CdS, CdSe, ZnS, CdTe, and GaAs) (Table II). A simplified version of the random phase approximation (the plasmon-pole approximation)^{135,105} and Hubbard's approximation^{65,97} have been used. Finally, a model of highly anisotropic systems (Subsection 3b2) was used in Ref. 136; calculations were carried out for multivalley polar semiconductors; lead and tin chalcogenides and thallium halides. In contrast with the situation in germanium and silicon, there are large discrepancies between the results of different calculations and also between the calculated results and the experimental results. Possible reasons for these discrepancies are inadequate information on the characteristics of the electron spectrum of these semiconductors and an inadequate accuracy of the calculation methods. The situation is aggravated by the circumstance that in polar semiconductors, φ is the difference among three large quantities, $\varphi = E_i^0 - E_p - E_{ex}$ (E_p is the

polaron shift), of which E_{ex} is usually not calculated but taken from experiments. For this reason, a 10% error in the determination of the E_i^0 can lead to large errors in the determination of φ . It may be concluded that the possibility of the formation of, and the characteristics of the ground state of, an electron-hole liquid in a semiconducting compound requires further study, both theoretical and experimental.

c) Surface properties

We have been discussing the properties of a spatially homogeneous electron-hole liquid. In reality an EHL exists in the form of droplets, whose surface inhomogeneity leads to several new properties. First, there is the finite surface energy, which can be estimated in order of magnitude by Langmuir's arguments⁶⁾ (see Ref. 137, for example):

$$\sigma \approx \frac{1}{5} \varphi (n_0^0)^{2/3}. \quad (3.13)$$

Second, near a surface there may be quantum oscillations in the carrier density, analogous to the Friedel oscillations in a metal (Fig. 3). Finally, the spatial profiles of the electron and hole densities are not identical near a surface because of the difference in their work functions, $W^{(e)}$ and $W^{(h)}$: A surface dipole layer must form on a droplet. In addition to this dipole layer, which arises even at $T = 0$, the difference between work functions should give rise at nonzero temperatures to the formation of a net surface charge on a droplet because of the preferential thermionic emission of carriers with the lower work function.

The surface tension of the EHL in germanium (and to a lesser extent in silicon) has been studied experimentally by various approaches: 1) on the basis of its effect on the con-

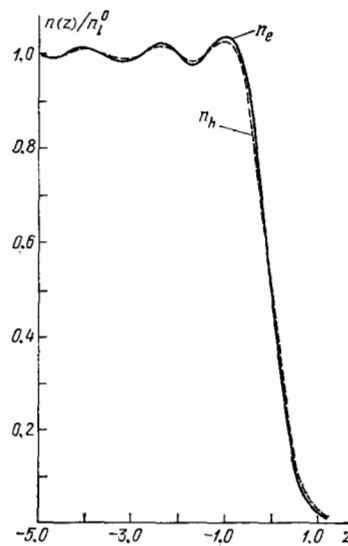


FIG. 3. Profiles of the electron and hole densities, n_e and n_h , near the surface of an electron-hole droplet in germanium.⁷⁵ The distance z is expressed in units of a_{ex} (177 Å in Ge). Since the binding energy of an electron is greater than that of a hole, n_e falls off more sharply than n_h .

⁶⁾More-rigorous arguments¹³⁸ lead to the following relation (which also holds for an EHL¹³⁹) among σ , the isothermal compressibility $\chi = [(n_i^0)^3 E^*(n_i^0)]^{-1}$ and the thickness of the transition layer at the surface, $L \sim a_{ex} \cdot \chi \sigma = L$.

densation kinetics of the EHL^{83-87,91-93} (Subsection 3e); 2) on the basis of the appearance of capillary resonances⁸⁸ (Subsection 4b and Section 2); 3) through the use of σ as an adjustable parameter determined by comparing the theoretical and experimental shapes of the phase diagram^{69,74} (Subsection 3d). The surface charge of electron-hole droplets in germanium was studied in Refs. 89 and 90 on the basis of the displacement of a droplet cloud in a static electric field.⁷⁾ Some results of this research are listed in Table I.

Theoretically, the surface properties of the EHL have been studied by the method of the Hohenberg-Kohn-Sham density functional method,^{141,142} which has proved successful for metals, nuclei, etc. (see, for example, the review by Lang¹⁴³). A gradient expansion and a variational method¹⁴¹ were used in Refs. 71, 72, 74, and 144-146; the self-consistent Kohn-Sham scheme¹⁴² was used in Refs. 73 and 75. Among the advantages of this self-consistent scheme is the possibility of obtaining quantum oscillations of the carrier density (Fig. 3); one of its disadvantages is the length of the numerical calculations. We might note in this connection that a modification of the self-consistent scheme as proposed in Ref. 147 was used in Ref. 73; this modification has been asserted by the authors to be simpler and stable in numerical calculations. Some results calculated for germanium and silicon are listed in⁸⁾ Table I. Also shown here are values of σ found from the Langmuir formula, (3.13). The agreement with experiment is good. The sign found for the charge on the electron-hole droplets in germanium by a variational method is incorrect—at odds with the experimental results. This discrepancy is not surprising since the gradient expansion can be justified for slightly inhomogeneous systems (on the scale of a_{ex}) but in the case of an electron-hole droplet the thickness of the transition layer near the surface is $\sim a_{ex}$ (Fig. 3).

We have two more comments on this topic. First, the papers cited here have generally dealt with the surface properties of an EHL occupying a half-space. This approach is not valid for an electron-hole droplet consisting of a few e-h pairs. The ground-state energy of a droplet with $j = 10-10\,000$ pairs in germanium was calculated in Ref. 149 by the density functional method. At $j < 120$, oscillations reminiscent of the shell effects in atoms were found in the ground-state energy. On the average, the energy can be described well by $E_j = -E_j^0 + 4\pi j^{2/3} \sigma (3/4\pi n_l^0)^{2/3}$ with $\sigma = 1.8 \times 10^{-4}$ erg/cm². Second, the anisotropy of the electron spectrum of a semiconductor gives rise to an anisotropy in the surface tension and to a deviation of the droplet from spherical shape. Electron-hole droplets in deformed germanium and silicon were analyzed theoretically in Ref. 150.

d) Exciton-EHL phase diagram

If the lifetime of the nonequilibrium carriers is substantially longer than the thermalization time, an equilibrium state which can be described by means of the ordinary ther-

modynamic relations is reached in the electron system. The partitioning of the system into phases at temperatures below the critical temperature occurs because at $T < T^c$ the density dependence of the chemical potential $\mu(n, T)$ becomes nonmonotonic, and the inverse function $n(\mu, T)$ becomes multivalued. The coordinates of the critical point, n^c and T^c , are determined from the condition for an inflection point in $\mu(n, T)$:

$$\left(\frac{\partial \mu}{\partial n} = \frac{\partial^2 \mu}{\partial n^2} \right)_{n=n^c, T=T^c} = 0. \quad (3.14)$$

At $T < T^c$ the densities of the liquid, $n_l(T)$, and of the gas, $n_g(T)$ are found by equating the chemical potentials and pressures in the two phases:

$$\mu(n_l, T) = \mu(n_g, T), \quad (3.15)$$

$$p(n_l, T) = p(n_g, T). \quad (3.16)$$

Since

$$\mu = f + n \frac{\partial f}{\partial n}, \quad p = n^2 \frac{\partial f}{\partial n}, \quad (3.17)$$

we must know the free energy $f(n, T)$ per e-h pair in order to determine the shape of the phase diagram. The free energy $f(n, T)$ has been calculated asymptotically exactly only for systems with a highly anisotropic spectrum (Subsection 3b and Section 2): layered (quasi-two-dimensional) semiconductors.⁶⁰ An exact equation of state and the exact shape of the phase diagram have also been derived.

The basic approximation used in the theory of the EHL in germanium, silicon, and other semiconductors which do not satisfy the conditions of a strong anisotropy consists⁶⁷ of using the expression for the free energy of a highly degenerate Fermi liquid (for $k_B T \ll E_F$):

$$f(n) = E(n) - \frac{1}{2} \gamma(n) (k_B T)^2, \quad (3.18)$$

where

$$\gamma(n) = \left(\frac{\pi}{3n\hbar^3} \right)^{2/3} (v_e^{2/3} m_{d,e} + m_{d,h}), \quad (3.19)$$

and $E(n)$ is the energy of the ground state of the metallic phase (Subsection 3b). This expression can be derived⁴⁷ for an EHL in the random phase approximation if $k_B T^c \ll \hbar \omega_p$ ($\omega_p = \sqrt{4\pi e^2 n_l^0 / \epsilon_0 m_l}$ is the plasma frequency), and only if the density is not too low ($r_s \lesssim 1$). This expression can be used to determine the coordinates of the critical point and the shape of the liquid branch of the phase diagram, but it cannot be used for the gas branch far from the critical point. For the gas phase, on the other hand, we can use the ideal gas approximation. The densities of free carriers, excitons, and biexcitons (n_c , n_{ex} , and n_b) at equilibrium are determined¹⁹ by the corresponding work functions of the EHL: $n_j \propto \exp(-W^{(j)}/k_B T)$, $W^{(c)} \sim 1/2 E_l^0$, $W^{(ex)} = \varphi$, $W^{(b)} = 2\varphi - E_D$. Since the condition $E_l^0 > 2\varphi$ holds in germanium and silicon (Table I), and the dissociation energy of a biexciton is small (Section 2), the "atmosphere" around an electron-hole droplet consists primarily of excitons. We thus have

$$f(n_g) \approx f_{ex}(n_{ex}) = -E_{ex} - k_B T \left\{ 1 + \ln \left[\frac{n}{v_{ex}} \left(\frac{2\pi \hbar^3}{k_B T m_{ex}} \right)^{3/2} \right] \right\}, \quad (3.20)$$

⁷⁾There is an alternative explanation for the drift of electron-hole droplets in an electric field: their entrainment by fluxes of electrons and holes.¹⁴⁰

⁸⁾The surface tension and the sign of the charge have also been calculated for deformed germanium and silicon^{72,74,75} and for GaP (Ref. 148).

where ν_{ex} and M_{ex} are the degeneracy and mass of the exciton state density. Far from the critical point the exciton pressure is low, and from the condition $p(n_i) = 0$ we find

$$n_i(T) = n_i^0 \left[1 - \frac{\delta_n}{2} (k_B T)^2 \right], \text{ where } \delta_n = \frac{\nu'(n)}{n E^0(n)} \Big|_{n=n_i^0}. \quad (3.21)$$

The equilibrium exciton density is determined from the condition $\mu_i = \mu_{\text{ex}}$:

$$n_{\text{ex}, T} = \nu_{\text{ex}} \left(\frac{k_B T M_{\text{ex}}}{2\pi\hbar^2} \right)^{3/2} \exp \left(-\frac{\Phi}{k_B T} \right). \quad (3.22)$$

This is the ordinary expression for the saturation vapor density in the ideal gas approximation (see Ref. 137, for example).

The values of n^c , T^c , and δ_n were derived theoretically for germanium and silicon⁹⁾ in Refs. 67 and 70. The ideal gas approximation cannot be used to determine the shape of the phase diagram near T^c . The nonideal nature of the electron gas and also the thermal dissociation of excitons were taken into account in Refs. 68 and 151. The heterophase fluctuations (liquid nucleation centers in the gas phase and gas bubbles in the liquid phase) were taken into account in Refs. 69, 70, and 66, with the result that it was possible to reproduce the experimental shape of the phase diagrams in germanium (Fig. 4) and silicon quite accurately. The results of this approach and of the previous approaches are shown in Table I. All the methods yield numerical values in order-of-magnitude agreement with the experimental values. The lowest values of T^c are found in the fluctuation model. In the case of germanium, these values are also the values which agree best with the experimental values.

The theoretical determination of the characteristics of the phase diagram simplifies substantially if approximation (3.6) (Refs. 126 and 132) or (3.11) (Ref. 129) for E_{Coul} is used. In each case the equation for n^c and T^c , in reduced exciton

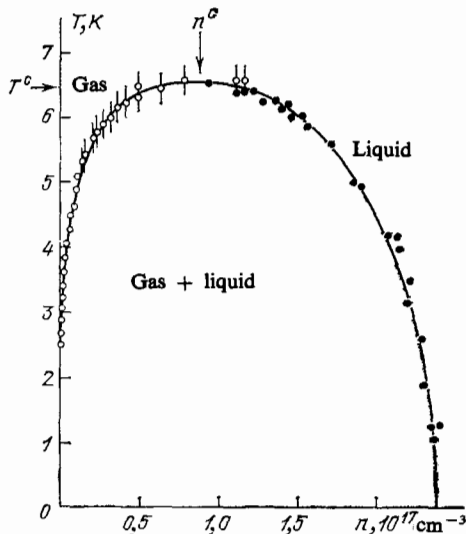


FIG. 4. Phase diagram for the transition between an exciton gas and an EHL in germanium. Points—experimental⁶¹; curve—theoretical.⁶⁹

⁹⁾And also for uniaxially compressed germanium and silicon^{64,130,132} and the polar semiconductor CdS, CdSe, ZnS, CdTe (Ref. 105), and GaAs (Refs. 64 and 105).

units, depends only on n_i^0 . In these models the following scaling relation thus holds:

$$\frac{n^c}{n_i^0} \sim \text{const.} \quad (3.23)$$

Using relation (3.11), we can also derive some other scaling relations, e.g.,¹²⁹

$$k_B T^c \sim 0.1 E_i^0. \quad (3.24)$$

A corresponding relation holds in the exactly solvable model of a highly anisotropic system,⁶⁰ mentioned above; this relation is apparently a common relation for first-order phase transitions.³⁶ The scaling relations for the EHLs in germanium and silicon have been checked experimentally.^{66,132,152}

The shape of the liquid branch of the phase diagram has been determined experimentally from the temperature dependence of the spectrum of the recombination radiation of an EHL (Subsection 4a), while the shape of the gas branch has been determined from the thresholds for the appearance of an EHL.^{56,58,92,153,154} Attempts to use (3.22) to describe the gas branch of the experimental phase diagram in germanium have yielded a value for φ (Refs. 58 and 153–156) which is substantially ($\sim 30\%$) lower than the spectroscopic value (Subsection 4a). A similar result has been observed in silicon.^{56,92} This matter is the so-called problem of the difference between the thermodynamic and spectroscopic values of φ (Subsection 3e).

e) Condensation and decay of an EHL; dimensions of an EHL

The finite carrier lifetime has been ignored in the study of the ground state and thermodynamics of EHLs. This simplification is justified for germanium and silicon, where the carrier lifetimes are more than 10^2 times the scale times for the thermalization and formation of excitons. Even in these semiconductors, however, recombination makes the transition between excitons and an EHL quite different from an ordinary gas-liquid transition. The EHL must be supplied a flux of electrons to compensate for recombining e-h pairs. The dimensions of the electron-hole droplets thus cannot be arbitrarily large, and the gas of excitons must be supersaturated; i.e., its density must exceed the thermodynamic-equilibrium value $n_{\text{ex}, T}$ in (3.22). We wish to stress that this supersaturation occurs in addition to the supersaturation which is characteristic of any first-order phase transition and which is associated with the positive sign of the surface energy of the interface. This supersaturation has a curious consequence: At extremely low temperatures, where the thermal evaporation of excitons from the droplets is slight, the exciton-EHL transition can occur without the hysteresis phenomena characteristic of first-order transitions.

In this subsection we will be discussing the processes which determine the size (R) and density (n_d) of electron-hole droplets and the density of the exciton gas between droplets (n_{ex}) in the case simplest to deal with theoretically: that of a spatially uniform excitation. (In the case of nonuniform excitation, the phonon wind has a decisive effect on the behavior of the EHL; see Section 6.)

Experimentally, the condensation and decay of EHLs have been studied most thoroughly in germanium and sili-

con. The exciton lifetime τ_{ex} in these semiconductors ($\sim 10^{-6}$ s) varies from sample to sample and is determined primarily by radiationless recombination processes, whose mechanisms have not been studied adequately. The carrier lifetime in an EHL, τ_l (measured for germanium in Refs. 125 and 157–159 and for silicon in Refs. 160–163), in contrast, is an internal characteristic of the EHL and does not change even if the sample is doped to a level of $0.1 n_l$. This lifetime is determined by radiative recombination (whose probability is proportional to n_l) and by radiationless Auger recombination, with the energy of the recombining pair being transferred to a third carrier (with a probability $\propto n_l^2$):

$$\tau_l^{-1} = Bn_l + Cn_l^2. \quad (3.25)$$

The quantum efficiency of the radiative recombination,

$$Q = Bn_l / (Bn_l + Cn_l^2)^{-1}, \quad (3.26)$$

is quite high in germanium^{125,157–159}: $Q \sim 0.25–0.8$. In silicon, the higher density of the EHL makes Auger recombination the dominant process, and we have¹⁶⁰ $Q \sim 5 \cdot 10^{-4}$. The value of C was calculated for germanium and silicon in Ref. 164, and the results agree well with experimental data.

For a given exciton generation rate $g(t)$ (per cm^3), the values of R , n_d , and n_{ex} are related by balance equations for the numbers of particles in the liquid and exciton phases, which were first used, in a simplified form, in Ref. 125 (see also Refs. 8 and 9) and, with surface tension, in Refs. 165 and 166:

$$n_l \frac{d}{dt} \left(\frac{4}{3} \pi R^3 \right) = -\frac{4}{3} \pi R^3 \frac{n_l}{\tau_l} + 4\pi R^2 [n_{ex} - n_{ex, T}(R)] v_{ex, T}, \quad (3.27)$$

$$\frac{dn_{ex}}{dt} = g - \frac{n_{ex}}{\tau_{ex}} - 4\pi R^2 [n_{ex} - n_{ex, T}(R)] v_{ex, T} n_d, \quad (3.28)$$

where $v_{ex, T} = \sqrt{k_B T / 2\pi M_{ex}}$ is the average thermal velocity of the excitons, and $N_{ex, T}(R) = n_{ex, T} \exp(2\sigma / n_l R k_B T)$ is the thermodynamic-equilibrium density of excitons at the surface of a droplet. Equation (3.27) describes the change in the number of pairs in a droplet due to recombination and the exchange of excitons with the gas phase. Equation (3.28) is constructed in an analogous way. [More-comprehensive balance equations, incorporating free carriers, were used in Refs. 153 and 167–170. Because of the low density, free carriers usually have little effect, but in magnetic and microwave fields they give rise to some interesting effects (Subsection 4e).]

Equations (3.27) and (3.28) must be supplemented with a condition determining the droplet density n_d . For steady-state excitation, however, n_d remains constant even for a substantial length of time after the excitation is turned off, and Eqs. (3.27) and (3.28) are sufficient for understanding many aspects of the situation. At low temperatures (at $T \lesssim 3$ K in germanium), for example, $n_{ex, T}$ is low, and the decay of droplets is exponential:

$$R(t) = R(0) \exp\left(-\frac{t}{3\tau_l}\right). \quad (3.29)$$

For a long time after the pumping is turned off the relation $n_{ex} \sim n_{ex, T}$ holds¹⁷¹ (Fig. 5). With increasing temperature, evaporation becomes important, and the functional depen-

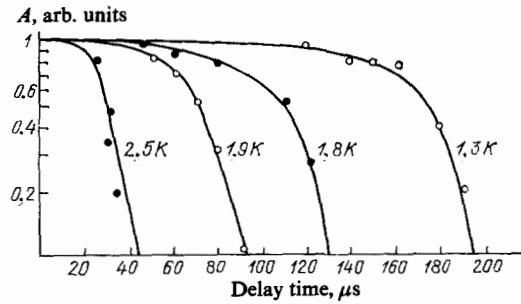


FIG. 5. The amplitude (A) of the microwave conductivity of a sample in a strong pulsed microwave field as a function of the delay of the puncturing pulse at various temperatures.¹⁷¹ ($A \propto n_{ex}$). The amplitude is normalized to a unit maximum value; the curves are labeled with the temperatures.

dence $R(t)$ becomes nonexponential.^{153,155}

From (3.27) we find an equation for the steady-state radius of an electron-hole droplet for a given value of n_{ex} (with $g = \text{const}$)¹⁶⁶:

$$n_{ex} = n(R), \text{ where } n(R) = n_{ex, T}(R) + \frac{n_l R}{3v_{ex, T}\tau_l}. \quad (3.30)$$

Figure 6 shows a typical function $n(R)$. Steady-state electron-hole droplets exist if $n_{ex} > n_{min}$ and if the radius is no less than R_{min} given by the condition^{165,166}

$$R_{min}^3 = 6 \frac{\sigma v_{ex, T}\tau_l}{n_l^2 k_B T} n_{ex, T}(R_{min}). \quad (3.31)$$

At $n_{ex} > n_{min}$, Eq. (3.30) has both stable and unstable solutions R^s and R^c ; R^s is the steady-state size of the droplet for a given n_{ex} . Experimentally, however, it is g which is given, and n_{ex} depends on the density of the droplets which form, as can be seen from (3.28). For this reason, a complete understanding of the processes requires an analysis of the droplet formation mechanism, to which we now turn.

The density of electron-hole droplets depends on the particular experimental conditions^{172,166,173} (see, for example, Fig. 7), and is not affected by the number of any sort of fixed nucleation centers. Heterophase fluctuations play a leading role in the formation of the nucleation centers.¹⁰

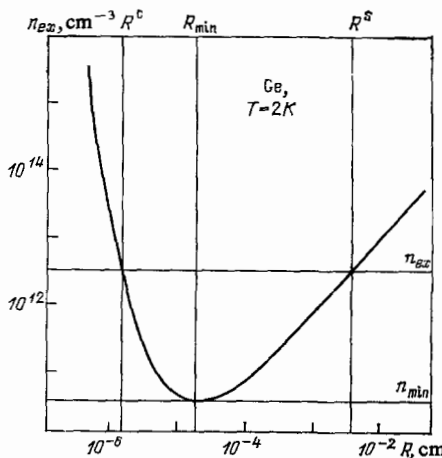


FIG. 6. The function $n(R)$ in (3.30) for an EHL in germanium at $T = 2$ K.

¹⁰Even in the purest germanium samples, the density of the electron-hole droplets, $n_d \lesssim 10^8 \text{ cm}^{-3}$, is far lower than the impurity density, $n_{im} > 10^{10} \text{ cm}^{-3}$; the impurities may serve as nucleation centers.

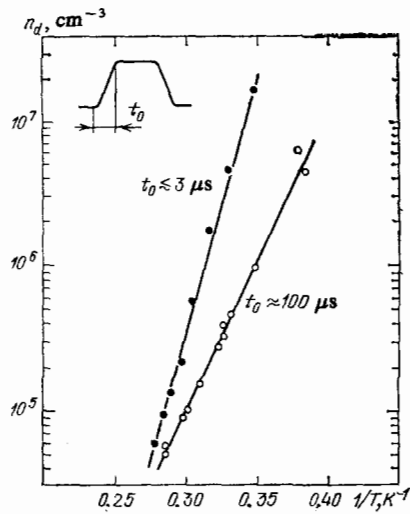


FIG. 7. Experimental temperature dependence of the density of electron-hole droplets in germanium for long and short rise times of the excitation pulses.¹⁶⁶ The inset at the upper left shows the shape of the exciting pulse.

This is a well-known circumstance in the case of ordinary gas-liquid transitions, characterized by the appearance of metastable states and hysteresis effects. Hysteresis effects are also observed in the course of condensation of excitons in germanium^{174-180,166,84,85,87} and silicon.^{92,93} These effects are seen as differences in the threshold excitation intensities when the pump is turned on and off and as a dependence of the density and sizes of the electron-hole droplets on the rate at which the excitation is turned on (Figs. 7 and 8). During steady-state excitation in germanium, the conditions under which the droplets appear are "remembered"¹¹¹ for 10^4 - 10^5 s (Ref. 85). The individual droplets may therefore exist long enough for a succession of $\sim 10^9$ generations of pairs in each droplet. (By way of comparison, 10^9 human generations would be the lifetime of the universe starting with the Big Bang.) The hysteresis effects in an e-h system with a finite particle lifetime of course have some distinctive features. At extremely low temperatures, $T < T^H$ ($T^H \sim 1.3$ K in germanium^{175,85} and $T^H \sim 10$ K in silicon^{92,93}), no hysteresis is observed. In this case the phase transition should be more reminiscent of a second-order transition. This may be the situation which we are observing at low temperatures in silicon, where the appearance of an EHL is preceded by the

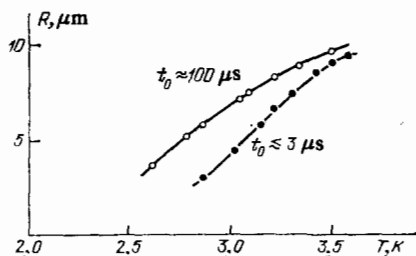


FIG. 8. Experimental temperature dependence of the radius of the electron-hole droplets in germanium for long and short rise times of the excitation pulses.¹⁶⁶

¹¹¹The hysteresis in silicon lasts a considerably shorter time,⁹³ $\sim 100\tau_l$, apparently because of a greater effect of the phonon wind.

formation of exciton-impurity complexes¹⁸¹ (see also Refs. 9 and 181a).

Essentially everything we know about the condensation of excitons (including the problem of the difference between the thermodynamic and spectroscopic values of φ) can be explained^{165,182,175,84,176} by the kinetic condensation theory of Becker, Döring, and Zel'dovich^{183,137} generalized to allow a finite carrier lifetime.¹² It turns out that the probability for the appearance of a liquid-phase nucleation center with j particles is proportional to $\exp(-\Phi_j/k_B T)$, where

$$\Phi_j = 4\pi R_j^3 \sigma - j k_B T \ln \frac{n_{ex}}{n_{ex,T}} + k_B T \sum_{p=2}^j \ln \left(1 + \frac{p^{1/3}}{\alpha_p \tau_l} \right), \quad (3.32)$$

$$\alpha_p = \pi r_s^2 v_{ex}, \tau n_{ex}, \tau(R_p), \quad R_p = r_s p^{1/3}.$$

The sum of the first two terms in (3.32) is the thermodynamic potential of a nucleation center in the limit $\tau_l \rightarrow \infty$: The first term is the positive surface contribution, while the second, equal to $(\mu_{ex} - \mu_l)j$, reflects the circumstance that condensation is thermodynamically favored if $n_{ex} > n_{ex,T}$. In an ordinary gas-liquid transition at small values of j , the surface contribution is predominant, and the gas phase turns out to be separated from the liquid phase by a barrier (Fig. 9a), which also explains the appearance of metastable states. The third term in (3.32) changes this picture substantially (Fig. 9b). At $n_{ex} < n_{min}$, Φ_j increases monotonically with increasing j , despite the condition $n_{ex} > n_{ex,T}$. There are no stable droplets. At $n_{ex} > n_{min}$, Φ_j becomes nonmonotonic. In addition to the unstable (critical) radius R^c (with the maximum Φ_j) there is a stable radius R^s (with a minimum Φ_j).

It is usually necessary to superheat a liquid in order to initiate the inverse transition to the gas phase. In this case the barrier can be overcome by fluctuations from the side of either the gas or the liquid at $n_{ex} > n_{ex,T}$. However, the barrier heights for these transitions Δ_c and Δ_d (Fig. 9b), are

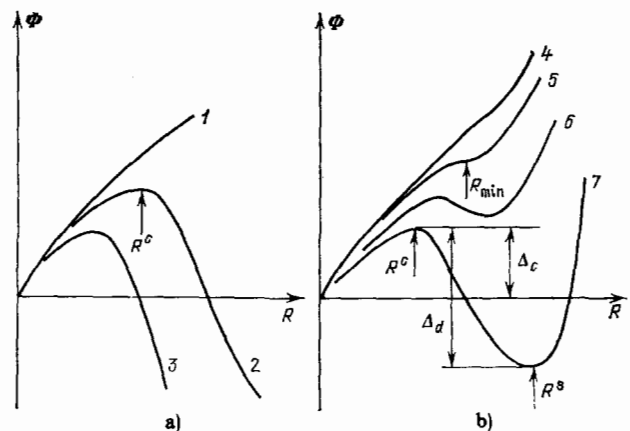


FIG. 9. The effective thermodynamic potential $\Phi(R)$ for nucleation center of radius R for (a) $\tau_l \rightarrow \infty$ and (b) $\tau_l < \infty$. The upper curves in both parts of the figure correspond to lower supersaturations: 1, 4— $n_{ex} = n_{ex,T}$; 2, 3, 5-7— $n_{ex} > n_{ex,T}$; 5— $n_{ex} = n_{min}$; 6, 7— $n_{ex} > n_{min}$.

¹²An intermediate approach was taken in Ref. 166: The finite lifetime τ_l was incorporated in equations like (3.27) and (3.28), while the classical Becker-Döring formula was used for the formation rate of nucleation centers. This approach yields good results if $T > T^H$ and $n_{ex} > n_{min}$. The results of some numerical calculations based on this theory are reported in Ref. 86.

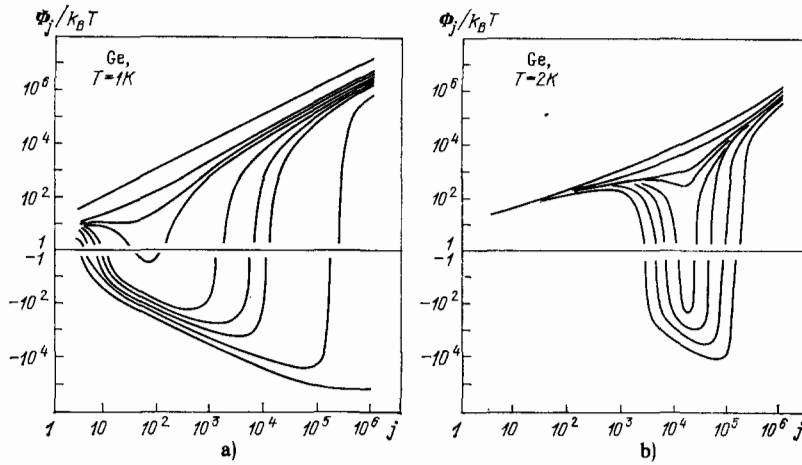


FIG. 10. Effective thermodynamic potential Φ_j in (3.32) for germanium at (a) $T = 1$ K and (b) 2 K. a— From top to bottom: $n_{ex}/n_{ex,T} = 1; 2 \cdot 10^4; 7 \cdot 10^4; 10^5; 2 \cdot 10^5; 3 \cdot 10^5; 4 \cdot 10^5; 10^6; 2 \cdot 10^6$ [$n_{ex,T}(1 \text{ K}) = 3 \cdot 10^5 \text{ cm}^{-3}$]; b—1; 1.25; 2; 2.1; 2.15; 2.2; 2.3; 2.5 [$n_{ex,T}(2 \text{ K}) = 1.7 \cdot 10^{11} \text{ cm}^{-3}$]. At $T = 1$ K, there is no barrier in Φ_j .

generally different and behave in different ways as functions of the degree of supersaturation. Specifically, Δ_d increases, and Δ_c decreases, with increasing n_{ex} . Since the rates of both processes are proportional to $\exp(-\Delta_{c,d}/k_B T)$, there may exist an interval of n_{ex} in which both the formation of new droplets and the fluctuational decay of existing droplets occur exponentially slowly. This situation would explain the existence of memory.¹⁷⁵

At extremely low temperatures, $T < T^H$, where recombination outstrips evaporation in the liquid, the barrier disappears from Φ_j (Fig. 10), taking with it the possible occurrence of hysteresis.^{175,184,185} The numerical values found for T^H in germanium and silicon in Refs. 175, 184, and 185 agree with the experimental results (as discussed above). For direct-band semiconductors with short values of τ_l , there should be no barrier anywhere in the region in which an EHL exists,¹⁸⁵ $0 < T < T^c$.

The disappearance of the barrier at low temperatures is a common feature of first-order transitions in systems with a finite particle lifetime.¹⁸⁶ In the limit $T \rightarrow 0$, the solution of (3.31), $R_{min} \rightarrow R_0 = 2\sigma/n_0^0\varphi$, becomes independent of τ_l . Using the Langmuir formula, (3.13), we find that the number of particles in such a droplet is $j_0 = 4/3\pi^3 R_0 n_0^0 \sim 0.3 < 1$. Since the condition $R^c < R_{min}$ holds for an arbitrary supersaturation, there is no barrier in Φ_j if the temperature is low enough (the barrier goes into the region $j < 1$). It is a simple matter to estimate¹⁸⁶ T^H :

$$k_B T^H \sim \varphi \left[\ln \left(\xi \frac{\tau_l \varphi}{\hbar} \right) \right]^{-1} \quad (3.33)$$

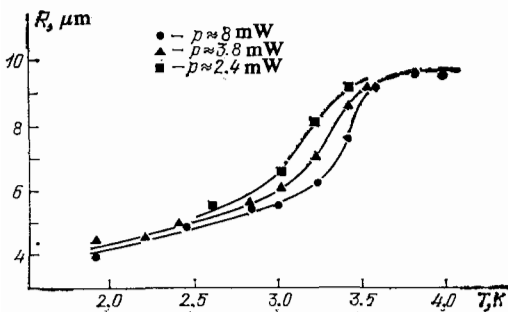


FIG. 11. Temperature dependence of the radius of electron-hole droplets in germanium at three excitation intensities P with $t_0 \leq 3 \mu\text{s}$ (see Fig. 7).¹⁶⁶

[a parameter $0 < \xi < 1$ to reflect the degree of inelasticity of the collisions of excitons with droplets can be introduced in (3.27) and (3.28)]. For an EHL in germanium with $\xi = 0.2-1$, expression (3.33) yields $T^H \approx 1.3$ K. Setting $\xi \sim 1$ for silicon, we find $T \approx 6$ K. Agreement with the experimental value of 10 K is achieved with $\xi \sim 10^{-2}$. This value corresponds to the value found in Refs. 92 and 93 by fitting the predictions of the condensation theory to experimental data.

We note in conclusion that many of the experiments carried out in germanium indicate that a mechanism is operating to retard or limit the growth of droplets with radii above 10–20 μm (Refs. 172, 166, 187, 188; see, for example, Figs. 8 and 11). This mechanism is not explained by the interpretation discussed above. An attempt was made in Ref. 166 to improve the agreement between theory and experiment by incorporating the diffusion of excitons in (3.27) and (3.28). The recombination instability of droplets due to the condensation flux of excitons to the droplets and the recombination flux of carriers within the droplets was studied in Ref. 189. Efforts to solve this problem have revealed the role played by the phonon wind (Section 6), which has also explained many other phenomena involving electron-hole droplets.^{190,191}

4. EXPERIMENTAL METHODS; EXTERNAL AGENTS

Figure 12 shows a schematic representation of experiments on EHLs. The semiconducting sample is placed in a cryostat and cooled to the desired temperature (1–6 K in the

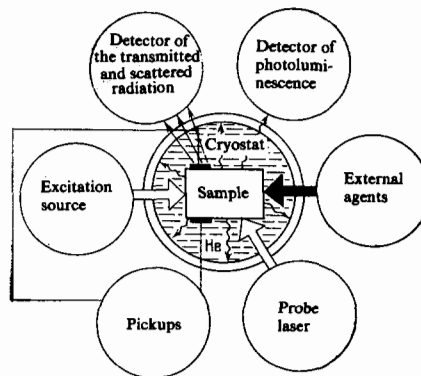


FIG. 12. Simplified diagram of the experiments with an EHL.

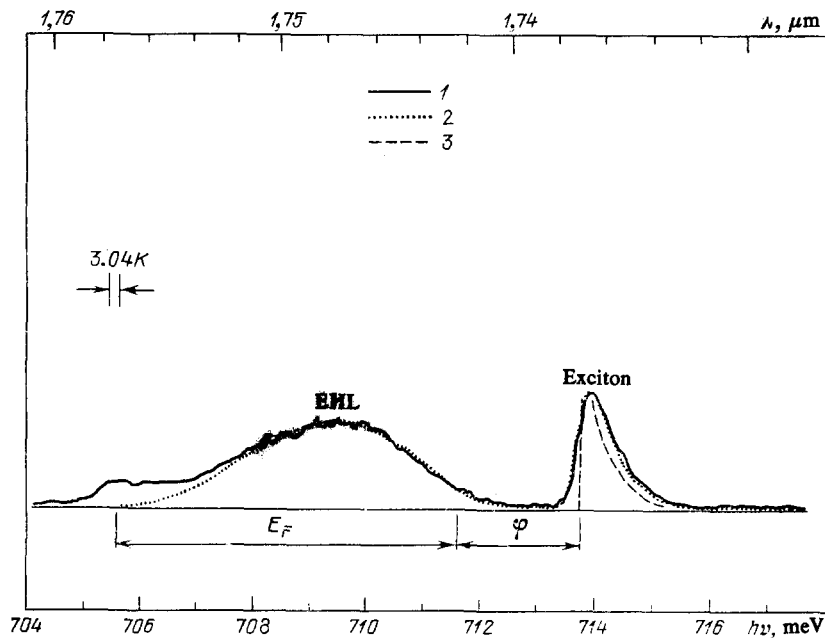


FIG. 13. Photoluminescence spectrum of germanium at $^{195} T = 3.04$ K. 1—Experiments; 2, 3—theoretical, with and without allowance for the finite width of the spectrometer slit.

case of germanium). The excitation source is usually a cw or pulsed laser. By using excitation sources with various wavelengths one can achieve either a surface excitation of the sample or a more or less uniform excitation. The recombination radiation can be detected with spectral, spatial, or temporal resolution. A laser beam whose wavelength is in the transparency region of the given semiconductor, is used to probe the EHL (the absorption or scattering of the light is measured). The pickups—various contacts on the surface of the sample—are used to measure the photocurrent, heat and sound pulses, etc. A wide variety of external agents can be used; for example, the sample can be placed between the pole tips of a magnet, in a microwave resonator, or in a clamp for the application of pressure.

a) Recombination radiation

Recombination radiation is one of the basic sources of information about nonequilibrium carriers. When an EHL forms, a characteristic line appears in the luminescence spectrum (Fig. 13). The basic features of this line can be understood by examining the energy diagram of the EHL (Fig. 1). The line is asymmetric; it has a width $\sim E_F$; and its high-energy wing is shifted on the low-energy side of the exciton line by a distance equal to the exciton work function φ . The shape of the line depends slightly on T (on the thermal spreading of the Fermi distribution at $k_B T < E_F$) but does not depend on the excitation intensity. Finally, in accordance with the characteristic features of a first-order transition, this line appears in the luminescence spectrum when a threshold is reached (as T is reduced or as the excitation intensity is raised). The electron-hole liquid has been discovered on the basis of these pieces of evidence.² Study of the luminescence has subsequently been used widely to determine the equilibrium parameters of the EHL,^{125,157,192-194} their temperature dependence,^{81,195,86,161,56,79} and their dependence on external agents (a magnetic field^{196-201,158} or deformation of the semiconductor^{5,202,157,24,79,163,66}). The

gas branch of the phase diagram has been determined^{174,153} from the thresholds for the appearance of the EHL line, and hysteresis phenomena have been studied.^{174,84,173,175,85,92} Extensive information on the appearance and decay of EHLs comes from study of the kinetics of the lines in the recombination spectrum in experiments with pulsed excitation.^{155,160,161,158,203,204} Spatially resolved measurements of the luminescence can be used to study the motion of electron-hole droplets and the formation and shape of the cloud of droplets.^{89,205-209} The intrinsic recombination radiation yielded the first photographic image of a huge droplet in nonuniformly compressed germanium²¹⁰ (Subsection 4b and Section 3).

In indirect semiconductors the radiative recombination is accompanied by the emission of phonons, and the line is shifted by the corresponding energy,¹³⁾ $\hbar\omega_{ph}$. The selection rules generally allow recombination involving phonons of several modes¹⁴⁾; the line doubles; and so-called phonon repetitions form (and may partially overlap). In the case of allowed transitions (e.g., transitions involving a longitudinal acoustic phonon in germanium), the spectral density of the recombination radiation of the EHL is

$$I(h\nu) = |M_0|^2 \int_0^{\infty} d\varepsilon^{(e)} d\varepsilon^{(h)} f_e(\varepsilon^{(e)}) f_h(\varepsilon^{(h)}) \rho_e \rho_h \delta(\hbar\nu + \hbar\omega_{ph} - E_g' - \varepsilon^{(e)} - \varepsilon^{(h)}), \quad (4.1)$$

where ν is the photon frequency, ρ_{eh} is the state density of the electrons and holes, M_0 is the transition matrix element for the band extrema, and $f_{e,h} = \{\exp[(\varepsilon - E_F^{(e,h)}(T))/k_B T] + 1\}^{-1}$ are the Fermi distribution functions. The shape of the line depends on two adjustable parameters: the EHL temperature T , which may differ from the sample tem-

¹³⁾A recombination of electrons and holes in an EHL in germanium involving a plasmon has recently been observed.^{210a}

¹⁴⁾The selection rules for such transitions in germanium were discussed in Ref. 76.

perature T_0 , and the density $n_i(T)$ [which determines $E_F^{(s,h)}(T)$]. The value of φ is found from the shift of the high-energy boundary of the EHL line with respect to the exciton peak.

Expression (4.1) gives a satisfactory description of the shape of the allowed phonon repetitions in germanium and silicon^{125,157,193,211,195,76} (Fig. 13). The reason for the deviation of the theoretical curve from the experimental data at low frequencies is that in this energy range the EHL remains in an excited state after the recombination. The corresponding correction was made in Refs. 212, 40, 194, 24, and 77. In the case of forbidden transitions, e.g., those involving a transverse acoustic phonon in germanium,^{193,213,76} expression (4.1) again gives a satisfactory description of the experimental line shape under the assumption that the matrix element is given by $M = M_e K^{(e)} + M_h k^{(h)}$.

When corrected at low energies, expression (4.1) can also be applied to direct-band semiconductors.¹⁰⁸ The line shape in this case may be distorted by stimulated emission. Special procedures are used to avoid this possibility.^{108,214} On the other hand, a study of the stimulated emission becomes an independent method for determining the characteristics of the EHL in a direct-band semiconductor.¹⁰⁷⁻¹¹² The absorption coefficient for light at frequency ν is related to $I(h\nu)$ in (4.1) by²¹⁵

$$\alpha(h\nu) \propto I(h\nu) \left\{ \exp\left[\frac{h\nu - E'_g - E_F(T)}{k_B T}\right] - 1 \right\} \quad (4.2)$$

and is negative (the absorption is replaced by a gain) at frequencies $E'_g < h\nu < E'_g + E_F(T)$. We note in this connection that EHLs can be used to achieve huge gains ($\alpha \gtrsim 10^3 \text{ cm}^{-1}$; Ref. 108).

We might add that at the threshold for their appearance, the electron-hole droplets are small, and the surface component of the energy of the liquid, $2\sigma/n_i R$, is appreciable. This component is seen as a shift of the recombination line toward a higher energy, so that σ or R can be measured.^{216,178}

b) Deformation of a semiconductor

The electron spectrum of a semiconductor changes upon deformation, with dramatic consequences for the properties of nonequilibrium carriers.

1) Uniform deformation

Experiments involving uniform uniaxial compression (Refs. 5, 202, 157, 217, 27, and 218 for germanium; Refs. 219, 24, 48, and 66 for silicon) provide a test of the theoretical methods for calculating the characteristics of the EHL upon changes in the band structure of the semiconductor. As pressure directed along certain crystal directions is increased, the structure of the filled bands of germanium and silicon simplifies (Fig. 2), leading to decreases in the density and binding energy of the EHL. In a highly compressed crystal, E^0 becomes comparable to E_b , so that luminescence of biexcitons can be observed.²³⁻²⁷

An interesting phenomenon occurs in uniaxially compressed germanium and silicon in connection with the slow pace of intervalley scattering of electrons (the scale time is

10^{-6} s; Refs. 28, 206, and 78). After excitation of a compressed sample by a short light pulse and rapid thermalization, all the valleys become populated with electrons identically; only then do the electrons begin to spill over slowly into the lower valleys. Accordingly, electrons of two types—“hot” (i.e., the electrons in the upper valleys) and “cold”—exist in the system for a long time (in comparison with the EHL formation time). Some very interesting phase diagrams have been predicted for such a Fermi system. In particular, the liquid may stratify into two phases with different relative densities of hot and cold electrons.^{131,220-222} The emission accompanying the recombination of holes with hot and cold electrons in EHLs in compressed germanium and silicon has been detected experimentally.^{223,78,206} Certain predictions of the model for the stratification of the liquid into two phases have also been confirmed.²²⁴ Nevertheless, the question still requires more-detailed study.

The first experiments with uniaxially compressed germanium revealed⁵ that the behavior of the EHL depends strongly on the uniformity of the applied pressure. The reason lies in the motion of electron-hole droplets in the strong fields created by a nonuniform deformation. The width of the band gap of the semiconductor and thus the energy of the e-h pairs depends on the deformation. If the deformation is nonuniform, the energy varies from point to point, and a force per pair¹⁵⁾

$$\mathbf{f}(\mathbf{r}) = -\text{grad } D_{ij} u_{ij}(\mathbf{r}) \quad (4.3)$$

is imposed on the carriers in the crystal; here $u_{ij} = (1/2)(\partial u_i / \partial r_j + \partial u_j / \partial r_i)$ is the strain tensor, $\mathbf{u}(\mathbf{r})$ is the displacement of the point \mathbf{r} of the crystal from its equilibrium position, and $D_{ij} = D_{ij}^{(e)} + D_{ij}^{(h)}$ is the resultant strain-energy tensor of the electrons and holes. This tensor is determined by the symmetry of the crystal and has been studied thoroughly for such semiconductors as germanium and silicon.²²⁶

The appearance of nonuniformities is unavoidable in experiments with deformed samples. Special methods for applying pressure are used to maximize the uniformity.^{218,27} On the other hand, in many experimental studies the deformation has deliberately been made nonuniform. These studies have been (1) experiments on the motion of electron-hole droplets in static nonuniform fields, (2) experiments in which a pressure field configuration with a maximum of the shear strain in the sample is used to produce and study so-called large electron-hole droplets (or γ -droplets, in distinction from the α -droplets in an undeformed semiconductor), and (3) experiments with ultrasound.

2) Motion of electron-hole droplets in static, nonuniform strain fields

If the force in (4.3) varies only slightly over distances of the order of the droplet radius, the droplets move without any change in shape at the drift velocity

$$\mathbf{v}_d = \frac{\mathbf{f}}{(m_e + m_h) \gamma} \quad (4.4)$$

¹⁵⁾Expression (4.3) applies only to nondegenerate bands. When relations of this type are used for germanium and silicon, the multivalley nature and the splitting of the valence band must be taken into account. The renormalization of the strain potential in the EHL must also be taken into account (see Ref. 225, for example).

where $\gamma = \tau_p^{-1}$ is the reciprocal of the momentum relaxation time of the EHL (Subsection 5a). Experiments with controllable strain gradients, in which the droplet velocity is measured, can be used to determine τ_p , which is an important characteristic of an EHL. A variety of methods have been used to produce nonuniform pressures: Samples with a varying cross section perpendicular to the axis of the applied pressure have been used,^{202,227,228,178} and also hemispherical²⁰⁶⁻²⁰⁹ and prismatic²²⁹ pistons. The velocity of the electron-hole droplets has been determined from the recombination radiation measured with spectral resolution and time resolution (and, in Refs. 206-209, with spatial resolution).

The motion of droplets has been studied in greatest detail in some recent studies of germanium^{206,209,229} and silicon.²⁰⁷ Relation (4.4) was tested in Refs. 207 and 209, and γ was studied as a function of the temperature and the velocity. The results can be explained in excellent fashion by assuming that the primary mechanism for the momentum relaxation of an EHL is the scattering of carriers by thermal lattice phonons (Subsection 5a). Kukushkin and Kulakovskii²²⁹ studied the motion in strain gradients which should have accelerated the droplets to a supersonic velocity, but it was found that the droplets are destroyed in such strong fields. These experiments did not unambiguously reveal whether the destruction resulted from the overheating of the droplets or from an instability in their shape as the sonic barrier was approached. We will discuss both possibilities in Section 5.

3) Potential well formed by a nonuniform deformation; large electron-hole droplets

When elastic bodies are in contact, the various components of their strain tensors depend in different ways on the distance from the contact surface. The band structure of germanium or silicon is sensitive to certain combinations of the components of the strain tensor, and it is possible to arrange a pressure configuration which produces a minimum of the band gap in the interior of the sample.²³⁰ In such a situation, a potential well arises, and near the bottom of this well the energy of the e-h pairs can be described by

$$E(\mathbf{r}) - E(\mathbf{r}_0) \propto (\mathbf{r} - \mathbf{r}_0)^2. \quad (4.5)$$

In order of magnitude, experiments with germanium²³⁰ yield $\alpha \sim 10$ meV/mm².

Pressure configurations of this sort have proved convenient in many experiments. In Subsection 4b2 we mentioned some studies^{206,207,209} which used such a configuration to study the motion of electron-hole droplets. The motion of excitons has also been studied.^{25,231} The momentum relaxation time of the excitons has been studied; in addition, the equilibrium distribution of excitons, the formation of biexcitons, and their equilibrium with excitons have been studied. The equilibrium distribution of excitons, studied on the basis of the spatial profile of the luminescence, has turned out to be a Boltzmann distribution: $n_{\text{ex}}(\mathbf{r}) \propto \exp[-E(\mathbf{r})/k_B T]$.

The most interesting possibility associated with the potential well in germanium is the formation of a huge elec-

tron-hole droplet (γ -droplet) in the well with a radius as large as¹⁶⁾ 0.5 mm. The γ -droplets were discovered²³² in experiments on the magnetoplasma Alfvén resonance (Subsection 4g), which can occur only in a unified conducting volume, not in a cloud of small droplets. Experiments with large droplets have made it possible to study the energetics of an EHL during high uniform compression.²³³ If the continuous excitation is not intense, the radius of the droplet will be small (50 μm , say), and the droplet will be in a region with a strain which varies only slightly. The reduced density and binding energy which are characteristic of the EHL in compressed germanium are also observed in γ -droplets. In accordance with (3.25), a decrease in n_i leads to an increase (by an order of magnitude) in the lifetime τ_i . In experiments with uniform pressure this increase would be difficult to observe because of surface recombination.

With increasing excitation intensity the size of the γ -droplet increases, and the nonuniformity of the strain becomes important. The potential well compresses the EHL (this effect was studied theoretically in Ref. 235), as can be seen in a decrease in τ_i , a broadening of the droplet emission line,²³³ and a decrease in the average density of the γ -droplet produced by a short pulse during the decay of the droplet.²³⁶ The degree of compression is determined by the isothermal compressibility of the EHL (see footnote⁶⁾), which can accordingly be measured "mechanically."

The behavior of a γ -droplet in a magnetic field is interesting. The shape of the droplet changes because of recombination magnetism (Subsection 4d); there is a magnetoplasma Alfvén resonance (Subsection 4g); and there are density oscillations (Subsection 4d). The research on γ -droplets is reviewed in detail in Ref. 14.

4) Ultrasound

The nature of the interaction of ultrasound with an electron-hole droplet depends on the relation between the wavelength of the ultrasound, λ , and the droplet radius R . If $\lambda \gg R$ (this condition corresponds to frequencies $\omega \lesssim 10^9$ s⁻¹ in germanium), the droplet will be in a uniform force field at all times, and it will move without any change in shape. The motion is accompanied by friction with the lattice, dissipation of energy, and thus absorption of the ultrasound.²³⁷ At a low ultrasound intensity,

$$I = \rho S^3 \frac{u_0^2}{2} \ll I_0 = \frac{(m_e + m_h)^2 \rho S^7}{D^3} \sim 10 \text{ W/cm}^2$$

(ρ is the density of the semiconductor, S is the longitudinal sound velocity, $u_0 = \text{Tr} u_{0ji}$ is the amplitude of the ultrasound; for this numerical estimate we have used some typical values for germanium: $\rho = 5$ g/cm³, $m_e + m_h \sim 10^{-27}$ g, $D \sim 10$ eV, and $S \sim 5 \cdot 10^5$ cm/s), the absorption coefficient is proportional to the average carrier density in the droplet,²³⁷ $n = 4/3\pi R^3 n_i n_d$:

¹⁶⁾What happens in silicon is apparently not the formation of one large droplet at the bottom of the potential well; the EHL exists as a dense cloud of small droplets. This conclusion is implied both by experiments¹⁶³ and by theoretical estimates²³⁴ of the effect of the phonon wind (Section 6).

$$\delta = n \frac{D^2}{\rho (m_e + m_h) S^5} \frac{\gamma \omega^2}{\gamma^2 + \omega^2}. \quad (4.6)$$

The droplet drift velocity along the sound propagation direction is

$$V_d = S \frac{\omega^2}{\omega^2 + \gamma^2} \frac{I}{I_0}. \quad (4.7)$$

At high intensities, $I \gg I_0$, the droplets are completely entrained by the ultrasound: $V_d = S$.

Strong absorption of ultrasound at the frequency $\omega \approx 10^9 \text{ s}^{-1}$ ($\lambda = 30 \mu\text{m}$) by electron-hole droplets in germanium has been observed experimentally.^{238,239} The temperature dependence of the absorption coefficient was described satisfactorily by (4.6) under the assumption that friction with the lattice was caused by scattering of carriers by thermal phonons (Subsection 5a). The strong temperature dependence of γ for this damping mechanism has the consequence that δ in (4.6) has a clearly defined maximum at the temperature corresponding to the condition $\gamma(T) = \omega$. We thus have a simple and reliable method for measuring τ_p . We wish to stress that, in contrast with the methods described in Subsection 4b and Section 2, these measurements are measurements of τ_p in undeformed germanium. That electron-hole droplets are entrained by ultrasound in accordance with (4.7) was proved experimentally in Ref. 240.

If $\lambda \sim R$, a droplet is subjected to nonuniform effects, and it not only moves with respect to the lattice but also changes shape. The interaction of a droplet with ultrasound at $\lambda \gtrsim R/10$ can be described²⁴¹ by the equations of the hydrodynamics of an incompressible fluid. Ultrasound excites capillary oscillations of the droplets with frequencies²⁴²

$$\omega_j = \sqrt{\frac{\sigma j(j+2)(j-1)}{n_l(m_e + m_h) R^3}}, \quad (4.8)$$

where $j = 2, 3, \dots$ (the case $j = 1$ with $\omega_1 = 0$ corresponds to the motion discussed above, without any change in shape). The absorption coefficient due to friction with the lattice and also to the internal viscosity of the EHL was calculated in Ref. 241. A simplified problem neglecting the viscosity of the EHL was solved in Ref. 88. The absorption coefficient has broad resonances at frequencies $\omega \cong \omega_j$, so that ultrasonic measurements can be used for a mechanical determination of the surface-tension coefficient of an EHL.^{144,88}

The interaction of droplets with short-wavelength phonons ($\lambda \ll R$) can be described by the ordinary equations for a degenerate e-h plasma (see Ref. 243, for example), provided only that the incomplete filling of the sample by the liquid is taken into account. The dominant process is the absorption of phonons; the scattering is slight, since it is described in second-order perturbation theory. The cross section for absorption of phonons by carriers, σ_{ph} , depends on the shape of the electron spectrum, the strain potentials, the wave vector, and the polarization of the phonons. In the simplest, isotropic, model (in which only longitudinal sound is absorbed), this cross section is

$$\sigma_{ph} = \frac{1}{8\pi} \frac{D^2 m^2 |\mathbf{k}|}{n_l \hbar^3 \rho S}, \quad \hbar |\mathbf{k}| < 2p_F. \quad (4.9)$$

Phonons with momenta $\hbar |\mathbf{k}|$ exceeding $2p_F$ are not absorbed because of the Fermi degeneracy of the EHL (this conclusion

also holds for semiconductors with an anisotropic spectrum). During absorption, the momentum of the phonon is transferred to the carriers. The phonon fluxes thus create force fields in the sample; consequences of these fields will be discussed in Section 6. The absorption of short-wavelength phonons by droplets in germanium was studied experimentally in Refs. 258 and 259 by a heat-pulse technique. The absorption of monochromatic phonons of frequency $\sim 3 \text{ meV}$ by droplets in compressed germanium was studied in Ref. 244. As the pressure changes, p_F of the EHL changes, as does σ_{ph} , in accordance with (4.9). Superconducting tunnel junctions were used in Ref. 244 to excite and detect phonons.

c) Photoconductivity in a static electric field

Study of the photoconductivity of a semiconductor upon the formation of an EHL in it can yield a wide variety of information. In such experiments, a static electric field is produced in the sample by means of contacts or at a p-n junction. It has been found^{7,245,246} that the conductivity increases sharply with increasing excitation intensity when a certain average exciton density $\sim 10^{16} \text{ cm}^{-3}$ is reached in a germanium sample. This sharp increase results²⁴⁶⁻²⁴⁹ from a percolation conductivity through the metallic electron-hole droplets under conditions such that the entire sample has not yet been filled by the metallic liquid. Another interesting effect²⁵⁰ stems from the destruction of the droplets in the strong electric field of a nonconducting p-n junction or of a metal-semiconductor contact. In such a case, current spikes are detected at the junction; the total charge in one spike is equal to twice the number of e-h pairs in a droplet, so that the dimensions of a droplet can be determined by measuring this charge. This effect has been exploited in order to study (by measuring the thresholds for the appearance of current pulses) the gas branch of the exciton-EHL phase diagram,^{174,154} the size distribution of the electron-hole droplets,²⁵¹ and the dependence of the droplet radius on the temperature and the excitation intensity.²⁵² Contacts on the surface of a sample are also used in studying the motion of droplets—to detect the presence of droplets in the corresponding part of a crystal¹⁷) (Refs. 253-257). Huge current pulses have also been detected in silicon upon the disintegration of a droplet at a p-n junction.²⁶⁰

d) Magnetic field

The behavior of an EHL in a static magnetic field is determined both by quantum-mechanical effects and by the finite carrier lifetime. We will begin with the quantum effects. They arise from the quantization of the carrier motion across the magnetic field: Landau quantization.²⁶¹ The electron and hole state densities change, as does the spectral shape of the recombination-radiation line of the EHL,^{196,200} in accordance with (4.1). In weak magnetic fields, $\hbar \omega_c^{(j)} \ll E_F^{(j)}$ ($\omega_c^{(j)} = eH/m_{c,j}c$ is the cyclotron frequency of the carrier of species $j = e, h$, with the cyclotron mass $m_{c,j}$), in which many Landau levels are populated, oscillation phenomena are observed in an EHL which are analogous to the De Haas-van-

¹⁷Superconducting bolometers have also been used for this purpose.²⁵⁷⁻²⁵⁹

Alphen and Shubnikov–de Haas effects in metals and which stem from the decrease in the number of filled Landau levels with increasing H . Oscillations have been detected in the integral intensity^{197,158,198} and polarization²⁶² of the recombination radiation of an EHL, in the half-width of an EHL line,¹⁹⁹ in the EHL lifetime,²⁰³ in the integral far-IR absorption,²⁶³ in the ultrasonic absorption coefficient,²⁶⁴ and in the velocity at which electron-hole droplets are entrained by the phonon wind¹⁸⁾ (Refs. 254–256). The detection of these oscillations confirmed the metallic nature of the EHL in germanium and also made it possible to determine independently the density of the EHL, since the period of the oscillation in the reciprocal of the field is proportional to the Fermi energy. A theory for the behavior of an EHL in a magnetic field satisfying $K_B T < \hbar\omega_c^{(j)} \ll E_F^{(j)}$ was derived in Ref. 265.

The most interesting quantum effects should occur in an EHL in an extremely strong magnetic field, $\hbar\omega_c^{(j)} \gg E_F^{(j)}$, when only the lower electron and hole Landau levels are occupied (the ultraquantum limit). For ordinary matter the ultraquantum limit is reached in fields $\sim 10^9$ Oe, which are possible only under astrophysical conditions (at the surface of a neutron star, for example). In the case of an EHL the energy scale is 10^{-2} – 10^{-3} Ry, the mass scale is $(0.1$ – $0.3)m_0$, and fields $\sim 10^5$ Oe, attainable in the laboratory, may prove sufficient for an experimental study of the behavior of a Coulomb system under these extreme conditions.¹⁹⁾ In such fields the carrier system becomes a quasi-one-dimensional system (the motion across the magnetic field is frozen), and the equilibrium properties of the EHL are described asymptotically exactly in the model of a semiconductor with a highly anisotropic spectrum^{128,127} (Subsection 3b2). Let us briefly review some of the predictions of this theory, which is described in detail in Refs. 269 and 270. An EHL in an extremely strong magnetic field should undergo a self-compression: $n_1^0(H) \sim a_{ex}^{-3} \tilde{H}^{8/7} \gg a_{ex}^{-3}$ ($\tilde{H} = \hbar^3 \epsilon_0^2 H / e^3 m_r^2 c$). Its binding energy should increase^{128,127}: $E_1^0(H) \sim E_{ex} \tilde{H}^{2/7} \gg E_{ex}$. The same is true of the parameters of the critical point²⁷¹: $n^c(H) \sim 0.05 \tilde{H}^{8/7} a_{ex}^{-3}$, $k_B T^c(H) \sim 0.1 \tilde{H}^{2/7} E_{ex}$. At densities satisfying $n_1^0(H) < n < a_{ex}^{-3} \tilde{H}^{4/3}$, a homogeneous state of an e-h plasma is unstable with respect to the formation of a density wave with a wave number $2p_F / \hbar$; an insulator gap should arise in the spectrum of one-particle excitations of the system.²⁷³ If $m_e \neq m_h$, the amplitudes of the electron and hole density waves will be different, and a charge density wave should form.²⁷³ With increasing magnetic field, the exciton binding energy also increases,²⁷² $E_{ex}(H) \sim (E_{ex}/2) \ln^2 \tilde{H}$, so that the formation of a metallic EHL becomes energetically favored only in very strong fields, $\tilde{H} > 10^7$ (i.e., even for semiconductors with $m_r \sim 0.01 m_0$ and $\epsilon_0 \sim 100$ at $H > 10^8$ Oe).²⁷⁰ It has been sug-

gested that an insulating EHL might form in weaker magnetic fields,²⁷⁰ but in polar semiconductors a metallic EHL should be favored, regardless of the magnetic field, because of the interaction with longitudinal optical phonons (Subsection 3b4).²⁶⁸

Some other interesting theoretical predictions have been made regarding the ultraquantum limit (see the review in Refs. 40 and 270). So far, there has been no experimental study of the behavior of an EHL in the ultraquantum limit. Some increase in the density (by a factor of four) and in the binding energy (by a factor of two) of an EHL in germanium has been observed²⁰¹ at $H \sim 1.9 \cdot 10^5$ Oe; this field would not yet be regarded as a superstrong field in the case of germanium. It has also been found²⁷⁴ that a magnetic field $H \sim 20$ – 50 kOe will stabilize an EHL in InSb, in qualitative agreement with the predictions of Refs. 182 and 127.

An interesting magnetic effect results from the finite carrier lifetime in an electron-hole droplet: recombination magnetism.²⁷⁵ A current of electrons and holes is established (directed from the surface of the sample toward its center) in order to replace the carriers which recombine in a droplet. In a magnetic field, these currents are deflected, and the droplet acquires a paramagnetic moment. The shape of the droplet changes.^{276–279} If the external flux of excitons to the droplet is isotropic, the droplet becomes flattened. Under certain anisotropic excitation conditions, however, a droplet may become elongated along the direction of \mathbf{H} (Ref. 278). This point has been tested experimentally for γ -droplets in germanium.²⁷⁹

e) Microwave methods

Methods involving the use of electromagnetic fields in the microwave range have proved extremely useful in studying the condensation of excitons.^{42,280,281,14} The primary advantages of these methods are the high sensitivity to even low densities ($\sim 10^{10}$ cm⁻³) of free carriers and the capability of studying separately the effects of the magnetic and electric components of the fields. In experiments by these methods, one studies the change in the microwave absorption which occurs during optical excitation and of the sample and which stems from the change in the imaginary part of the polarizability upon the formation of electron-hole droplets and of the gas of free carriers around the droplets. (Although the density of excitons near a droplet is usually many orders of magnitude greater than the density of carriers, the excitons make only a small contribution to the polarizability.) A change in the real part of the polarizability leads to a shift of the frequency of a resonator (a deviation from resonance) and can also be measured experimentally.

The EHL in germanium usually forms as a cloud (with a radius $R_{cl} \sim 1$ mm) of droplets of radius $R = 2$ – 10 μ m, surrounded by free carriers and excitons. The dielectric permittivity of an EHL or of a gas of free carriers at the frequency of a microwave field, ω , is given in the Drude approximation by

$$\epsilon_j(\omega) = \epsilon_0 \left(1 - \frac{\omega_{p,j}^2}{\omega(\omega + i\nu_j)} \right) \equiv \epsilon_0 (\epsilon_j' + i\epsilon_j''), \quad (4.10)$$

where $\omega_{p,j} = \sqrt{4\pi e^2 n_j / \epsilon_0 m_r}$, n_j and ν_j are the plasma frequency, density, and collision rate in an EHL ($j = l$) and in

¹⁸⁾ These experiments were carried out in germanium. The oscillations (at $H < 30$ kOe) were caused by light electrons. Oscillations due to hole Landau levels were observed in Ref. 266 (with $\mathbf{H} \parallel \langle 111 \rangle \sim 160$ kOe). Slight oscillations in the intensity of an EHL line have also been observed in silicon.²⁶⁷

¹⁹⁾ The next-to-last Landau hole level in germanium is emptied at $H_{cr} \sim 2 \cdot 10^6$ Oe. In germanium subjected to high uniaxial compression, H_{cr} should decrease by nearly an order of magnitude.²⁰¹ The critical field is $H_{cr} \sim 10^5$ – 10^6 Oe in highly anisotropic polar semiconductors: lead and tin chalcogenides.²⁶⁸

the gas of free carriers ($j = c$). For both a cloud of carriers and an individual droplet, the conditions for the applicability of the Rayleigh limit of the Mie problem of an isotropic conducting sphere in an alternating electromagnetic field hold in the microwave range²⁸²: $k_0 r_j \ll 1$, $|k_j r_j| \ll 1$ ($k_0 = \omega \sqrt{\epsilon_0}/c$, $k_j = \omega \sqrt{\epsilon_j}/c$), $r_i \equiv R$, $r_c \equiv R_{c_i}$. In this case, the most important electric component of the absorption of the microwave field is the electric dipole (E1) absorption, and the most important magnetic component is the magnetic dipole (M1) absorption. The cross sections for the absorption by the droplets of an EHL or by a carrier cloud are

$$\sigma_{E1}^{(j)} = \frac{12\pi k_0 r_j^3 \epsilon_j''}{(\epsilon_j' + 2)^2 + (\epsilon_j'')^2}, \quad (4.11)$$

$$\sigma_{M1}^{(j)} = \frac{12\pi}{15} k_0^3 r_j^5 \epsilon_j''^2. \quad (4.12)$$

In order to find the cross section for the absorption by all the droplets, we must multiply $\sigma^{(j)}$ by the number of droplets in the cloud, $(4/3)\pi R_{c_i}^3 n_d$. Estimates based on (4.11) and (4.12) with $\omega = 10^8 - 10^{11} \text{ s}^{-1}$, $\nu_1 \sim 10^{11} \text{ s}^{-1}$, $\nu_c \sim 10^9 \text{ s}^{-1}$, $n_c \sim 10^{11} \text{ cm}^{-3}$, and $n_d \sim 10^5 \text{ cm}^{-3}$ (typical values for germanium at $T \sim 2 \text{ K}$) lead to the following conclusions: 1) Free carriers dominate the microwave absorption in the electric component of the field ($\sigma_{E1}^{(c)} \gg \sigma_{E1}^{(d)} \cdot 4/3\pi \cdot R_{c_i}^3 n_d$); 2) The M1 absorption by the carriers is slight. 3) The M1 absorption by the droplets is far stronger than the E1 absorption by the droplets (since $|\epsilon_j| \gg 1$), and if the droplets are large enough, with $R \sim 10^{-3} \text{ cm}$, this absorption may be comparable in magnitude to the E1 absorption by free carriers. (The question of microwave absorption and the deviation from resonance were analyzed in detail in Ref. 283.)

The microwave methods are thus sensitive primarily to the gas of free carriers. Since these carriers are at equilibrium with the droplets and the excitons, their behavior yields extensive information about the overall system. For example, the time dependence of the carrier density at extremely low temperatures, where the primary source of the carriers is the ejection of Auger carriers from the droplets, yields an estimate of the mean free path of the hot carriers in the EHL.^{167,280,284} From the temperature dependence of n_c at higher temperatures, where thermal evaporation from the droplets is predominant,

$$n_c \sim n_{c,T} \propto (k_B T)^{3/2} \exp\left(-\frac{E_i}{2k_B T}\right), \quad (4.13)$$

we can determine the EHL binding energy.^{285,286}

The microwave absorption results in a heating of the free carriers. The probability for impact ionization of the excitons increases, and at a certain threshold microwave power breakdown of the exciton gas becomes possible. In the presence of electron-hole droplets, the breakdown has a characteristic peaked behavior: The free carriers formed during the breakdown are captured by droplets rapidly, over times $(4\pi R^2 n_d v_{c,T})^{-1} \sim 10^{-7} \text{ s}$ ($v_{c,T} = \sqrt{k_B T_c/m} \sim 10^7 \text{ cm/s}^{-1}$ is the average carrier velocity). This phenomenon is observed in both continuous²⁸⁷ and pulsed¹⁶⁷ microwave fields. Keldysh *et al.*¹⁶⁷ have derived a theory which explains the basic aspects of the peaked breakdown of excitons.

Pulsed microwave breakdown has turned into an effective tool for studying the droplet-carrier-exciton system.^{280,281} Data on breakdown were used in Ref. 167 to esti-

mate the density and radius of the droplets; the lifetime of the EHL was found in Refs. 167 and 204 and turned out to agree with that found from data on the kinetics of the recombination radiation; and the lifetime of the free carriers and the dependence of the probability for the impact ionization of excitons on the microwave power were found in Ref. 288. This method has also made it possible to study¹⁷¹ the time evolution of the exciton density at low temperatures at times after the exciting pulse long in comparison with τ_j (at which the recombination radiation of the excitons was not detected experimentally because of the small number of excitons). At a microwave power far above the threshold, the density of free carriers at the breakdown maximum is equal to the density of excitons at the time at which the microwave field is applied. By varying the delay of the microwave pulse with respect to the excitation pulse, it becomes possible to study the time evolution of the density of excitons. It turns out¹⁷¹ that the exciton density in the cloud remains essentially constant at $n_{ex,T}$ given by (3.22) for a long time after the excitation pulse (Fig. 5). This result is attributed to the evaporation of excitons from droplets and is characteristic of a gas-liquid phase transition.

The heating and the increase in the density of free carriers in a microwave field affect the volume and temperature of the electron-hole droplets, since there are changes in the flux of carriers away from the droplets and in the energy which they carry.^{179,170,289} These changes have a particularly significant effect on formation of nucleation centers, causing a shift of the thresholds for the appearance of the EHL.¹⁷⁰ Furthermore, the relaxation of the carriers is accompanied by the generation of a phonon wind (Section 6) sufficient to drive the droplets to the surface of the sample.²⁹⁰ Another consequence of the perturbations caused by a microwave field is the appearance of fluctuations in the microwave conductivity.^{291,169} The reasons for these fluctuations have not yet been definitely identified, although it is obvious that self-excited oscillations and autowave processes may occur in the complex carrier-exciton-droplet system, with its nonlinear relationships. Some possibilities were analyzed in Refs. 292–295 and 169.

The relatively strong magnetic dipole absorption by the droplets makes it possible in principle to measure ϵ_j'' and thus the conductivity of the EHL.^{296,276,14} However, studies of the kinetics of the absorption in the magnetic component of the microwave field have shown^{297,298} that absorption by free carriers is detected in experiments with undeformed germanium. It thus becomes possible to estimate an upper limit on the conductivity of the droplets.²⁹⁷ In the case with γ -droplets (Subsection 4b3), we have the opposite situation. The conductivity of γ -droplets and its dependence on the temperature and impurity concentration were determined in Ref. 299.

f) IR methods

1) *Probing of electron-hole droplets by electromagnetic radiation in the far-IR region ($\lambda = 10^{-3} - 10^{-1} \text{ cm}$)*

This method was historically one of the first used to study the droplets. A broad resonance near $\hbar\omega = 9 \text{ meV}$

($\lambda = 140 \mu\text{m}$) was discovered⁴ in the absorption spectrum of photoexcited germanium and attributed to a plasma resonance at the frequency $\omega_p/\sqrt{3}$ in electron-hole droplets with dimensions small in comparison with the wavelength of the radiation in the sample, $\lambda_0 = \lambda/\sqrt{\epsilon_0}$. At $R \ll \lambda_0$, the cross section for the absorption of droplets with a dielectric permittivity (4.10) is given by (4.11), which can easily be put in the form

$$\sigma_{E1}^{(l)} = \frac{4}{3} \pi R^2 k_0 \frac{\omega_p^2 v_l \omega}{[\omega^2 - (\omega_p^2/3)]^2 + \omega^2 v_l^2}. \quad (4.14)$$

Working from the experimental value of ω_p , Vavilov *et al.*⁴ determined the density of an EHL in germanium for the first time (and extremely accurately). The simple expression (4.14) gives a poor description of absorption in the short- and long-wavelength parts of the spectrum. The primary reason for this failure is that the Drude formula, (4.10), does not apply to the EHL in germanium at $\hbar\omega \sim 3\text{--}40 \text{ meV}$, at which transitions between the light- and heavy-hole bands are important.^{300–304,187} The leading terms in the Mie expansion were also taken into account in those studies: The Rayleigh limit, (4.11), does not apply to droplets with radii $R > 2 \mu\text{m}$. Comparison with experimental results yielded refined values of n_l (Refs. 300, 302, and 303) and of v_l in the IR region [$\sim 4 \cdot 10^{12} \text{ s}^{-1}$ (Refs. 300 and 187) and 10^{12} s^{-12} (Ref. 304)] and revealed an increase in the dimensions of the droplets with increasing excitation level^{187,304} and with increasing concentration of small impurities.¹⁸⁷ Finally, Zayats *et al.*¹⁸⁷ concluded that the droplets in germanium at $T = 1.5\text{--}2 \text{ K}$ have a distribution of sizes (a Junge distribution).²⁰ The IR absorption has also been studied for γ -droplets in nonuniformly compressed germanium.³⁰⁵ A plasma resonance involving droplets has also been discovered in silicon.³⁰⁶

We note in conclusion that a study of the absorption and photoconductivity in the submillimeter range ($\hbar\omega \sim E_{ex}$) is a direct and very sensitive technique for studying the spectrum and density of free excitons (see Ref. 42, for example). This method has made it possible to study the gas branch of the exciton-EHL phase diagram at low temperatures in germanium.^{156,58}

2) Near-IR range

Electron-hole droplets with a refractive index different from that of the crystal constitute optical inhomogeneities which scatter and absorb light at wavelengths in the transparency range of the semiconductor. The droplets in germanium are usually studied with the beam from a He-Ne laser with $\lambda = 3.39 \mu\text{m}$. Scattering is the most direct method for studying the macroscopic structure of an EHL. The droplet radius can be determined from the angular distribution of the intensity of the scattered light (described by the Rayleigh-Gans theory³⁰⁷). Simultaneous measurements of the optical absorption also reveal the number density of the droplets and the mass density of the EHL. Scattering of light by droplets in germanium was first observed in Ref. 308. This scattering arose at the same time as the recombination

radiation of an EHL, and this coincidence became an important argument in favor of the formation of droplets. The method has subsequently been used to determine the densities and radii of droplets,^{172,309–312} the spatial distribution of droplets,^{311,312} the size distribution of droplets,¹⁸⁸ the surface tension of an EHL,⁸³ the kinetics of condensation and hysteresis phenomena,¹⁶⁶ and the motion of droplets.^{190,313–315} It has also been used to study γ -droplets²¹ (Ref. 316). The method is discussed in detail in Refs. 317 and 42. We might add that the frequency shift of the scattered light depends (by virtue of the Doppler effect) on the velocity distribution of the droplets in the cloud. An interference method has been developed³¹⁸ for measuring droplet velocities.

The cross section for absorption by carriers in droplets in germanium at wavelengths $\lambda \sim 3\text{--}4 \mu\text{m}$ (Ref. 319) is far larger than the values derived in the Drude approximation. The difference results³²⁰ from transitions from a heavy-hole band to a band split off by the spin-orbit interaction. The absorption cross section at $\lambda = 10.6 \mu\text{m}$, $\sim 2 \cdot 10^{-16} \text{ cm}^2$ (Ref. 321), is also greater than the cross section in the free-carrier model. During the absorption of IR radiation, the droplets become heated. An increase in the phonon wind which is generated (Section 6) due to continuous radiation at $\lambda = 2.1 \mu\text{m}$ was detected in Ref. 322 (from an increase in the velocity at which droplets move out of their excitation region). The behavior of droplets in intense pulsed light at $\lambda = 10.6 \mu\text{m}$ (a CO_2 laser beam) was studied in Refs. 323 and 324. Evaporation and subsequent recondensation of the droplets was observed. With increasing light intensity, the number of carriers which recondense decreases; this effect is explained by arguing that the phonon wind blows some of the e-h pairs to the surface of the sample, and the pairs rapidly recombine.

One of the first indications of the formation of droplets in germanium was found³ from a change in the absorption spectrum at the threshold for direct interband transitions ($\hbar\omega = 0.88\text{--}1 \text{ eV}$). A detailed theory for this effect was derived in Ref. 325.

g) Magnetoplasma microwave and IR phenomena

The microwave and IR methods involving a static magnetic field are closely related to the methods described above. The most important of these methods is the cyclotron resonance involving the free carriers around droplets. This resonance has been used to study the decay kinetics of small and large droplets^{153,286} and the density and collision rate in the carrier gas near the surface of γ -droplets.²⁸⁶ In Ref. 326 cyclotron resonance of free carriers was detected not in the usual way, on the basis of microwave absorption, but from the intensity of droplet recombination radiation.

Many experimental studies have been carried out on magnetoplasma resonances involving electron-hole droplets in germanium (in the far-IR and submillimeter ranges^{263,327–330} and in the microwave range^{331,332}). In a stat-

²⁰Roughly analogous results with pulsed excitation have been obtained¹⁸⁸ by a light-scattering method (Subsection 4f2).

²¹In particular, the vanishing of the scattering became an important argument in favor of the formation of a single large electron-hole droplet in nonuniformly compressed germanium.³¹⁶

ic magnetic field the dielectric permittivity of an EHL is a gyrotropic tensor, so the Mie theory breaks down. There are some other difficulties: the complicated band spectrum of germanium and the change in the droplet shape in a magnetic field. For small droplets (under the conditions $k_0 R, |kR| \ll 1$), however, both electric and magnetic fields can be assumed uniform over a droplet. This assumption simplifies the theoretical analysis, making it possible to incorporate both the anisotropy of the effective electron masses³³³ and the change in the droplet shape.^{333,334} Comparison of theory with experiment³³⁴ has revealed the carrier density in droplets, an increase in this density with increasing magnetic field, the collision rate in an EHL as a function of the field frequency, and the renormalization of the carrier masses in an EHL. The magnetic dipole resonances in the submillimeter range,³²⁹ which are relatively sensitive to the droplet shape, have been used to determine the extent to which droplets are flattened in fields of 10–20 kOe.

The Alfvén microwave size resonance involving γ -droplets in compressed germanium was studied in Refs. 232, 335, and 336. The studies in Refs. 232 and 335 also led to the discovery of huge droplets. Alfvén waves are circularly polarized electromagnetic waves which can propagate in a neutral plasma along the direction of a strong magnetic field H . The dispersion law for an Alfvén wave in an infinite medium with $v_l \ll \omega \ll \omega_c$ is²⁸²

$$\omega = \frac{Hk}{\sqrt{4\pi n_l(m_e + m_h)}}. \quad (4.15)$$

If the electromagnetic wave excites Alfvén waves in a sphere, resonances may occur at $kR > 1$ which correspond to the excitation of an integer number of standing waves in the sphere. The resonant magnetic field H_{res} is proportional to R ; in Refs. 335 and 336, the shift of H_{res} as a function of the delay with respect to the excitation pulse was used to study the kinetics of the decrease in the radius of a γ -droplet and its lifetime. The theory here becomes far more complicated than that in the case of magnetic dipole resonances, since the Rayleigh limit is no longer sufficient. All the experiments with Alfvén resonances, however, have been carried out at frequencies corresponding to the condition $k_0 R \ll 1$. An asymptotically exact scheme for numerical calculations has been constructed for this case.³³⁷ It was used in Ref. 338 to calculate the microwave absorption coefficient of a γ -droplet in germanium.

5. MOTION OF ELECTRON-HOLE DROPLETS

Electron-hole droplets can be moved through a crystal by a nonuniform deformation,⁵ ultrasound,^{237,238} a phonon wind,^{190,191} electric fields,⁸⁹ nonuniform magnetic fields,^{8,339} exciton density gradients^{340,189} electron and hole fluxes,¹⁴⁰ and radiation pressure.¹⁸⁷ This motion is possible because of (on the one hand) the high sensitivity of the electron system to these agents and (on the other) the relatively slight friction of the EHL against the lattice, which is suppressed by the Fermi degeneracy of the carriers in the liquid.

a) Friction mechanisms

The primary mechanism for friction in a pure nonpolar semiconductor is the emission and absorption of acoustic phonons by carriers, described by the strain-energy method²² (Subsection 4b). The friction level depends on the droplet velocity v_d and the temperature. At $v_d = S$, where S is the longitudinal sound velocity in the semiconductor, the friction is viscous, and the friction force is proportional to v_d . The kinematic friction coefficient, equal to the reciprocal of the momentum relaxation time, τ_p^{-1} , was calculated in Refs. 8 and 237 for the simplest case, of isotropic, nondegenerate bands:

$$\gamma = \tau_p^{-1} = \frac{2}{3(2\pi)^2} \frac{m_e^2 D_e^2 + m_h^2 D_h^2}{(m_e + m_h) \rho S} \left(\frac{k_B T}{\hbar S} \right)^5 \int_0^{\xi_0} d\xi \cdot \xi^5 \frac{\exp \xi}{(\exp \xi - 1)^2}, \quad (5.1)$$

where $\xi_0 = \tilde{T}/T$ and $k_B \tilde{T} = 2p_F S$ (in germanium, $\tilde{T} \sim 13$ K). The temperature dependence of γ is analogous to that of the resistance of a metal: at $T \lesssim 0.1\tilde{T}$ the dependence is $\gamma \propto T^5$, while at higher temperatures the dependence becomes linear, $\gamma \propto T$ (Fig. 14).

Expression (5.1) gives a satisfactory description of the friction of droplets in germanium and silicon.^{238,209} We might expect a strong screening of the strain potential in an EHL and an effect of the crystal anisotropy, but detailed calculations^{342,225} show that γ differs from expression (5.1) only by a factor ~ 2 . In impure semiconductors the phonon relaxation may be accompanied by an impurity relaxation of the droplet momentum; the contribution of this relaxation to γ was calculated in Ref. 341. We might add that studies of hysteresis effects and the diffusion of droplets in germanium indicate^{180,343} the existence of static friction for the droplets. This friction can be attributed to, for example, a binding of droplets with impurities.^{344,345}

b) Motion at velocities near the sound velocity

Experiments have revealed that the electron-hole droplets in germanium can move at velocities up to the longitudi-

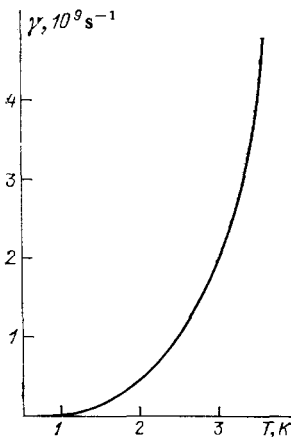


FIG. 14. Temperature dependence of the reciprocal of the momentum relaxation time of an EHL in germanium.²³⁷

²²In polar semiconductors there is a competing piezoelectric interaction with phonons; its contribution to the friction was studied in Ref. 341.

nal sound velocity.²⁵⁷ Can droplets overcome this sound barrier? At least three circumstances oppose this possibility: an increase in the friction, overheating, and an instability of the droplet shape.

The dependence of the friction on the velocity of the droplet was studied theoretically in Refs. 346, 342, and 347. As v_d approaches S , the average momentum of the emitted phonons increases, and with it the coefficient of friction. The friction increases most rapidly at $v_d > S$. Furthermore, a coherent emission of sound by droplets analogous to a Cherenkov emission begins at $v_d > S$. This emission causes an abrupt onset of retardation by radiation.^{347,348} Accordingly, droplets can be accelerated to supersonic velocities only by extremely large forces, difficult to produce experimentally.

Because of the anisotropy in a crystal, a droplet can emit transverse Cherenkov phonons at $v_d > S_t$, where S_t is the transverse sound velocity. The retardation force for a cubic crystal was calculated in Ref. 349 and found to be far weaker than the force due to the emission of longitudinal phonons at $v_d > S$. It would apparently not prevent the attainment of velocities³⁴⁹ $v_d > S_t$.

The noncoherent emission and absorption of acoustic phonons by carriers change the internal energy of an EHL⁸ and can cause overheating of a moving droplet. At $v_d < S$, however, this overheating is generally insignificant³⁵⁰:

$$1 - \frac{v_d}{S} < \frac{T}{T_0} < 1 + \frac{v_d}{S}, \quad (5.2)$$

where T is the droplet temperature, and T_0 is the temperature of the semiconductor. A droplet may in fact become cooler because of the intensified emission of phonons in the course of its motion.³⁵¹ The overheating, like friction, begins to increase rapidly only at³⁵¹ $v_d > S$. The most serious obstacle to the crossing of the sound barrier by the droplets appears to be the shape instability of a droplet as $v_d \rightarrow S$ (Refs. 348 and 352). As the droplet moves, its intrinsic strain field (Subsection 5c) creates stresses in the droplet which tend to flatten it out along the direction in which it is moving. As the sound barrier is approached, this flattening should increase without bound (unless an instability of some sort occurs).

Friction in the case of motion of droplets at high velocities in silicon has been studied experimentally.³⁰⁷ Up to $v_d = 0.9S$, the v_d dependence of this friction can be described well in terms of a noncoherent interaction with acoustic phonons. With a further increase in the force accelerating the droplet, the velocity reaches saturation, apparently indicating the onset of Cherenkov radiation. Kukushkin and Kulakovskii²²⁹ have observed breaking up of electron-hole droplets in germanium in strong fields, which should have caused supersonic motion of the droplets. Whether the effect was caused by overheating or by a shape instability has not yet been determined, however.

c) Intrinsic strain field of an electron-hole droplet; mass transfer by a moving droplet

A droplet, which is a macroscopic cluster of nonequilibrium carriers, causes a deformation of the surrounding region of the semiconductor. Two effects associated with this deformation have already been discussed: the Cherenkov

emission of sound during motion at supersonic velocity³⁴⁷⁻³⁴⁹ and a change in the shape of a moving droplet.^{348,352} Furthermore, a droplet acquires an additional deformation mass³⁴⁷; a droplet in nonuniform motion emits sound even at³⁴⁷ $v_d < S$. Several effects are associated with the anisotropy of the elastic properties of the lattice: a change in the shape of a droplet at rest,³⁵³ an attraction of droplets to the surface of the semiconductor,^{354,355} and an interaction between droplets.³⁵⁵ All these effects can be described in classical mechanics by means of the Lagrangian

$$L = L_0 + L_d + L_{int}, \quad (5.3)$$

where (in the isotropic case)

$$L_0 = \int d^3r \left[\frac{\rho}{2} \left(\frac{\partial \mathbf{u}}{\partial t} \right)^2 - \frac{\mu}{2} \left(\frac{\partial \mathbf{u}_i}{\partial r_j} \right)^2 - \frac{\lambda + \mu}{2} (\text{div } \mathbf{u})^2 \right]$$

is the Lagrangian of the semiconductor, λ and μ are Lamé coefficients, L_d is the Lagrangian of the droplet, $L_{int} = -D \int n_l(\mathbf{r}, t) \text{div } \mathbf{u} d^3r$, and the carrier density in the droplet, $n_l(\mathbf{r}, t)$, is an explicit function of the coordinates of the center of mass of the droplet, \mathbf{r}_d , and its shape, $R(\mathbf{r} - \mathbf{r}_d)$. By varying the action for (5.3) with respect to \mathbf{u} , R , and \mathbf{r}_d , we can easily derive equations for the intrinsic field and shape of a droplet and an equation of motion for the droplet. We cannot analyze these effects in detail here; we will discuss only the mass transfer by a droplet, which has not yet been discussed in detail in the literature.

The mass of the carriers constituting a droplet is an effective mass, and its motion—the transfer of excitation energy accumulated by the carriers—is not accompanied by a real transport of matter²⁰ (by analogy with the situation involving excitons³⁸). At first glance the situation would seem to change if we took into account the displacement of the strain field of the droplet following the droplet—the region in which the lattice is compressed or stretched (depending on the sign of D).

In the isotropic model, the strain field of a droplet is longitudinal ($\text{curl } \mathbf{u} = 0$) and satisfies the equation^{351,348}

$$\left(\Delta - \frac{1}{S^2} \frac{\partial^2}{\partial t^2} \right) \mathbf{u} = -\frac{D}{\rho S^2} \text{grad } n_l(\mathbf{r}, t). \quad (5.4)$$

A spherical droplet of radius R at rest causes a strain

$$u \equiv \text{div } \mathbf{u} = \begin{cases} -\frac{D n_l}{\rho S^2}, & r < R, \\ 0, & r > R. \end{cases} \quad (5.5)$$

In germanium we have $D < 0$, and the density of the crystal inside the droplet decreases by an amount $\delta\rho/\rho = -u \sim 10^{-6}$. The energy of an e-h pair decreases by only $\sim 10^{-2}$ meV in the case of such a strain. On the other hand, we have $\rho S^2 a_0^2 \sim 1$ Ry and $D \sim 1$ Ry (a_0 is the lattice constant) and thus $|\delta\rho/\rho| \sim a_0^{-3} n_l$. In other words, each e-h pair displaces approximately one atom of the semiconductor from the region occupied by the droplet (or draws approximately one atom into this region, in the case $D > 0$). As the droplet moves, the pairs "entrain" these extra atoms (or vacancies), as can be seen from an expression which follows from (5.4) for the momentum of the strain field of a droplet moving at a velocity \mathbf{v}_d :

$$\Pi \approx -\frac{1}{1 - (v_d^2/S^2)} \frac{D n_l}{\rho S^2} \frac{4}{3} \pi R^3 \rho \mathbf{v}_d. \quad (5.6)$$

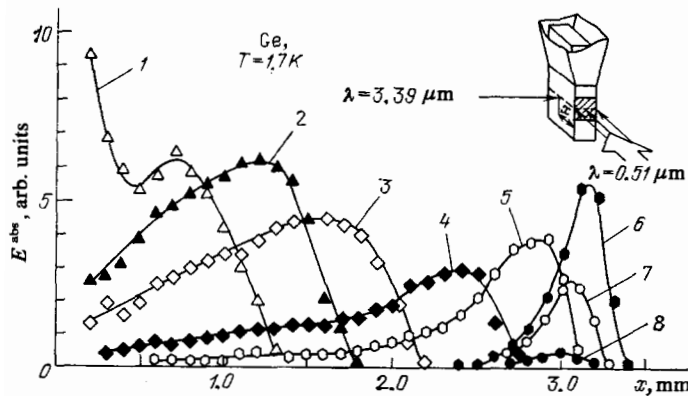


FIG. 15. Evolution of a cloud of electron-hole droplets in germanium after its production at $t = 0$ by a short pulse with $\lambda = 0.51 \mu\text{m}$ (pulse length of 10 ns, pulse energy of 120 erg), according to measurements of the absorption of a probe beam with a wavelength $\lambda = 3.39 \mu\text{m}$ (Ref. 358). The curves were recorded at various times t (μs): 1— ~ 0 ; 2—0.5; 3—1.0; 4—2.0; 5—3.0; 6—7.0; 7—30; 8—75. The experimental arrangement is shown by the inset at the upper right.

How could such a large mass (of real matter!) transported by a droplet fail to be detected in experiments on the motion of droplets? To answer this question we need to look at the appearance of the mass flux in (5.6) during the acceleration of a droplet to the velocity v_d . It turns out that over the entire time interval of the accelerated motion of the droplet the droplet is emitting sound in such a fashion that the resultant transport of mass by the whole crystal is exactly zero. This emission of sound causes a renormalization of the mass of a droplet (the renormalization is by an amount equal to the deformation mass mentioned above) and a retardation by radiation. The deformation mass is an effective mass: It appears in the equation of motion of a droplet and is unrelated to mass transfer.

6. PHONON WIND

The EHL in germanium forms as a cloud of droplets with $R < R_m \sim 10\text{--}20 \mu\text{m}$ (Refs. 172 and 166); the average density of this cloud does not change with increasing excitation intensity, while its dimensions increase.^{356,311,312} The mechanism for the formation of this cloud is not a diffusion mechanism, as can be seen particularly clearly in the case of pulsed surface excitation, in which case a layer of electron-hole droplets arises and moves rapidly into the interior of the semiconductor.³¹³ This motion, which continues for several microseconds, terminates a few millimeters from the excitation surface. The large friction with the lattice ($\tau_p \sim 10^{-9}$ s) rules out a free, ballistic, motion of the droplets and indicates the existence of some force fields which entrain the droplets. These effects were explained in Refs. 190 and 191 as being due to a phonon wind: fluxes of nonequilibrium phonons produced during the generation and recombination of carriers. As they are absorbed by carriers, the phonons create

force fields in the semiconductor which influence the spatial distribution of the EHL.

The phonon-wind model quickly found experimental support. It was shown that the electron-hole droplets move over macroscopic distances under the influence of various origins.^{190,253,258,256} Measurements of the droplet velocity distribution during steady-state surface excitation have confirmed that the motion of the droplets is not a diffusive motion.^{318,322,357} It has been shown that it is the phonon wind which is responsible for the formation of a cloud of droplets.^{314,358-361,187,254-256} The various stages of the evolution of a cloud during pulsed excitation (Fig. 15) were studied in Refs. 314, 35, and 359, and average characteristics of the phonon wind were determined. The cloud produced by a sharply focused surface excitation was found to be sharply anisotropic in Refs. 362, 205, 208, and 209. This effect was attributed to an anisotropy of the force exerted by the phonon wind (including the focusing of phonons) (Fig. 16). The shape of a cloud may be distorted near dislocations,³⁶³ and there is a tendency toward isotropy with increasing impurity concentration²⁰⁶. Droplets can be used to determine the quality of semiconductor crystals. Studies of the phonon wind are closely related to research on the properties of non-equilibrium phonons, which has recently been developing actively (see Refs. 364 and 365, for example). Superconducting bolometers or tunnel diodes are usually placed on the surface of the sample to detect phonons. Electron-hole droplets can be used to study the behavior of phonons directly in the interior of the semiconductor, so that some interesting experimental opportunities are opened up.

Research on the phonon wind is reviewed in Ref. 365; here we will discuss the formation of the phonon wind and describe a simplified model for its effect on the electron-hole droplets.

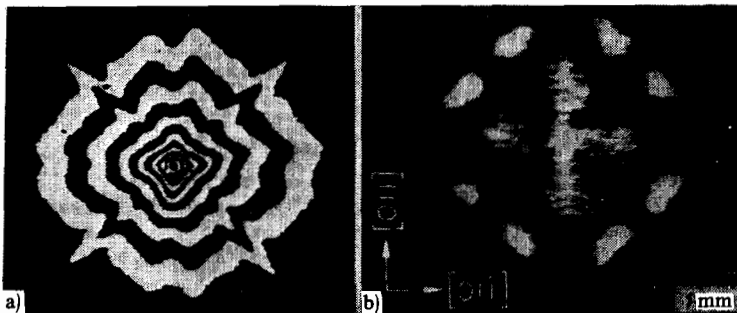


FIG. 16. Infrared image of a cloud of electron-hole droplets produced by exciting light sharply focused on the (100) surface of a germanium sample. The image was obtained across a (100) surface.^{205,209} a: Continuous excitation; the black and white bands are contours of constant intensity of the recombination radiation of an EHL. b: Pulsed excitation, recorded 5 μs after the exciting pulse (300 ns long, energy of 200 erg).

A degenerate EHL absorbs only phonons with $\hbar k < 2p_F$ (Subsection 4b4). Such phonons (especially those from the lower transverse branch) have a long lifetime at low temperatures and propagate ballistically over large distances (of the order of several centimeters). They are generated during the thermalization and recombination of carriers.²³⁾ Correspondingly, there are two types of phonon wind—the thermalization wind and the recombination wind—which are generally formed in different parts of a sample and which have different effects on an EHL.

The energy of the carriers which are produced, especially in the case of surface pumping, is far higher than the energy of an optical phonon: $\varepsilon > \hbar\omega_{\text{opt}}$ (in germanium, $\hbar\omega_{\text{opt}} \sim 37$ meV). Thermalization begins with the emission of a cascade of optical phonons which lasts 10^{-12} – 10^{-11} s. The remaining energy $\varepsilon_T \lesssim \hbar\omega_{\text{opt}}$ is emitted in the form of acoustic phonons, with a momentum $\hbar k \sim \sqrt{2m\varepsilon_T} \sim 2p_F$. Phonons with $k < 2p_F/\hbar$ may also arise from the decay of optical phonons into high-energy acoustic phonons and the subsequent degradation of the latter (which we will call “secondary” to distinguish them from the “primary” phonons which arise directly during the thermalization). Experiments with steady-state excitation at various frequencies^{357,206,365} apparently indicate that this pathway for the generation of a thermalization phonon wind is inefficient.³⁶⁶ During pulsed excitation, however, motion of electron-hole droplets is also observed after the primary phonons should have left the cloud.^{313,358} An effect of this sort is also observed during the generation of phonons by a heat pulse²⁵⁸ and is attributed to the appearance of a “hot spot”: a region in which high-frequency phonons are localized. As they decay, long-wavelength phonons form and cause the droplets to move.

The recombination phonon wind apparently forms during the thermalization of hot carriers produced during Auger recombination, which occurs highly efficiently in an EHL^{190,191} (Subsection 3e). During their thermalization in a dense EHL, another thermalization mechanism also operates, and this mechanism is efficient in terms of the generation of a phonon wind.^{293,254–256,358,366,365} This mechanism involves the generation of a phonon wind through collisions with carriers and the emission of plasmons (in germanium, $\hbar\omega_p \sim 15$ meV). The energy of a hot carrier becomes “spread out” over the electron system and is ultimately expended entirely on the emission of acoustic phonons with $k < 2p_F/\hbar$.

We turn now to the action of the phonon wind on an EHL. We assume that each event involving the recombination or production of an e-h pair is accompanied by the emission of phonons with $\hbar k < 2p_F$, with a total energy ε_R or ε_T , respectively; the average cross section for the absorption by carriers is $\bar{\sigma}_{\text{ph}}$. The conditions $\varepsilon_T \lesssim \hbar\omega_0$ and $\varepsilon_R > \varepsilon_T$ presumably hold, and we can estimate $\bar{\sigma}_{\text{ph}}$ from (4.9) with

²³⁾Generation of phonons should also accompany the formation of excitons and of an EHL.³⁶⁶ In several experiments the phonon wind has been produced by an external source: so-called heat pulses (a brief laser heating of a metal film deposited on the surface of the semiconductor,^{258,259,256} an additional carrier excitation source,¹⁹⁰ microwave breakdown of excitons,²⁹⁰ or IR heating of nonequilibrium carriers^{322–324}).

$\hbar k \sim 2p_F$. The average carrier density in a cloud, $n = \frac{4}{3}\pi R^3 n_l n_d$, must satisfy the following system of equations (in the isotropic approximation):

$$\frac{\partial n}{\partial t} + \text{div } n \mathbf{v}_d = -\frac{n}{\tau_l} + g, \quad (6.1)$$

$$\gamma (m_e + m_h) \mathbf{v}_d = \mathbf{f}_{\text{ph}}(\mathbf{r}, t) + \mathbf{f}(\mathbf{r}, t), \quad (6.2)$$

where

$$\mathbf{f}_{\text{ph}}(\mathbf{r}, t) = \frac{\sigma_{\text{ph}}}{4\pi s \tau_l} \int_V d^3 r' [\varepsilon_R n(\mathbf{r}', t') + \varepsilon_T g(\mathbf{r}', t') \tau_l] \frac{\mathbf{r} - \mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|^3}, \quad (6.3)$$

$t' = t - (|\mathbf{r} - \mathbf{r}'|)/s$, V is the volume of the sample, $g(\mathbf{r}, t)$ is the rate at which carriers are produced, and $\mathbf{f}(\mathbf{r}, t)$ is a force unrelated to the phonon wind. Expression (6.3) for the force of the phonon wind incorporates the delay between the emission and absorption of phonons, but it ignores the delay in their formation. Consequently, this expression describes the behavior of a cloud with an accuracy up to temporal and spatial intervals over which the phonon wind is generated. For primary phonons, these intervals are 10^{-9} – 10^{-10} s and 10^{-4} – 10^{-3} cm, respectively. A greater resolution is not required here. The effect of the secondary phonons of the hot spot can be taken into account only by abandoning the delay and by phenomenologically introducing a hot-spot lifetime^{358,366} τ_{ph} (usually, $\tau_{\text{ph}} \sim 1$ – 5 μs). We might add that Eqs. (6.1)–(6.3) ignore the effect of the phonon wind on the condensation of the EHL (it is assumed that all the carriers which are generated condense).

In the steady state, with $\partial g/\partial t = \partial n/\partial t = 0$, the force \mathbf{f}_{ph} in (6.3) is analogous to the force which would act on e-h pairs if they had charges

$$e_R = \sqrt{\frac{\sigma_{\text{ph}} \varepsilon_R}{4\pi s \tau_l}} \quad (6.4)$$

and were in a region in which background charges $e_T = e_R (\varepsilon_T/\varepsilon_R)$ were distributed with a density $g\tau_l$ (the analogy with electrostatics was first pointed out in Ref. 191). The phonon “charge” of an e-h pair can be determined experimentally (more on this below). In germanium the value $e_R \sim 1.5 \cdot 10^{-15}$ esu has been found²⁴⁾ (Ref. 358), in agreement with an estimate found from (4.9) with $\varepsilon_R \sim \hbar\omega_{\text{opt}}$.

Because of the effective mutual repulsion of e-h pairs, large volumes of an EHL cannot be confined by surface tension.¹⁹¹ Droplets with radii exceeding

$$R_m = \left(\frac{15}{2\pi} \frac{\sigma}{e_R^2 n_l^2} \right)^{1/3} \quad (6.5)$$

should break up. This tendency corresponds to the capillary instability of droplets with a space charge which is well known in nuclear fission. In germanium we have $R_m \sim 2 \cdot 10^{-3}$ cm, in approximate agreement with the largest droplet size observed. Furthermore, the recombination phonon wind causes a mutual repulsion of droplets, which has been observed experimentally.^{314,359} This repulsion apparently retards the formation of γ -droplets in nonuniform-

²⁴⁾The quantity $\rho = e_R n_l$ was determined in Ref. 358. The value of τ_p used in the analysis of the experimental results was too high. A recalculation with the correct value of τ_p yields the value of e_R given here.³⁶⁵

ly compressed germanium^{234,367} and prevents small droplets from merging into a single large droplet in nonuniformly compressed silicon.^{234,163} Incidentally, a potential well strongly improves the stability of droplets with respect to breakup.³⁶⁸

Introducing, by analogy with electrostatics, a phonon potential $\varphi(\mathbf{r})$ which satisfies the equations $\Delta\varphi = -4\pi(e_R n + e_T g\tau_l)$ and $\mathbf{f}_{ph} = -e_R \nabla\varphi$, we can easily show that for spatially uniform excitation the average cloud density is

$$n = -\frac{a_T g \tau_l + 1}{2a_R} + \sqrt{\left(\frac{a_T g \tau_l + 1}{2a_R}\right)^2 + \frac{g \tau_l}{a_R}}, \quad (6.6)$$

where

$$a_R = \frac{4\pi e_R^2 \tau_l}{\gamma(m_e + m_h)} = \frac{\bar{\sigma}_{ph} e_R}{\gamma(m_e + m_h) S},$$

$$a_T = \frac{4\pi e_R e_T \tau_l}{\gamma(m_e + m_h)} = \frac{\bar{\sigma}_{ph} e_T}{\gamma(m_e + m_h) S}.$$

It is easy to see that as g increases the cloud density reaches saturation and becomes independent of the excitation level; specifically, at $g \gg a_T^{-1} \tau_l$ we have $g \gg a_T^{-1} \tau_l$, $n \sim n_{\max} = a_T^{-1}$. This effect is observed in germanium^{356,311,187,205} and silicon.³⁶⁹ In germanium, we have $n_{\max} \sim 10^{15} \text{ cm}^{-3}$. We thus find $e_T \sim 10^{-15} - 10^{-16} \text{ esu}$, and this result is consistent with the estimates above. We might note that if we ignore the thermalization of phonon wind we would be unable to explain the density saturation.³⁶⁶

If the excitation is time-varying, but if the variation is only slight over times of the order of the transit time of phonons through the cloud of droplets, we can ignore the delay in (6.3), and the analogy with electrostatics remains in force. This approach is ordinarily used to describe the expansion of a cloud of carriers during pulsed excitation.^{191,385,366} It makes it possible to incorporate the hot spot, and it leads to a good description of the observed motion at times $\geq \tau_{ph}$ after the existing pulse. This model, however, fails to describe the initial stage of the evolution of a cloud of nonequilibrium carriers produced by a short ($t_i \approx 10^{-8} \text{ s}$) surface-excitation pulse: the formation, in a time shorter than $1 \mu\text{s}$, at the front of the cloud, of a layer of electron-hole droplets which moves into the interior of the sample at velocity near the sound velocity.³¹⁵ It turns out that this effect can be described in terms of the action of primary thermalization phonons if the delay between their emission and their absorption is taken into account. A simple model for the expansion of a plane layer of carriers was proposed in Ref. 315 on the basis of Eqs. (6.1)–(6.3). Under the condition $t_i \ll a/s$ (a is the initial layer thickness), and a plane geometry, these equations can be solved analytically. The shape of the droplet trajectories is determined by the dimensionless parameter $V_0 = \sigma_{ph} e_R n_0 / 4s\gamma m$ (n_0 is the initial carrier density in the cloud). The displacement of the droplets from their initial positions is small if $V_0 \ll 1$ and large if $V_0 \geq 1$. Figure 17 shows some typical droplet trajectories for $V_0 = 0.1$ and 1. The most interesting feature in Fig. 17 is the formation of a bunch of carriers at the front of the expanding cloud.²⁵¹ Near the front, the density of the cloud diverges in accordance with

²⁵¹A bunch is also formed if the cloud initially has a spherical or cylindrical shape.

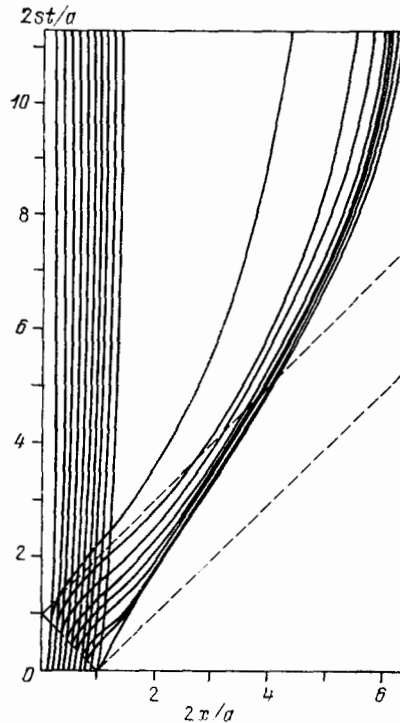


FIG. 17. Families of the trajectories of carriers produced at the time $t = 0$ by a short exciting pulse in a layer of thickness a . The carriers are being driven apart by primary thermalization phonons.³¹⁵ The nearly vertical lines correspond to $V_0 = 0.1$, the others to $V_0 = 1$.

$$\frac{n(x, t)}{n_0} \propto [x_f(t) - x] \frac{1}{V_{1+4V_0^2}^{-1}}, \quad (6.7)$$

where $x_f(t)$ is the coordinate of the front at the time t . A dense layer of carriers forms because the droplets immediately behind the front move under the influence of a greater force and overtake the front of the cloud. When the diffusion of carriers is taken into account, the front should of course spread out, and the divergence in (6.7) should be eliminated.

The dependence of the velocity of the front on its coordinate predicted by this model agrees well with the experimental result.³¹⁵ This model can also explain the behavior of a system of nonequilibrium carriers in germanium subjected to a brief IR heating pulse³²⁴ (Subsection 6d).

7. CONCLUSION

I had intended at least to mention all the research directions in the field of the electron-hole liquid. However, several directions have been omitted from this review: the two-dimensional EHL, the EHLs in impure semiconductors, the many interesting effects which occur in magnetic fields, and (unfortunately) many other directions. Some of the missing information can be found in some other reviews.⁸⁻¹⁴

I would like to express my gratitude to L. V. Keldysh, A. A. Manenkov, V. A. Milyaev, G. N. Mikhailova, N. N. Sibel'din, and A. P. Silin for many discussions and useful comments.

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Translated by Dave Parsons