V. N. Murzin. Submillimeter spectroscopy of collective and bound carrier states in semiconductors. At low temperatures, the Coulomb interaction of carriers in semiconductors results in a range of phenomena that are quite unusual for solid-state physics and includes the formation of quasiatomic bound states (excitons) and states of the molecular type in the carrier system and, finally, a phase transition of the carriers to a condensed state—that of the electron-hole (EH) Fermi liquid, which exhibits unique quantum properties. Studies of the exciton condensation, the possibility of which was suggested by L. V. Keldysh in 1968¹ and confirmed experimentally in Refs. 2–5, gave rise to a new trend in semiconductor physics that has come to occupy one of the central positions in this field.

This paper is devoted to the results of the spectroscopic approach to this problem that was developed in Refs. 4 and 6-23 and is based on studies in the range of photon energies that correspond to the characteristic bonding energies of the Coulomb states $\hbar \omega = m^* e^4/2\hbar^2 \kappa_0^2$ $= 10^{-3} - 10^{-2}$ eV ($\lambda = 50 - 1000 \ \mu$ m), i.e., in the longwave IR or submillimeter band.²⁴ These investigations have yielded one of the first experimental proofs⁴ of the existence of the exciton-condensation phenomenon; the nature of the condensed phase in Ge has been studied and several of its characteristic properties have been observed.

1. Exciton photoexcitation spectra. Structural features of quasiatomic bound states. For the first time since the experimental observation of excitons by E. F. Gross and N. A. Karryev in 1952, intrinsic exciton photoexcitation spectra from transitions of a crystal from ground exciton to excited states were observed in Refs. 6-10, i.e., exciton spectroscopy in the sense usually invested in the concept of atomic or molecular spectroscopy came into being. Figure 1 shows a typical Ge exciton spectrum. Similar spectra were observed in Ref. 25. These studies, with investigations of the photoexcitation spectra of minor impurities in several semiconductors (Ge, Si, InSb),¹¹⁻¹⁴ made it possible to study quasiatomic-state energy-structure features governed by complex dispersion relationships between energy and carrier quasimomentum in the crystal and to demonstrate effects governed by the limits of validity of



FIG. 1. Absorption spectra of free excitons in ultrapure germanium, measured using optical generation of carriers in a crystal. α is the absorption coefficient and d is the thickness of the crystal.¹⁰

the effective-mass approximation.

2. Bound states of molecular type. Since electrons and holes have similar masses, excitonic molecules in semiconductors should be characterized by low binding energies. For this reason, it has been possible to observe excitonic molecules in Ge and Si only when the crystal was deformed in a special way.²⁶ In the case of impurities, submillimeter-spectroscopy methods have been used to investigate several molecular-type complexes,^{12,14} as well as effects of the interaction of impurity centers¹²⁻¹⁴ rigidly embedded in the crystal.

3. Observation of exciton condensation. Phenomena of plasma (PR) and magnetoplasma (MPR) resonance in EHDs. A highly unusual new phenomenon in the form of resonant absorption ($\lambda_{max} = 150 \ \mu m$) was observed in Refs. 4 and 15-18; it appeared in threshold fashion as the temperature was lowered and the level of carrier generation raised in pure Ge. This phenomenon, which has been interpreted as a result of electrodipole interaction $(r \ll \lambda)$ of radiation with plasma oscillations of EH drops (EHDs),⁴ was one of the first experimental demonstrations of the existence of the exciton condensation in semiconductors and made possible the first estimate of the density of the condensed phase and the size of the EHD. A whole set of resonances of the electricdipole and magnetic-dipole types appears in a magnetic field in the phenomenon of magneto-plasma resonance (MPR) in EHDs.^{7,19-23} Study of the observed phenomena made it possible to obtain information on important characteristics of the EHD in Ge.

4. Ground-state energy and other parameters of the condensed phase in Ge. PR studies resulted in determination of the particle density $n_k = 2 \cdot 10^{17}$ cm⁻³ and the most important energy parameters of EHDs in Ge (energy of Fermi particles, work function for EHD, etc.), which characterize the change in the ground-state energy of the particles on transition to the condensed state.^{4,15-18} The observation of intensity oscillations of plasma absorption in EHDs in a magnetic field,¹⁹ an analog of the de Haas-van Alphen oscillations in metals, confirmed the Fermi-liquid nature of the condensed phase.

5. Renormalization of effective carrier masses in the condensed phase. Studies in the region of the cyclotron branches of MPR in EHDs in Ge^{20, 22, 23} made possible the first measurements of carrier masses in the condensed phase. It was found that they differ from the masses of free electrons and holes in the same crystal $(m_{c1}^* = 1.15m_{c1}, m_{c1}^* = 1.0m_{c1}, m_h^* = 1.15m_h)$.^{20, 23} Thus, it was shown that the collective interaction of quasiparticles in the EH liquid not only shifts, but also bends the energy bands of the crystal.^{20, 22-23, 27}

6. Electron-hole collisions in EHDs. The damping of EHD oscillations can, in principle, be determined by a number of single-particle and multi-particle mechanisms.^{21,23} It was shown in Refs. 15–16, 21, and 23 that the electron-hole collision mechanism predominates in the case of EHDs in Ge, and the frequency dependence $\gamma(\omega)$ was traced through a broad spectral interval below and above the Fermi carrier energy. In the case of or-



FIG. 2. Particle density in condensed phase in Ge plotted against magnetic field intensity with various orientations of H. 1) Measurements based on shift of plasma absorption band of $EHD^{19,23}$ 2) The same data processed in a more complex MPR model^{21,23}; 3) data of Ref. 30; 4) Ref. 31; 5) Ref. 32; the dotted curve represents the data of Ref. 33.

dinary metals, this is practically impossible, owing to the super-position of interband transitions. It was found,^{21, 23} that the characteristic quantum-mechanical dependence $\gamma \sim \omega^{2, 28}$ is satisfied up to $h\omega^{\approx}(2-3)\varepsilon^{F}$.

7. Macroscopic characteristics of EHDs in Ge. Studies made at various excitation levels made it possible to estimate the average radius of the EHD $(1-3 \ \mu m)$ and to determine the nature of the drop size distribution.^{15,18}

8. Spontaneous compressibility of EH liquid in a magnetic field. The EH liquid is a highly unusual substance, notably because it is characterized by a very low particle binding energy (on the usual atomic scales). Submillimeter-wavelength studies have made it possible to trace the variation of several EHD parameters in magnetic fields^{19, 23} and to detect an increase in the density of the EH liquid in fields H = 20-40 kOe.²¹ Figure 2 shows that as H increases, the concentration n_k first oscillates and then settles on a nearly linear $n_k(H)$ curve in agreement with the theory.²⁹ A change in drop shape was observed on application of a magnetic field (flattening in the plane perpendicular to H) due to recombinational magnetization of the EHD.^{22, 23}

Conclusion. Further investigation in this area appears to be promising, both with respect to study of electron states in semiconductors and from the standpoint of carrying out unique model analyses of the behavior of ordinary matter under the extreme conditions of ultrastrong fields, pressures, etc. The application of methods whose physical content and informational capability are on a par with those of atomic spectroscopy will open up opportunities for development of a quasiatomic nonlinear spectroscopy and other new areas in semiconductor physics. in collection: Éksitony v poluprovodnikakh [Excitons in Semiconductors], Nauka, Moscow, 1971, p. 5.

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