Phase diagram of nonequilibrium-carrier gas and electron-hole liquid in the straight-band semiconductor PbI_2

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We report the first experimental determination of the phase diagram for the transition of electrons and holes to a condensed state for a straight-band semiconductor.

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The results of a number of experiments indicate the possibility of phase separation of a uniform system of nonequilibrium carriers in straight-band polar semiconductors into a gaseous and a denser liquid phase.[1] The energetic stability of the electron-hole condensate in such compounds is the result of the interaction of the carriers with optical phonons.[2]

A phase transition leading to the formation of an electron-hole liquid differs from the usual (for example, water–vapor—liquid–water) phase transition in that even after it is complete the condition that the chemical potentials of the initial and final phases be equal is violated. This deviation from thermodynamic equilibrium arises owing to the finite lifetime τ of the carriers forming the electron-hole liquid and is most clearly manifested at temperatures far from the critical temperature T_c. Therefore, one expects that in straight-band semiconductors ($\tau \sim 10^{-10}$ sec) the region of thermodynamic instability of a uniform system of electrons and holes will be extremely narrow.

In this letter we present the results of studies to determine the phase diagram for condensation of carriers in sandwich structures of the straight-band semiconductor PbJ_2 (Ref. 3).

We studied the recombination emission arising during illumination of PbI_2 by an N_2 laser (peak power 3.2 kW, pulse duration 10^{-8} sec). The spectra were recorded by a photoelectric method using a strobe integrator. The experiments were done on single crystals located either in liquid helium or in helium vapor which was held stable in temperature to within ± 0.05 K.

The temperature dependence of the equilibrium density n_0 of the electron-hole liquid was determined from the gain spectra, as was done in Ref. 4. The gain spectra were obtained[1] by amplifying the spontaneous photoluminescence of PbI_2.[5] It should be noted that the negative absorption that was observed in the experiment in the region of the emission band of the electron-hole liquid (L band) and the fact that the width of the gain spectrum is independent of the excitation intensity confirm the existence of electron-hole droplets in PbI_2.

The boundary of the phase diagram on the gas side was found by measuring the threshold excitation density I_t for the appearance of the L band in the spectrum of the spontaneous photoluminescence. In such measurements, especially under conditions of surface excitation, it is difficult to determine the absolute density of carriers at each point in temperature. However, by taking the law of corresponding states into account, one can normalize the experimental values of I_t in the region of the critical point to the universal phase-equilibrium diagram and assuming that the coefficients relating I_t to the carrier density are temperature independent, one can complete the phase diagram.

The diagram of the phase transition to the electron-hole liquid in PbI_2 is shown in Fig. 1. The best coincidence of the experimental points for the function $n_0(T)$ (represented by crosses) with the standard phase diagram[6] (dashed curve) was obtained for $T_c = 52$ K. The corresponding value of the critical density is $n_c = 4\times 10^{17}$ cm^{-3}. The experimental dependence of n_0 on T is well described all the way up to 25 K by the expression $n_0(T) = n_0(0)[1 - \delta_n(kT)^2]$ ($\delta_n = 0.014$ meV^{-2}), which follows from Landau theory for a quantum Fermi liquid.

The experimentally determined phase boundaries on the gas side (solid dots in Fig. 1) are strongly shifted toward larger densities from the thermodynamic equilibrium value n_s. For example, at $T = 4.2$ K the degree of saturation is $\ln(n_t/n_s) = 10.8$ (n_t is the threshold concentration for the appearance of the electron-hole liquid).

It is of interest to compare the experimental values of $n_t(T)$ with the theoretical curve. To construct the theoretical curve we used the expression from Ref. 7 for the difference of the free energies $\Phi(\nu)$ of the condensed particles and also an equivalent number of gas molecules ν.

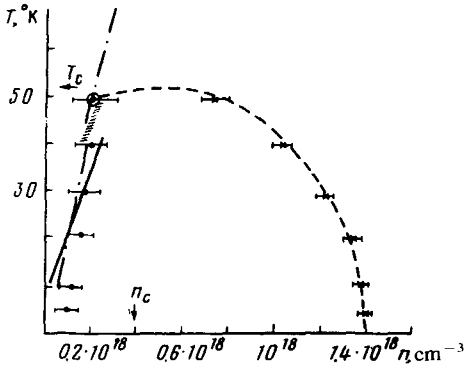

FIG. 1. Phase diagram of electron-hole liquid in PbI_2. The point at which the threshold I_t was normalized to the standard phase-equilibrium diagram is enclosed by a circle. To the left of the shaded region the electrons are not degenerate.

From the conditions $\partial\Phi/\partial v = 0$ and $\partial^2\Phi/\partial v^2 = 0$, we determined the minimum density of carriers for which drops of the electron-hole liquid can exist in PbI_2. However, such a state of the system is unstable against fluctuations, and additional supersaturation is required. In practice, the theoretical threshold of condensation under these conditions is determined by the equality of the thermodynamic barriers impeding the formation and breakup of the electron-hole liquid.

The agreement between the experimental and theoretical (solid line in Fig. 1) functions $n_t(T)$ is more qualitative than quantitative. In our view the main reason for this is the nonideality of the gas of carriers for concentrations at which condensation is possible in straight-band semiconductors.[2] If the polariton nature of the gaseous phase is taken into account, exciton-exciton collisions can lead to a lower value of the chemical potential of this phase compared to that of an ideal gas at the same density.[8] It is clear that this effect will only increase the threshold of condensation.

Finally, we note that the experimental points $n_t(T)$ do not agree badly with the Mott-transition line (dot-dash line in Fig. 1) calculated from the condition $ga_{ex} = 1.19$ (g is the screening length and a_{ex} is the Bohr radius of an exciton). This allows one to hope that the distortion[9] of the phase diagram obtained is insignificant.

[1)] These measurements will be described in detail elsewhere.

[2)] A calculation shows that for $T = 4.2$ K and $n = 10^{15}$ cm^{-3} the probability of an exciton-exciton collision in PbI_2 is 10^{12} sec^{-1}.

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