Dependence of the phase diagram for an exciton gas and an electron-hole liquid on the thickness of the germanium crystal

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(Submitted 3 June 1985)
Pis'ma Zh. Eksp. Teor. Fiz. **42**, No. 3, 81–84 (10 August 1985)

The gas boundary of the phase transition between an exciton gas and an electron-hole liquid is studied as a function of the thickness of the germanium sample. The results agree with a new model recently developed for the exciton condensation kinetics {V. M. Asnin *et al.*, Zh. Eksp. Teor. Fiz. **84**, 2129 (1983) [Sov. Phys. JETP **57**, 1239 (1983)]; Solid State Commun. **48**, 611 (1983)}.

The kinetics of the nucleation of a liquid in a first-order phase transition is usually analyzed in a model in which there is a quasiequilibrium in the system of liquid-phase nucleation centers in the region in which their size is close to the "critical" size.[1,2] A gas-liquid transition can be described by this approach if the deviation from equilibrium in the system is not too great. The phase diagram in this case is determined entirely by the thermodynamic characteristics of the system.

We have recently proposed a new model[3,4] for the kinetics of the condensation of an exciton gas into an electron-hole liquid. This model holds in the opposite case of a pronounced deviation of the system from equilibrium, caused by an intense diffusion of nucleation centers out of the gas phase and their destruction through surface recombination at the surface of the crystal. It has been shown that the properties of the phase transition in this case depend on only the kinetic characteristics of the system. The reason can be easily seen from the following arguments. As usual,[1,2] we assume that a droplet containing ν electron-hole pairs forms as the result of a sequential trapping of free excitons and that we may ignore the rate at which a nucleation center evaporates in comparison with the rate at which it is transported and consumed at the surface. The latter rate is determined by the quantity[3,4] $T_\nu^{-1} = \pi^2 D_0/\nu d^2$ (D_0 and $D_0\nu^{-1}$ are the diffusion coefficients of the exciton and of a nucleation center of size ν, respectively, and d is the thickness of the crystal). The probability for a transition of a nucleation center from a size ν to a size $\nu+1$ is then given by

$$W(\nu \to \nu+1) = \frac{\tau_\nu^{-1}}{\tau_\nu^{-1} + T_\nu^{-1}} = \left(1 + \frac{\tau_\nu}{T_\nu}\right)^{-1}, \tag{1}$$

where $\tau_\nu^{-1} = \pi r_0^2 \nu^{2/3} v n$ is the rate at which the nucleating center traps excitons, $r_0 = 3/(4\pi n_0)^{1/3}$, n_0 is the density of the electron-hole liquid, and v and n are the thermal velocity and density, respectively, of the excitons. We then find the following expression for the size distribution of the nucleating centers:

$$g_{\nu+1} = n \prod_{j=1}^{\nu} \left(1 + \frac{\tau_j}{T_j}\right)^{-1} = n \exp\left[-\sum_{j=1}^{\nu} \ln\left(1 + \frac{\tau_j}{T_j}\right)\right] = n \exp(-\Psi_\nu/kT), \tag{2}$$

 0021-3640/85/150095-04$01.00

For droplets of macroscopic size we have $\nu \gg 1$, so that in the approximation of intense escape, with $\tau_1/T_1 \gg 1$, we have

$$\Psi/kT \approx \int_1^{\infty} \ln\left(1+\frac{\pi D_0}{r_0^2 v\, nd^2 j^{5/3}}\right) d_j \approx \pi\left(\frac{D_0 n_0^{2/3}}{v\, nd^2}\right)^{3/5}. \quad (3)$$

Here Ψ represents a potential barrier which must be overcome by the nucleation center if it is to convert into a macroscopic droplet. The height of this barrier determines the rate of the condensation, which in this case depends on only the diffusion coefficient and thermal velocity of the excitons—not the thermodynamic characteristics of the system (the temperature, the surface-tension coefficient, and the condensation energy). The barrier height increases rapidly with decreasing thickness of the crystal, according to (3), so that a pronounced supersaturation of the exciton gas would be required for observing the condensation process. As a result, the phase-transition boundary shifts toward higher exciton densities and ceases to depend strongly on the temperature.

The phase diagram for the transition between an exciton gas and an electron-hole liquid in germanium was calculated as a function of the crystal thickness in Refs. 3 and 4 through a solution of the Becker-Döring system of kinetic equations. It was shown that this "kinetic" phase transition is observed in thin ($d \approx 10^{-3}$ cm) germanium crystals. In the present letter we report an experimental study of the phase diagram over a broad range of sample thicknesses. We compare the results with the calculations of Refs. 3 and 4.

The experimental samples are ultrapure germanium crystals with a density $N_i \approx 3\times 10^{10}$ cm^{-3} of shallow impurity centers, at which nucleation occurs by a homogeneous mechanism.[3-5] The diffusion of the nucleating centers through the sample may be accompanied by their trapping by impurity centers,[6] for which the probability increases with increasing droplet size. That characteristic droplet size ν_t at which trapping first becomes important can be found from the condition $\tau_t \approx T_\nu$, where $\tau_t^{-1} = \pi r_0^2 \nu^{2/3} N_i v/\nu^{1/2}$ is the trapping time:

$$\nu_t \approx \pi D_0 / (r_0^2 v N_i d^2). \quad (4)$$

In the crystals studied we find $\nu_t \gtrsim 40$ at $d \lesssim 0.05$ cm. It follows from expression (3) that the barrier height Ψ is determined primarily by the nucleation centers with small values of $\nu, < 10^2$, for which the scale time for escape by diffusion is much shorter than the scale time for trapping of the nucleating centers by a center. For a homogeneous nucleation mechanism we would thus expect the escape of nucleation centers to affect the condensation threshold at low temperatures even at sample thicknesses $d \lesssim 0.05$ cm.

To find the phase diagram, we studied the threshold characteristics of the emission of the electron-hole liquid at various temperatures. The excitation source is an LG-106M argon laser or an LGN-406 krypton laser. The threshold for the appearance of an electron-hole liquid (this is a metastable threshold) is measured by chopping the excitation for ≈ 0.02 s periodically at a frequency ≈ 10 Hz. During the interruptions, there is a complete recombination of the nonequilibrium electron-hole pairs in the

sample. This procedure makes it possible to carry out all the threshold measurements at a fixed value ($\approx$0.1 s) of the time interval alloted for condensation. It tends to reduce the role played by the trapping of nucleation centers by other centers.[1)] The stable threshold (at which the electron-hole liquid disappears) is measured during continuous excitation by additionally illuminating the sample with pulses $\approx 10^{-6}$ s, with a power $\approx$5 W, at a frequency $\approx$1 Hz from a GaAs laser. This method, developed in Ref. 7, makes it possible to find the absolute position of the stable threshold corresponding to the minimum possible droplet radius under the given excitation conditions. A hysteresis and a stable threshold for the electron-hole liquid can occur only for the trapped droplets.[2,6] The position of this threshold is determined by the thermodynamic characteristics of the system and thus does not depend on the sample thickness. This circumstance was exploited in fitting the experimental data to the theoretical curves.

One crystal is used in each measurement cycle. Its thickness is reduced in steps by polishing and etching. Figure 1 shows the comparative threshold behavior of the light for samples with $d = 0.085$ and 0.01 cm. The thresholds for the descending branches coincide. We see that a decrease in the sample thickness leads to a substantial shift of the threshold for the appearance of an electron-hole liquid. Figure 2 shows the measured position of the phase boundary for samples of various thicknesses. Also shown here are phase diagrams for the pertinent sample thicknesses calculated from the kinetic model of condensation developed in Refs. 3 and 4. The adjustable parameter in the calculations is the quantity $D_\nu = kT\tau_s/(m_{ex}\nu)$, where τ_s is the time scale of the scattering of an electron-hole pair by acoustic phonons in the electron-hole liquid, and m_{ex} is the exciton mass. The calculations give a satisfactory description of the experimental data under the assumption $\tau_s = 5\times 10^{-9}$ s at $T = 1.6$ K, and the temperature dependence is characteristic of macroscopic droplets. The value found for τ_s in this manner agrees with the data available on this time.[8,9] The good agreement between the experimental data and the theoretical predictions proves that this new model for the kinetics of the condensation of excitons into an electron-hole liquid is correct, and it confirms the homogeneous mechanism for nucleation in germanium.

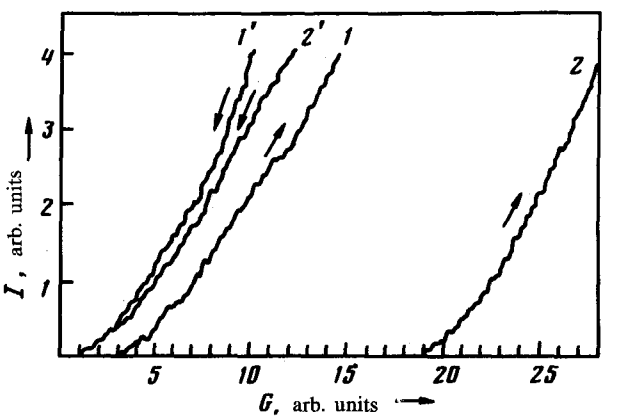

FIG. 1. Threshold behavior of the emission of the electron-hole liquid for samples with (1) $d = 0.085$ cm and (2) $d = 0.01$ cm. 1, 2—Ascending branch of the emission; 1', 2'—descending branch. $T = 1.6$ K.

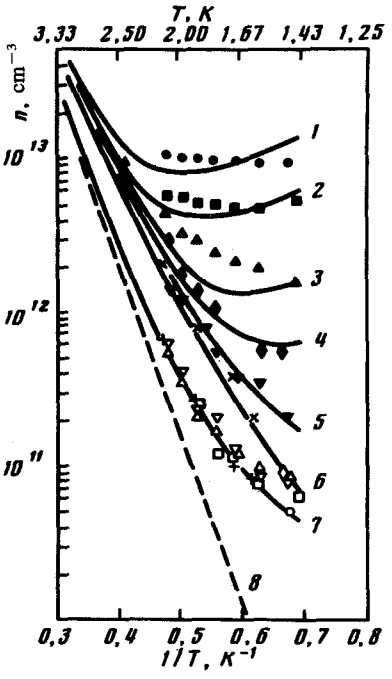

FIG. 2. Phase diagram of the transition of an exciton gas into an electron-hole liquid in germanium for samples with various thicknesses d (cm): 1—0.003; 2—0.005; 3—0.011; 4—0.021; 5—0.085; 6—0.3; 7—stable boundary of the phase diagram. Solid lines—Calculated from the theory of Refs. 3 and 4; points—experimental; open symbols—stable threshold; filled symbols—metastable threshold; dashed line—saturation vapor density.

[1)]It was observed that a decrease in the condensation observation time from several seconds to 0.1 s causes a 10–20% shift in the threshold toward higher densities. A further decrease in the time, to 10^{-3} s, leaves the position of the threshold essentially unaffected. This behavior apparently reflects the time variation of the nucleation, due to the slow relaxation of the height (Ψ) of the potential barrier due to the trapping of nucleation centers by other centers. This conclusion is supported by the circumstance that the magnitude of the effect falls off with decreasing sample thickness.

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Translated by Dave Parsons