Kinetics of condensation of excitons into an electron-hole liquid in finite-size crystals

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A model is proposed of the kinetics of condensation of excitons into an electron-hole liquid (EHL) in crystals whose dimensions are small compared with the exciton diffusion length. It is shown that for a homogeneous mechanism of formation of nucleation centers, allowance for the capture and destruction of the liquid phase centers at the surface differs in principle from allowance for the finite lifetime in the bulk of the semiconductor and leads to a strong inhibition of the condensation process. As a result, in thin crystals a strong shift of the phase boundary toward the region of very high supersaturation of the exciton gas occurs, its position being virtually constant in a broad temperature range. The conclusions of the model are in qualitative agreement with the experimental data obtained by investigating the exciton condensation threshold in 5 to 30 μm thick germanium crystals. A hysteresis of the EHL emission is observed near the phase boundary, its properties being different from the hysteresis observed in large size crystals. It is shown that the hysteresis of a thin crystal may be due to the formation at the condensation threshold of a thin EHL layer pressed between the crystal surfaces and existing in the metastable state.

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§1. INTRODUCTION

The kinetics of condensation of excitons into an electron-hole liquid (EHL) in semiconductors is usually considered in the model of classical nucleation theory[1,2] or in its generalization to the case of the finite lifetime of the liquid.[3,4] The crystal dimensions are disregarded in this case, this being justified if they exceed the diffusion-displacement length of the excitons, and also if the liquid is nucleated at impurities or defects. In the case of the homogeneous nucleation mechanism, however, when the nuclei of the liquid phase move freely through the crystal, its limited dimensions can lead to a radical change in the basic characteristics of the phase transition.

The reason for this is the following. If any one of the crystal dimensions is shorter than the diffusion length of the nuclei, they remain on the surface for a time $\tau_\nu \sim d^2/D_\nu$ (D_ν is the diffusion coefficient of a nucleus containing ν electron-hole pairs). The interaction of the drop with the surface centers should lead to sticking to the surface and to the loss of the nuclei within a time of the order of r_ν s^{-1}, where r_ν is the radius of the nucleus and s is the rate of the surface recombination of the electron-hole pairs in the nucleus. The nuclei captured on the surface cannot grow into large drops if the exciton density is less than $n_{\max} = 4n_0 s/v$, where n_0 is the density of the EHL and v is the thermal velocity of the excitons. At $n < n_{\max}$ the nuclei can develop into large drops only if during the growth time they do not experience even a single collision with the surface. This, as will be shown below, is highly improbable in thin samples and leads to an ultrahigh degree of supersaturation of the exciton gas at the condensation threshold at $T \lesssim 2$ K for germanium. As a result, in contrast to equilibrium systems, where the presence of a surface usually stimulates condensation and lowers the phase-transition threshold,[1] in the considered nonequilibrium case the surface plays the role of an effective brake on the exciton-condensation process. The sample thickness starting with which one should expect the surface to influence the phase-transition kinetics is determined by the relation $d \lesssim (D_{\nu^*}\tau_0)^{1/2}$, where τ_0 is the bulk lifetime of the EHL, $D_{\nu^*} = D_0/\nu^*$ is the diffusion coefficient of the critical nucleus, and D_0 is the diffusion coefficient of one electron-hole pair. In germanium, $\nu^* \approx 50$ particles,[4] $D_0 \approx 10^3$ cm^2 sec^{-1} (Ref. 5), and $d \leqslant 3\cdot 10^{-2}$ cm.

The data obtained in Refs. 6 and 7 offer evidence that the exciton condensation threshold in thin germanium crystals ($d \lesssim 10^{-3}$ cm) turns out to be at $T \leqslant 2$ K higher by two or three orders of magnitude than in thick samples ($d = 10^{-1}$ cm), and is almost independent of temperature, i.e., it does not satisfy the Clapeyron-Clausius relation.

We develop in this paper a model of exciton condensation in thin crystals, in which account is taken of the role of the surface recombination in the nucleation kinetics. The main conclusion of this model agree both with those obtained earlier[6,7] and with new results of the investigation of condensation kinetics, which will be presented below.

Hysteresis is observed at the threshold of the appearance of EHL in thin crystals, and the properties of the hysteresis differ from those of the hysteresis that exists near a "thermodynamic" phase-transition boundary.[4]

§2. MODEL OF EXCITON CONDENSATION KINETICS IN A THIN CRYSTAL

Following the standard models,[1–4] we shall describe the formation of a nucleus of the liquid phase as a chain of successive captures of excitons, assuming that nuclei of all sizes, starting with $\nu > 1$, are stable. We shall assume also a homogeneous nucleation mechanism, which apparently is realized in germanium. We consider a plane-parallel plate of thickness d and assume that when the nuclei of any size

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($\nu > 1$), land on the surface of the crystal they stick to it and are annihilated as a result of surface recombination. The kinetic equation that describes the distribution of nuclei in the dimensions g_ν, with allowance for their diffusion in coordinate space, takes the form

$$\frac{\partial g_\nu}{\partial t} = J_\nu - J_{\nu+1} + D_\nu \frac{\partial^2 g_\nu}{\partial x^2}, \tag{1}$$

$$J_\nu = g_{\nu-1}\beta n(\nu-1)^{2/3} - g_\nu(\alpha_\nu \nu^{2/3} + \nu/\tau_0) \tag{2}$$

with boundary conditions $g_\nu(x = 0, d) = 0$, which obviously corresponds to an infinite rate of surface recombination. Here

$$\beta = \pi r_0^2 v, \quad r_0 = (3/4\pi n_0)^{1/3}, \quad \alpha_\nu = \beta n_s \exp(8\pi r_0^2\sigma/3\nu^{1/3}kT),$$
$$n_s = N_c \exp(-\varphi/kT),$$

n_s is the density of the saturated vapor of the excitons over the flat surface of the liquid, N_c is the reduced density of states for excitations, φ is the binding energy of the excitons into EHL, σ is the surface-tension coefficient, and τ_0 is the volume lifetime of the EHL. The first term in (2) describes capture of excitons by the nucleus, the second describes their evaporation and volume recombination. Equations (1) and (2) differ from those considered in Ref. 4 only by the presence of the diffusion term.

In the stationary case, in which we are interested, and assuming exciton generation uniform over the volume, we have

$$J_\nu - J_{\nu+1} + D_\nu d^2 g_\nu/dx^2 = 0. \tag{3}$$

Then, considering that $D_\nu = D_0\nu^{-1}$, we readily see that we have an equation with separable variables, whose solution with allowance for the boundary conditions takes the form

$$g_\nu(x) = \sum_l g_\nu^{(l)} \sin\frac{\pi l}{d}x. \tag{4}$$

In the first harmonic we introduce the density of the nuclei, averaged over the plate thickness, and denote it as before by g_ν. We obtain then in place of (3), taking (2) into account,

$$g_{\nu-1}n\beta(\nu-1)^{2/3} - g_\nu[\nu^{2/3}(\beta n + \alpha_\nu) + \nu/\tau_0 + \pi^2 D_0/\nu d^2] + g_{\nu+1}[\alpha_{\nu+1}(\nu+1)^{2/3} + (\nu+1)/\tau_0] = 0. \tag{5}$$

The term containing D_0 is obviously the rate of loss of the nuclei on the surface of the crystal, determined by the "lifetime" $\tau_\nu = \nu d^2/\pi^2 D_0$.

Knowing the distribution function of the nuclei $g_\nu(n)$, we can determine from the solution (5) the condensation rate[1,2]

$$(dg/dt)_{\nu^*} = g_{\nu^*}(n)/\tau^*, \tag{6}$$

where g_{ν^*} is the density of the critical nuclei that correspond to the minimum of the distribution function, and τ^* is the time of passage of the nucleus through a space of size equal to the region $\Delta\nu$ near ν^*. The condensation threshold n_+ can be easily found by equating the right-hand side of (6) to the condensation rate corresponding to the experimentally observed number of macroscopic drops, in the excited volume of the crystal.[4]

To analyze Eqs. (5) we follow the procedure developed in Refs. 3 and 4 and introduce a function $\Psi(\nu)$ with the aid of which g_ν can be expressed in the form

$$g_\nu = G_\nu \exp[-\Psi(\nu)/kT]. \tag{7}$$

Substituting (7) in (5) and assuming that for sufficiently large ν the dependence of the pre-exponential factors on ν is weak compared with $\exp(-\Psi/kT)$, so that

$$g_{\nu\pm1} = G_{\nu\pm1}\exp[-\Psi(\nu\pm1)/kT] \approx g_\nu \exp(\mp\Delta\Psi/kT),$$

we obtain for $\Delta\Psi$ an equation whose solution is of the form

$$\Delta\Psi(\nu) = kT\ln\{{}^1/_2(1+a+b) + [{}^1/_4(1+a+b)^2 - a]^{1/2}\},$$
$$a = \frac{\alpha_\nu}{\beta n}\left(1 + \frac{\nu^{2/3}}{\alpha_\nu\tau_0}\right), \qquad b = \frac{\pi^2 D_0}{\beta n d^2 \nu^{5/3}}. \tag{8}$$

Under conditions when the diffusion can be neglected we have $b = 0$, and from (8) we obtain $\Delta\Psi(\nu) = kT\ln a$, from which it follows that

$$\Psi(\nu) = \sum_{j=2}^{\nu}\Delta\Psi(j) = 4\pi r_0^2\sigma\nu^{2/3} - \nu kT\ln\frac{n}{n_s} + kT\sum_{j=2}^{\nu}\ln\left(1 + \frac{j^{1/3}}{\alpha_j\tau_0}\right). \tag{9}$$

This expression, in which the first two terms represent the change of the thermodynamic potential upon appearance of liquid-phase nuclei in the gas,[1] and the last term is due to the finite lifetime of the EHL in the volume of the crystal, constitutes the so-called quasi-thermodynamic potential used to describe the nonequilibrium system exciton gas plus EHL.[3,4] We shall accordingly regard the function $\Psi(\nu)$, which can be obtained with the aid of (8), as a generalization of the quasi-dynamic potential (9) to include the case when an additional disequilibrium is present in the considered system and is connected with the loss of nuclei on the surface. The quantity G_ν in (7) is then the reduced density of states for nuclei with dimension ν.

The function

$$\Psi(\nu) = \sum_{j=2}^{\nu}\Delta\Psi(j),$$

obtained by numerical integration of (8) is shown in Fig. 1. The calculation was carried out using the same values of the parameters of the excitons and EHL in germanium as in Ref. 4. The diffusion coefficient D_ν is assumed equal to $D_\nu = kT\tau_r/m_{ex}\nu$, where m_{ex} is the exciton mass and τ_r is the momentum-relaxation time of the current carriers in the EHL. The value of τ_r was assumed to be the same as large drops ($\tau_r \approx 10^{-9}$ sec at $T = 1.6$ K), and its temperature dependence was approximated by the relation $\tau_r \propto T^{-2}$ (Ref. 5),[1)] so that $D_0 = 1.2\cdot10^3\cdot T^{-1}\cdot\text{cm}^2\cdot\text{sec}^{-1}$.

The maximum value of $\Psi(\nu)$ determines the stationary concentration of the critical nuclei and, consequently, the rate of nucleation in accordance with (6).

It follows from (8) that the contribution of the diffusion term b is most substantial at small ν, in contrast to the term that contains the bulk lifetime. For this reason, at $\nu \approx \nu^*$ the

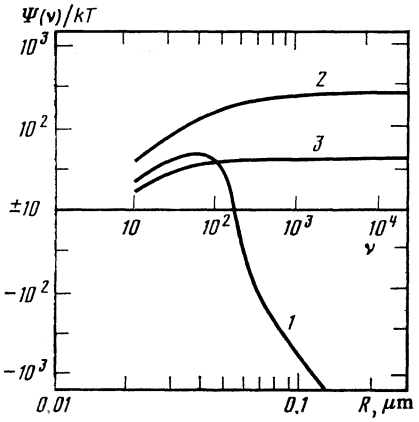

FIG. 1. Quasi-thermodynamic potential of excitons + EHL system in germanium at $T = 2$ K for crystals of different thickness: 1) $d = 0.1$ cm, $n/n_s = 7$; 2) $d = 10^{-3}$ cm, $n/n_s = 7$; 3) $d = 10^{-3}$ cm, $n/n_s = 80$.

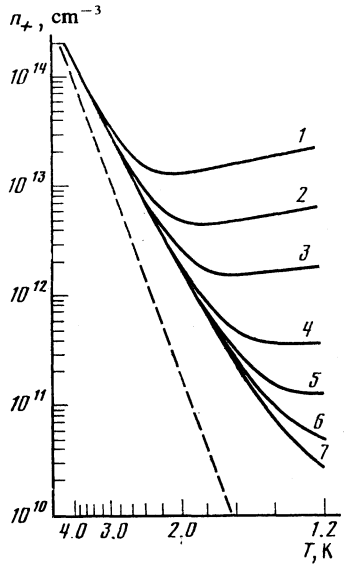

FIG. 2. Excitons + EHL phase boundary in germanium for crystals of different thickness, d [cm]. 1) 10^{-3}; 2) $2\cdot10^{-3}$; 3) $4\cdot10^{-3}$; 4) 10^{-2}; 5) $2\cdot10^{-2}$; 6) $4\cdot10^{-2}$; 7) 10^{-1}. Curve 7 coincides with the excitons + EHL phase boundary calculated in Ref. 4. The dashed line shows the $n_s(T)$ dependence.

maximum of the potential increases with decreasing d, which leads to a deceleration of the condensation process. This effect is illustrated in Fig. 1, which shows the comparative behavior of the potential $\Psi(\nu)$ for crystals of different thickness at $T = 2$ K and at a degree of supersaturation $n/n_s = 7$ corresponding to the threshold of condensation in a large crystal.[4] The height Ψ_{max} of the potential barrier necessary to observe condensation in a crystal with $d = 10^{-3}$ cm can be attained only by increasing the supersaturation of the exciton gas to a value $n/n_s \approx 80$ and by a corresponding shift of the threshold by more than 10 times.

So high a supersaturation at the condensation threshold causes a strong deviation of the temperature dependence of the threshold from that predicted by the Clapeyron-Clausius law. Indeed, as can be seen from (8), at sufficiently small d and low temperature it is possible to neglect in the expression for the potential the evaporation terms, so that up to $\nu \lesssim \nu^*$ we have $a \ll b$. In this case $\Delta\Psi \approx kT \ln(1+b)$ and

$$\frac{\Psi_{max}}{kT} \approx \sum_{j=2}^{\nu^*} \ln\left(1 + \frac{\pi^2 D_0}{\beta n d^2 j^{5/3}}\right), \qquad (10)$$

so that the rate (and consequently the threshold) of the condensation is practically independent of temperature. At the same time, at high temperatures, when $a \gg b$, the potential $\Psi(\nu)$ satisfies expression (9) and (for the case of germanium, where the volume recombination makes no contribution to Ψ at small ν)

$$\frac{\Psi_{max}}{kT} \approx \frac{16\pi\sigma^3}{3(kT)^3[n_0 \ln(n/n_s)]^2}, \qquad (11)$$

leads to an exponential dependence of the position of the phase boundary on the temperature.

A calculation of the phase diagram of the excitons + EHL system in germanium was carried out with the aid of expression (6). The value of g_{ν^*} was determined by direct numerical solution of Eq. (5). To simplify the calculation procedure in accordance with (7) it was approximately assumed that $g_{\nu+1} = g_\nu^2/g_{\nu-1}$. The time τ^* was assumed equal to the time required to capture ν^* excitons by a nucleus of critical size. The threshold was taken to be a value $(dg/dt)_{\nu^*}$ such that the rate of formation of the macroscopic drops[2)] amounted to 10^3 cm^{-3} sec^{-1}. The parameters that enter in (5) were taken to be the same as above in the calculation of $\Psi(\nu)$.

The results are shown in Fig. 2. It can be seen that allowance for the finite dimensions of the crystal leads to a strong change in the characteristics of the phase transition. With decreasing temperature, when the time of emergence of the nucleus to the surface turns out to be less than the time of its development into a large drop, an abrupt decrease takes place in the rate of condensation. As a result, the "thermodynamic" exponentially decreasing $n_+(T)$ dependence gives way to a weakly increasing one, corresponding to an increase of the degree of supersaturation at the condensation threshold, a degree which reaches for a crystal with $d = 10^{-3}$ cm and $T = 1.5$ K a value $\approx 5\cdot10^3$. The power-law growth of $n_+(T)$ at low temperatures is due to the temperature dependence of D_0.

The accuracy of the considered model of the condensation is determined by the assumption that Eqs. (1) and (2) are valid at small $\nu \lesssim 10$. In the case of germanium, for the thinnest samples, the diffusion approximation used in (1) is valid likewise only at $\nu \gtrsim 10$, when, as follows from the value given above for τ_r, the mean free path of the nuclei is $l \lesssim 3\times10^{-4}$ cm. However, trial calculations show that even a considerable deviation of the distribution function g_ν from that given by Eq. (5) lead at small ν to the same numerical values of the condensation threshold, accurate to a factor of the order of unity. The obvious reason for this is that the dimension of the critical nucleus corresponds to large values of ν ($\nu \gtrsim 10^2$, Fig. 1). More significant is the stationarity assumption and the uncertainty in the diffusion coefficient at small ν, since the threshold density of the excitons in the "nonthermodyna-

mic" region increases approximately linearly with increasing D_ν. With the approximation of the diffusion coefficient for large drops in the region of small ν, which is used in the calculations, is quite rough. The inaccuracy in the determination of the condensation threshold is obviously due also to the simplifications made in the derivation of (5).

The region of applicability of the model is bounded by the density of the excitons $n_{max} = 4n_0 s/v$, where s is the rate of surface recombination of the electron-hole pairs into the EHL. This quantity is the limiting value to which the condensation threshold tends when the crystal thickness is decreased. For a well etched surface of germanium, as will be shown below, $s \approx 10^2$ cm·sec^{-1} and consequently $n_{max} \approx 10^{14}$ cm^{-3}.

§3. EXPERIMENTAL PROCEDURE AND RESULTS

In the experiments we used the threshold behavior of the radiative recombination of EHL in germanium plates of thickness $d = 5$–$30\,\mu$m with shallow impurity center density $N_i = 10^{10}$–10^{15} cm^{-3}. The surfaces of the crystals, after polishing, were etched in one part of H_2O_2 + 0.02 parts KOH at $t = 80 \pm 3$ °C for 8–10 min, or in a polishing etchant with 3 parts HNO_3 + 1 part HF. The samples were freely secured inside a helium bath and were excited with a LG–106 M1 cw argon laser whose intensity could be smoothly varied with a rotating polarizer.[8] The signal was modulated via chopping the radiation from the sample at a frequency 170 Hz.

We measured the dependence of the EHL radiation intensity I on the excitation level G. To investigate hysteresis phenomena we recorded the EHL radiation in a regime in which the excitation was gradually increased from zero level (the threshold of the ascending or metastable branch G_+) and the character of the vanishing of the EHL radiation as the excitation was smoothly decreased from a level exceeding by many times the value of G_+ (the threshold of the descending or stable branch G_-).

To investigate the kinetics of the radiation relaxation and to determine from it the rates of the surface recombination for the electron-hole pairs in the EHL, we used excitation pulses of duration $\approx 1\,\mu$sec from a GaAs laser of ≈ 10 W power. The measurements were performed on samples in which the EHL lifetime obtained in this manner was not less than 5 μsec. Since the excitation level corresponded in this case in practice to complete filling of the thinnest samples with the liquid, the rate of the surface recombination of the particles could be estimated at $s \approx d/2\tau \approx 10^2$ cm·sec^{-1}.

Figure 3 shows the dependence of the EHL radiation intensity I on the excitation level G for two different samples of thickness $d = 7\,\mu$m. In all the cases investigated by us the $I(G)$ behavior exhibited hysteresis, but the properties of the ascending (metastable) branch (curves 2, 3) depended on the sample. A feature of curve 2 is the jumplike appearance of radiation at the threshold G_+. Estimates show that the size of the jump corresponds to formation of a volume of liquid containing not less than 10^{-9} particles.[3)] This means that in a sample of thickness $\approx 10^{-3}$ cm there can appear at the nucleation threshold a layer of liquid of thickness $3 \cdot 10^{-3}$ cm. We note that in the "usual" hysteresis behavior observed in bulky samples[4] a drop with dimension $R \approx 10^{-4}$ cm, containing not more than 10^7 particles, can grow out of one nucleus. In a number of cases a smooth $I(G)$ dependence is observed near G_+ in place of a jump (curve 3). The causes of the different behavior of the metastable branch near the threshold are not clear. There exists, however, a definite correlation between the width of the hysteresis, i.e., the ratio G_+/G_-, and the behavior of this branch, namely, the broader the hysteresis the more probable that a jump of radiation will be observed near G_+.

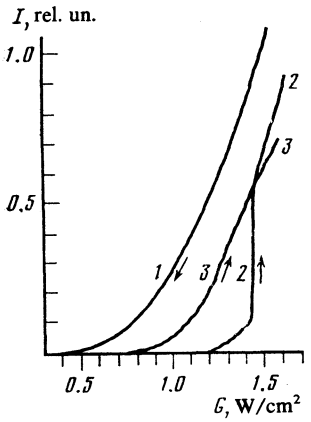

FIG. 3. Threshold behavior of the EHL radiation in germanium crystals of thickness $d \approx 7 \cdot 10^{-4}$ cm with $N_i \approx 10^{10}$ cm^{-3}: 1) stable branch; 2, 3) different types of metastable branch; $T = 1.7$ K

Figure 4 shows a comparison of the behavior of $I(G)$ in samples of different thickness and different degree of doping. It is known that the density of the nonequilibrium carriers in a plate whose thickness is less than the diffusion length is

$$n = \frac{G}{d}\left(\frac{1}{\tau} + \frac{2s_{ex}}{d}\right)^{-1}.$$

If the rate of surface recombination is large enough, so that $2s_{ex}/d \gg 1/\tau$; we have

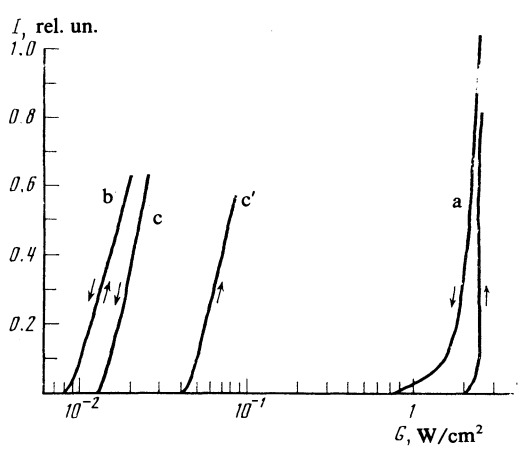

FIG. 4. Threshold behavior of the EHL radiation in germanium crystals of different thickness and different degree of doping: a) $d \approx 10^{-3}$ cm, $N_i \approx 10^{10}$ cm^{-3}; b) $d \approx 10^{-3}$ cm, $N_i \approx 10^{15}$ cm^{-3}; c, c') $d \approx 0.1$ cm, $N_i \approx 10^{10}$ cm^{-3}; $T = 1.7$.

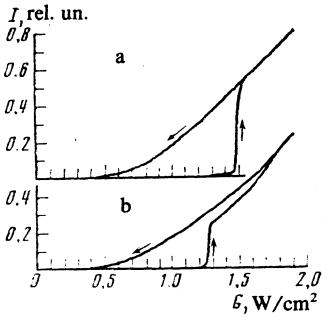

FIG. 5. Threshold behavior of the EHL radiation in germanium crystals with thickness $d \approx 10^{-3}$ cm at different temperature: a) $T = 2.0$ K; b) $T = 1.6$ K.

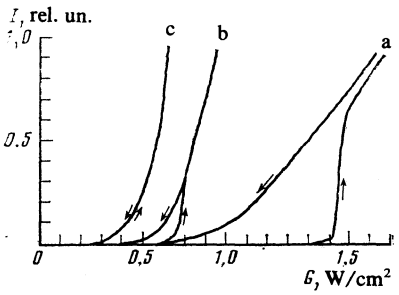

FIG. 6. Dependence of threshold properties of EHL radiation in germanium on the crystal thickness, obtained for a wedge-shaped sample with $N_i \approx 3 \cdot 10^{13}$ cm^{-3}: a) $d \approx 8 \cdot 10^{-4}$ cm; b) $d \approx 2 \cdot 10^{-3}$ cm; c) $d \approx 3 \cdot 10^{-3}$ cm; $T = 1.7$ K.

$$n \approx G/2s_{ex}.$$

In germanium, the rate of surface recombination of the excitons is $s_{ex} \sim 10^5$ cm·sec^{-1} (Ref. 4). Consequently, at $d \lesssim 10^{-1}$ cm the exciton density is proportional to the excitation level and does not depend on the sample thickness (see §4). As can be seen from Fig. 4, the threshold values for a thin sample exceed the corresponding values for the bulky one by almost two orders of magnitude. Another distinguishing feature of thin samples is that the threshold values of G and the hysteresis character are preserved also in doped samples up to a shallow-impurity-center density $N_i \approx 10^{14}$ cm^{-3}. At $N_i > 10^{14}$ cm^{-3} the condensation threshold in a thin crystal drops steeply and becomes close in value to the threshold in a thick samples (curve b of Fig. 4).

Figure 5 shows the hysteresis behavior of $I(G)$ for a thin sample at temperatures 1.6 and 2.1 K. It can be seen that there is practically no temperature dependence, in agreement with the data of Refs. 6 and 7, and with Fig. 2. In thick samples, in the same temperature range, the threshold excitation increased by one order of magnitude (see Fig. 2). We note that if the increase of the excitation threshold level in thin samples were due only to a decrease of the effective lifetime of the excitons, the temperature dependence of the excitation would not differ from that observed in a thick sample.

The threshold characteristics of the radiation as functions of the crystal size were investigated using a wedge-shaped sample, whose thickness varied from $3 \cdot 10^{-3}$ to $5 \cdot 10^{-4}$ cm with a gradient $2.5 \cdot 10^{-4}$. The results, shown in Fig. 6, indicate that with increasing sample thickness the threshold G_+ shifts towards lower excitation levels. In this case the hysteresis becomes narrower and vanishes completely for a sample $d = 30\,\mu$m thick.

§4. DISCUSSION OF RESULTS

1. Condensation threshold

The model developed in §2 explains qualitatively two most significant (and previously not understood) features of the condensation of excitons in thin germanium samples: the anomalously high threshold and its independence of temperature. A quantitative comparison of the experimental data with calculation (see Fig. 2) requires a determination of the numerical value of the threshold exciton density n_+. This can be done by comparing the threshold excitation intensity G_+ at $T = 4.2$ K when the threshold is independent of the crystal thickness (Fig. 2), and at temperatures at which the location of the threshold is determined by the limited size of the sample. Such a comparison gives $G_+(4.2)/G_+(1.7) \approx 5$ at $d \approx 10^{-3}$ cm, whence, using for the threshold density at $T = 4.2$ K the value[4] $n_+ \approx 2 \cdot 10^{14}$ cm^{-3} (Fig. 2), we obtain $n_+(1.7) \approx 4 \cdot 10^{13}$ cm^{-3}. With the aid of the data of Fig. 3 we obtain in this case for the exciton surface recombination rate $s_{ex} = G_+/n_+ \approx 10^5$ cm·sec^{-1}, which agrees with the result obtained in Ref. 4. Therefore one more estimate of n_+ can be obtained by comparing the threshold G_+ at one and the same temperature for a thin and for a thick sample, for which the threshold density is known.[4] Such a procedure also leads to the value $n_+(1.7) = (3 - 4) \cdot 10^{13}$ cm^{-3} for a sample with $d \approx 10^{-3}$ cm.[4)] This is close to the value expected in accordance with the condensation model developed above (Fig. 2).

It seems to us that the most important conclusion that follows from the qualitative agreement between experiment and theory is the confirmation of the homogeneous mechanism of nucleation of EHL in germanium. In the case of nucleation on impurity centers or crystal defects, the phase-transition diagram would be independent of the crystal size. It is known, however, that the drops can be captured by shallow impurity centers,[9] and consequently a criterion for a "thin" sample should be taken to be the ratio of the times of capture of the nuclei by the impurity center and of the emergence to the surface. As a result, when the impurity density is increased the crystal thickness corresponding to a "thin" sample will decrease. Indeed, as seen from the data of Fig. 4, at $N_i \approx 10^{15}$ cm^{-3} the condensation threshold in a sample with $d \approx 10^{-3}$ cm hardly differs from the value measured for a crystal with $d = 0.1$ cm.

2. Dimensions and shape of electron-hole drops in a thin crystal

The large supersaturation of the exciton gas at the condensation threshold in a thin crystal causes the resultant viable nuclei to induce an abrupt increase in the volume of the EHL, as is manifest by a jumplike occurrence of EHL radiation. The drop exists in the volume of the crystal, its size

corresponds to the condition of stationary existence of a spherical drop,[5] which has a radius

$$R_0=3\tau_0 vn/4n_0, \tag{12}$$

from which it follows that for a sample with $d = 10^{-3}$ cm at $n_+\approx 4\cdot 10^{13}$ cm^{-3} we have $R = 5\cdot 10^{-3}$ cm $> d$.[5)] This means that the liquid in such a sample can exist in the form of a layer that joins together the opposite surface of the crystal. Then the lifetime of the drops will be determined principally by the rate of surface recombination of the electron-hole pairs in the EHL. Approximating for simplicity the drop shape by a cylinder, we can estimate its size from the ratio of the balance of the fluxes of the surface recombination and of the excitons incident on the surface:

$$\frac{R_c}{d}=\frac{1}{4}\frac{n}{n_0}\frac{v}{s}. \tag{13}$$

For a crystal with thickness $d = 10^{-3}$ cm at the condensation threshold $n_+\approx 4\cdot 10^{13}$ cm^{-3} and at $s\approx 10^2$ cm·sec^{-1} we obtain $R_c/d = 1$ and $R_c\approx 10^{-3}$ cm. This corresponds to $\approx 10^9$ particles in the drop, which exceeds by approximately one order the sensitivity threshold of our apparatus.

An investigation of the kinetics of relaxation of radiative recombination of EHL shows that the liquid, in all probability, wets the surface of the sample. Indeed, otherwise the relaxation kinetics would include inevitably a component with a time of the order of the bulk lifetime of the liquid ($\tau_0\approx 40$ μsec), something not observed in experiment.

An experimental confirmation of the assumption that the EHL on the descending branch in a thin sample can have the form of a layer "clamped" between the surfaces of the plate was obtained from experiments that made it possible to measure the lifetime of the EHL. In these experiments, when the descending branch was recorded, the excitation of the crystal was interrupted periodically for a short time with a mechanical chopper. The duration of the "dark pulse" could vary in the range 10^{-5} sec $< \Delta t < 10^{-3}$ sec. The idea of the experiment was that the chopping of the excitation should lead to a rapid decrease of the size of the drops because the exciton flux to the drop is stopped. If the duration of the dark pulse is such that the drops do not have time to recombine completely, their size is restored to the initial value after the end of the pulse, and the action of the "dark pulses" does not manifest itself in the behavior of the stable branch of $I(G)$. In the opposite case, breakaway will take place to the metastable branch at the point where the duration Δt is sufficient for complete recombination of the drops. The results of such measurements for a sample of thickness $d\approx 10^{-3}$ cm are shown in Fig. 7. From the data of this figure, by measuring the amplitudes of the radiation signals corresponding to breakaway to the metastable branch, depending on the duration of the dark pulse, one can determine the lifetime of the liquid (inset in Fig. 7). The radiation relaxation time is $\approx 10^{-5}$ sec, corresponding to a lifetime $\tau = d/s$ of the EHL layer on the surface at $s = 10^2$ cm·sec^{-1}. These data are also in agreement with the described results of the measurements of τ under intensive pulse excitation of thin samples, corresponding to filling them with the EHL. We note that when

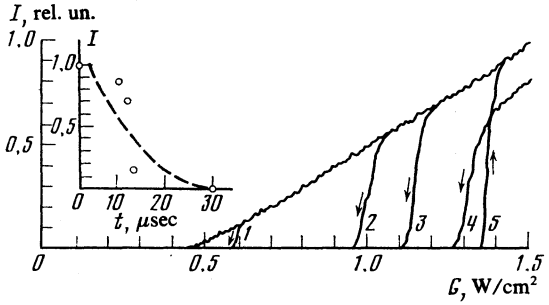

FIG. 7. Effect of "dark pulses" of different duration on the behavior of the stable branch of EHL radiation in a germanium crystal of thickness $d\approx 10^{-3}$ cm. Δt (μsec): 1) 19; 2) 20; 3) 22; 4) 30; 5) ascending metastable branch; $T = 1.7$ K. In the inset is shown the EHL kinetics obtained from the data of the figure.

the EHL is fixed in the volume, the radius of the drops would be, in accordance with (12), not less than 3 μm even near the threshold G_-, and breakaway from the stable branch at $T = 1.7$ K could be observed only at $\Delta t \gtrsim 2\cdot 10^{-4}$ sec.

3. Hysteresis of the appearance and vanishing of the liquid layer

A remarkable feature of the behavior of EHL in a thin sample is the existence of hysteresis of $I(G)$ near the threshold.

The nucleation model considered above makes it possible to determine the behavior of the threshold of the metastble branch, but is not complete enough for the description of the hysteresis phenomena. Nonetheless, we can qualitatively describe the observed hysteresis by assuming that the EHL in a thin sample ($d\approx 10^{-3}$ cm) exists in the form of a layer. In fact, if the drops are fixed in the sample volume and do not touch the surface, the threshold of the stable branch, first, should not depend on the dimensions of the crystal and, second, its width should be $G_+/G_-\approx 10^2$, since $n_-\approx 10^{11}$ cm^{-3} at $T = 1.7$ K (Ref. 4).[6)]

If, however, a drop is on the surface, the excitation level that ensures its stationary state depends on the shape of the drop. An EHL in the form of a flat layer on one of the surfaces of the crystal can exist only at an exciton density $n \gtrsim n_{max}$ which, as shown above, is not reached at the condensation threshold G_+. If the liquid drop joins together the opposite surfaces of the crystal and its shape is close to cylindrical, the condition of its stationary state can be satisfied in accordance with (13) at smaller exciton densities the smaller the ratio R_c/d. The hysteresis can be explained in the following manner: at the threshold G_+ there is produced a cylindrical drop that short circuits the opposite surfaces of the crystal, and has a radius that decreases gradually with decreasing G, so that at $G = G_-$ the drop breaks into two segments and vanishes. The point $G = G_-$ corresponds to the limit of static instability, when the surface energies of the cylindrical layer and of the segments are equal. Estimate of the stability limit of an EHL layer clamped between the surfaces of a sample of thickness $d = 10^{-3}$ cm show that one can expect a hysteresis with $G_+/G_- = 2$, which is close to the one observed in experiment.

There are, however, a number of circumstances that complicate the situation. The value of G_+, as seen from Fig. 2, should depend very strongly on the sample thickness. The thickness dependence observed in the experiment (Fig. 6) is weaker (and, unfortunately, not very well defined, since different samples can have thresholds that differ by a factor 1.5–2).

The model developed in the paper does not take into consideration the possibility of capturing nuclei by impurity centers, which apparently can influence the character of the phase diagram also at $N_i < 10^{14}$ cm^{-3}.[7)]

CONCLUSION

We have consider for the first time a model of exciton condensation in to an electron-hole liquid in a semiconductor, with account taken of the influence of the surface recombination of the drops on the condensation kinetics and of the hysteresis of the phase transition. It is shown that allowance for surface recombination differs in principle from allowance for the volume lifetime of the EHL and leads to an effective increase of the potential barrier for nucleation, i.e., it inhibits the condensation process. As a result, in thin semiconductor plates the oversaturation of the exciton gas at the condensation threshold reaches tremendous values $\approx 10^3$–10^4. This makes it possible to realize in principle in the exciton system a unique situation at which it is possible, for example, to observe sinusoidal decay in a liquid-gas transition.[11] So far, the theoretical predictions that such a phase transition is possible have not been experimentally verified because of the difficulty of realizing ultrahigh supersaturation of the gas.

The model developed describes satisfactorily the results of the experiment, primarily the abrupt shift of the condensation threshold into the region of high excitation levels, and the violation of the Clapeyron-Clausius law in the case of thin crystals. The proposed scheme of considering the condensation kinetics can apparently be used to describe the phase transition under conditions of existence of any mechanism that takes the nuclei out of the crystal excitation region, such as phonon wind, inhomogeneous deformation, etc.

In conclusion, the authors thank B. M. Ashkinadze for helpful discussion and Yu. M. Lomasov for help with the experiment.

[1)]Such a relation describes satisfactorily the behavior of τ_r in EHL in germanium at $1.5 < T < 4.2$ K, but underestimates the diffusion coefficient at lower temperatures, then a gradual transition takes place to the relation $\tau_r \propto T^{-5}$. At $1.5 < T < 4.5$ K, the times τ_r for excitons, electrons, and holes in EHL are close in value.

[2)]This value is to a considerable degree arbitrary and is determined by the sensitivity of the experimental setup. However, the condensation threshold is practically independent of the assumed value of the condensation rate when the latter is varied within several orders of magnitude.[1–4]

[3)]The number of radiating particle was determined by two methods: by direct estimates of the sensitivity of the radiation receiver, and by comparison with the radiation signal of a bulky sample near the onset threshold of the EHL. In the latter case, if $Gd^{-1} = n\tau_{ex}^{-1} + vg_v\tau_0^{-1} \approx 2n/\tau_{ex}$, i.e., the radiation threshold is overestimated by a factor of 2, then $n\tau_0^{-1} \approx n\tau_{ex}^{-1}$, and from this we can obtain v. Both methods gave approximately the same estimate of the number of radiating particles.

[4)]In Ref. 6, in the calibration of the scale of G, it was assumed that the excitons and of the electron-hole pairs in EHL in thin samples have equal lifetimes, and this lead to an overestimation of the value of n_+ at the same excitation level G_+.

[5)]Equation (12), just as Eq. (5), was derived neglecting the diffusion restriction on the exciton flux, which becomes substantial in germanium at $R \gtrsim 10^{-3}$cm ($v \gtrsim 10^9$). Allowance for this circumstance leads to a decrease of the stationary radius of the drops by an approximate factor of 2, leaving the arguments presented above in force.

[6)]This hysteresis can in fact be observed in samples of intermediate thickness (from 30 to 100 μm), if the stable branch is plotted by the procedure described in Ref. 8: the sample is illuminated by infrequently repeated powerful light pulses from a GaAs laser. It is known[4] that in bulky samples ($d \gtrsim 1$ mm) hysteresis is observed only at $N_i \approx 10^{10}$ cm^{-3}; the hysteresis practically vanishes even at a impurity density $N_i \approx 10^{13}$ cm^{-3}. If the sample is made thinner, then at $N_i \gtrsim 10^{10}$ cm^{-3} and $d \approx 100\,\mu$m the width of the hysteresis decreases rapidly because of the increase of G_+, so that $G_+/G_- \approx 50$. Exactly the same effect is observed in impurity samples, but at a lower thickness: at $N_i \approx 10^{13}$ cm^{-3} and $d \approx 30\,\mu$m. The preliminary results of an investigation of this effect indicate that the position of the threshold of the metastable branch is explained by the model of §2 with allowance for the dependence of the effective diffusion coefficient on the density of the defects (impurities) that restrain the drops.

[7)]We note that in principle it is possible to explain the condensation singularities observed in thin crystals, using the model of surface nucleation, if it is assumed that the rate of surface recombination of the electron-hole pairs in the EHL depends on the size of the drop. Such a possibility was considered in Ref. 10, where the hypothesis was advanced that capillary pressure is capable of changing the surface-recombination rate. In this case, at a given exciton density, when a small drop (nucleus) located on the surface cannot be maintained by the electron flux and recombines, a large one turns out to be stable.

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