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Lifetime, surface tension, and impurity effects in electron-hole condensation*†

Richard N. Silver

Los Alamos Scientific Laboratory,‡ Los Alamos, New Mexico 87544
and California Institute of Technology, Pasadena, California 91109

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A theory of electron-hole condensation in germanium and silicon is developed in which recombination, evaporation, and exciton collection are treated as random processes. An expression is derived for the probability distribution of the number of electron-hole pairs bound to a nucleation center. Consideration of the effects of lifetime, surface tension, and nucleation center leads to: (i) the relation of multiexciton complexes to electron-hole droplets; (ii) stable droplet sizes which are strong functions of temperature but only weak functions of pair-generation rate; (iii) the possibility of determining the surface tension from size measurements; and (iv) deviations from the usual phase diagram for a liquid-gas transition at very low temperatures. Detailed numerical calculations are carried out for uniform excitation of germanium and compared to data available from laser excitation experiments.

I. INTRODUCTION

The equilibrium between liquid and gas phases of most systems is maintained by the dynamical processes occurring at the interface between the two phases. For the electron-hole liquid-gas transition in germanium and silicon[1-3] a new volume effect is also present arising from the finite carrier lifetimes. One obvious result is that in the steady state the crystal must be continually excited to make up for recombination. In this paper it shall be shown that other less obvious physical phenomena should also be expected. These include multiexciton complexes attached to impurities and stable droplet sizes on the order of many microns if the excitation level is not too high.

Pokrovsky[1] was the first to observe in doped silicon crystals a series of narrow peaks in the recombination radiation extending from the bound-exciton line to the peak of the droplet line. The detailed study of the radiation as a function of excitation level and impurity level by Sauer[4] and Kosai and Gershenzon[5] gave strong evidence that the radiation arose from recombination of electrons and holes in multiexciton complexes bound to impurities. Since then Martin[6] has observed a similar series of peaks in doped germanium suggestive of multiexciton complexes. The nature of the connection between multiexciton complexes and electron-hole droplets has remained an important question, although most physicists would agree with Pokrovsky's initial speculation[1] that impurities act in some way as nucleation centers for electron-hole condensation.

A seemingly unrelated question has been why the electron-hole liquid comes in the form of "electron-hole droplets." An important concept in the description of usual liquid-gas transitions is Landau's idea of a critical size below which a droplet evaporates and above which a droplet grows indefinitely, i.e., no droplet size is stable. Electron-hole droplet sizes on the order of many microns have been determined by both light-scattering experiments[1] and shot-noise experiments[7,8] in which droplets are pulled apart in the high electric field of a p-n junction and the total charge measured. More recently it has been observed that the droplets increase in size with increasing temperature.[9,10] There have been observations of millimeter-size droplets[11] but only under extremely high excitation conditions. We shall discuss this rather special case separately.

Several workers on electron-hole droplets have taken data on the dependence of the amount of liquid phase on excitation level, and on the decay and evaporation of the liquid after the excitation source is turned off. Such data have been fit to rate equations governing evaporation, recombination, and exciton collection.[1,12] An assumption made in these fits, which is not correct in the view of the present paper, is that the droplet number is fixed and the droplet size depends strongly on excitation level. (This approach may have been motivated by some initial reports of such behavior in light-scattering experiments, but from the present viewpoint it is probable that the temperature was increasing with excitation level. Temperature control is a well-known difficulty of both laser excitation and double-injection experiments.[13,14]) It shall be argued that at fixed temperature it is droplet number rather than droplet size which varies strongly with excitation level.

In order to understand droplet-size measurements and establish the connection between multiexciton complexes and electron-hole droplets, in Sec. II a description of electron-hole condensation as a stochastic process is developed. In the calculations of this paper it shall be assumed that the exciton density and the temperature are uniform throughout the sample. Comparison of the theory with experiment will be carried out, with educated guesses for the parameters, in Sec. III. In actual laser-excitation or double-injection experiments there are both density and temperature gradients. Improved agreement with experiment should be obtained once the ideas developed here are employed in understanding transport effects in real experiments. Some remarks on this transport problem along with a discussion of other directions of future work will be presented in Sec. IV.

II. STOCHASTIC VIEW OF ELECTRON-HOLE CONDENSATION

Consider a single nucleation center. Denote by $P(n, t)$ the probability that at any given time t there are n electron-hole pairs bound to this center. This section will be devoted to establishing rate equations governing $P(n, t)$ and exploring their consequences. It will be assumed for simplicity that the distribution of the n pairs among the infinity of possible energy levels is given by equilibrium statistical mechanics, and that the temperature of the n pairs is the same as the temperature of the lattice. It shall also be assumed for simplicity that free electrons and holes can be ignored. Extension of the present theory to include nonequilibrium effects within complexes and free carriers should be straightforward once the relevant cross sections and energy levels are in some way established.

A. Rate equations

The rate equations governing $P(n, t)$ should include gain and loss due to the collection of excitions, recombination, and evaporation. For exciton collection the contribution to $dP(n, t)/dt$ is

$$+v_{\text{ex}}\rho_{\text{ex}}4\pi R_{n-1}^2 P(n-1, t) - v_{\text{ex}}\rho_{\text{ex}}4\pi R_n^2 P(n, t), \tag{1}$$

where v_{ex} is the average exciton velocity, ρ_{ex} is the exciton density, and $4\pi R_n^2$ is the surface area of an n-pair complex. The first term represents the collection of an exciton by an $(n-1)$-pair complex to become an n-pair complex, and the second term represents the collection of an exciton by an n-pair complex to become an $(n+1)$-pair complex.

The contribution to $dP(n, t)/dt$ from recombination is

$$\frac{n+1}{\tau_{n+1}} P(n+1, t) - \frac{n}{\tau_n} P(n, t), \tag{2}$$

where τ_n is the lifetime of a pair in an n-pair complex. The first term represents the decay of an $(n+1)$-pair complex to become an n-pair complex, while the second represents the decay of an n-pair complex to become an $(n-1)$-pair complex.

In determining a form for the evaporation contribution to $dP(n, t)/dt$ it is necessary to take into account the effects of surface energy and the nucleation center in altering the work function of an n-pair complex. Let Φ_∞ denote the work function of the infinite liquid, S the surface tension, and $B(n)$ the contribution of the nucleation center to the energy of an n-pair complex. $B(n)$ should be determined by the presently unknown energy-level structure of an n-pair complex but generally should be important only for small n. Assuming spherical droplets the Gibbs free energy of an n-pair complex is

$$G(n) = -n\Phi_\infty + S4\pi R_n^2 + B(n). \tag{3}$$

Taking, for large n,

$$n = \tfrac{4}{3}\pi R_n^3 \rho, \tag{4}$$

where ρ is the liquid phase density, the work function is

$$\Phi_n = \Phi_\infty - \frac{2S}{R_n \rho} - \frac{dB(n)}{dn}. \tag{5}$$

Then the contribution to $dP(n, t)/dt$ from evaporation is

$$\begin{aligned} &-P(n, t)4\pi R_n^2 A T^2 e^{-\Phi_n/k_B T} \\ &+P(n+1, t)4\pi R_{n+1}^2 A T^2 e^{-\Phi_{n+1}/k_B T}, \end{aligned} \tag{6}$$

where A is the thermionic emission constant.

Combining all these effects, the rate equation for $P(n, t)$ is

$$\begin{aligned} \frac{dP(n, t)}{dt} = {} & v_{\text{ex}}\rho_{\text{ex}}4\pi R_{n-1}^2 P(n-1, t) - v_{\text{ex}}\rho_{\text{ex}}4\pi R_n^2 P(n, t) + \frac{n+1}{\tau_{n+1}} P(n+1, t) - \frac{n}{\tau_n} P(n, t) \\ & + P(n+1, t)4\pi R_{n+1}^2 A T^2 e^{-\Phi_{n+1}/k_B T} - P(n, t)4\pi R_n^2 A T^2 e^{-\Phi_n/k_B T}; \end{aligned} \tag{7}$$

except that for $n = 0$

$$\frac{dP(0, t)}{dt} = -v_{\text{ex}}\rho_{\text{ex}}4\pi R_0^2 P(0, t) + 1/\tau_1 P(1, t) + P(1, t)4\pi R_1^2 A T^2 e^{-\Phi_1/k_B T}. \tag{8}$$

Of course, for small n, (4) is not true and $4\pi R_n^2$ is only to be thought of as a surface area. Let sines of this nature be absorbed into $B(n)$. It shall be argued that the conclusions of this paper do not depend on the detailed form of $B(n)$.

B. Steady-state probability distribution

It shall now be shown that with the use of Eqs. (7) and (8) the "steady excitation thermodynamics" of electron-hole condensation can be discussed, like the "equilibrium thermodynamics" of a usual liquid gas transition, in terms of free-energy minimization.

In the steady-state, Eqs. (7) and (8) may be readily solved. Simple algebra gives

$$4\pi R_n^2 P(n) = 4\pi R_{n+1}^2 P(n+1)\left(\frac{AT^2 e^{-\Phi_{n+1}/k_BT}}{v_{\text{ex}}\rho_{\text{ex}}} + \frac{n+1}{\tau_{n+1}4\pi R_{n+1}^2 v_{\text{ex}}\rho_{\text{ex}}}\right). \tag{9}$$

In anticipation of the results to follow, a function $G(n)$ is defined by

$$\exp\left(\frac{1}{k_BT}\frac{dG(n)}{dn}\right) = \frac{AT^2 e^{-\Phi_n/k_BT}}{v_{\text{ex}}\rho_{\text{ex}}} + \frac{n}{\tau_n 4\pi R_n^2 v_{\text{ex}}\rho_{\text{ex}}} . \tag{10}$$

Then, iteration of (9) gives

$$4\pi R_n^2 P(n) = 4\pi R_{n_0}^2 P(n_0)\exp\left[-\frac{1}{k_BT}\left(\frac{dG(n_0+1)}{dn} + \frac{dG(n_0+2)}{dn} + \cdots + \frac{dG(n)}{dn}\right)\right] , \tag{11}$$

where $n > n_0$. If $dG(n)/dn$ does not vary too rapidly with n it is a good approximation to treat n as a continuous rather than a discrete variable. Then

$$\frac{dG(n_0+1)}{dn} + \frac{dG(n_0+2)}{dn} + \cdots + \frac{dG(n)}{dn} = \int_{n_0}^{n} dn' \,\frac{dG(n')}{dn'} \cdot \tag{12}$$

For slowly varying $G(n)$,

$$4\pi R_n^2 P(n) = 4\pi R_{n_0}^2 P(n_0)\exp\left(-\frac{G(n)}{k_BT} + \frac{G(n_0)}{k_BT}\right) . \tag{13}$$

It should be apparent that $G(n)$ is the steady excitation thermodynamics analog of the Gibbs free-energy difference between an n–electron-hole-pair complex and the exciton gas.

It can be established by direct calculation that $G(n)$ reduces to the equilibrium thermodynamics Gibbs free energy in the limit of infinite carrier lifetime. Consider a single n-pair complex in equilibrium with its gas. If N_{ex} is the number of excitons, m the exciton mass, and g the exciton degeneracy, then the free energy of the gas phase is

$$G_{\text{ex}} = -N_{\text{ex}} k_BT \times \ln\left(g\int \frac{d^3k}{(2\pi)^3}\, e^{-\beta\hbar^2k^2/2m}/\rho_{\text{ex}}\right) . \tag{14}$$

The free energy of the n-pair complex has already been given by Eq. (3). For this system and two different size complexes n and n_0,

$$N_{\text{ex}} - N_{\text{ex}}^0 = -n + n^0 . \tag{15}$$

When (3), (5), (14), and (15) are combined, the total free energy is found to be

$$G(n) - G(n_0) = k_BT(n-n_0) \times \ln\left(g\int \frac{d^2k}{(2\pi)^3}\, e^{-\beta\hbar^2k^2/2m}/\rho_{\text{ex}}\right) - \int_{n_0}^{n} dn'\,\Phi_n' . \tag{16}$$

This can be compared with what would be calculated from Eq. (10) in the infinite-lifetime limit. The result is the same as Eq. (16) if

$$AT^2/v_{\text{ex}} = g\int \left[d^3k/(2\pi)^3\right] e^{-\beta\hbar^2k^2/2m} . \tag{17}$$

The proof of (17) is left to the reader.

The "generalized free energy" of steady-excitation thermodynamics is given by

$$G(n) - G(n_0) = k_BT\int_{n_0}^{n} dn' \times \ln\left(\frac{AT^2 e^{-\Phi_{n'}/k_BT}}{v_{\text{ex}}\rho_{\text{ex}}} + \frac{n'}{\tau_{n'} 4\pi R_{n'}^2 v_{\text{ex}}\rho_{\text{ex}}}\right). \tag{18}$$

In order to get a feeling for the behavior of (18), consider first the rate equations which would govern electron-hole condensation if the stochastic nature of exciton collection, evaporation, and recombination were ignored. One has

$$\frac{d}{dt}\left(\tfrac{4}{3}\pi R_n^3\rho\right) = v_{\text{ex}}\rho_{\text{ex}}4\pi R_n^2 - 4\pi R_n^2 AT^2 e^{-\Phi_n/k_BT} - n/\tau_n , \tag{19}$$

which reduces to

$$\frac{dR_n}{dt} = \frac{v_{\text{ex}}\rho_{\text{ex}}}{\rho}\left(1 - \frac{AT^2 e^{-\Phi_n/k_BT}}{v_{\text{ex}}\rho_{\text{ex}}} - \frac{n}{v_{\text{ex}}\rho_{\text{ex}}4\pi R_n^2\tau_n}\right) . \tag{20}$$

The quantity inside the parentheses in (20) is very simply related to the rate of change of the droplet radius. In order to maintain this logical connection, define

$$\mathcal{R}(n) \equiv 1 - \frac{AT^2 e^{-\Phi_n/k_BT}}{v_{\text{ex}}\,\rho_{\text{ex}}} - \frac{n}{\tau_n\, 4\pi R_n^2\, v_{\text{ex}}\,\rho_{\text{ex}}} \tag{21}$$

so that from (13)

$$4\pi R_n^2 P(n) = 4\pi R_{n_0}^2 P(n_0) \times \exp\left(-\int_{n_0}^{n} dn' \ln[1-\mathcal{R}(n')]\right) . \tag{22}$$

Consider the probability distribution $P(n)$ about a size n_0 where $\mathcal{R}(n_0)=0$. Expand $\mathcal{R}(n)$ about n_0:

$$\mathcal{R}(n) = 0 + \frac{d\mathcal{R}}{dn}(n_0)(n-n_0) + \cdots . \tag{23}$$

Keeping only the first nonzero term in (23) and expanding the logarithm in (22) gives

$$4\pi R_n^2 P(n) = 4\pi R_{n_0}^2 P(n_0) \exp\left(\frac{1}{2}\,\frac{d\mathcal{R}}{dn}(n_0)(n-n_0)^2\right) . \tag{24}$$

Clearly, if $d\mathcal{R}(n_0)/dn$ is positive then n_0 is a minimum in the probability distribution. On the other hand, if $d\mathcal{R}(n_0)/dn$ is negative, n_0 is a maximum in the probability distribution.

This behavior can be given a very simple physical interpretation. Consider first the case where $d\mathcal{R}(n_0)/dn$ is positive. If n is increased slightly above n_0 the rate of change of the radius given by Eq. (20) is positive and the droplet would keep growing. If n is decreased slightly below n_0 the rate of change of the radius is negative and the droplet will continue to shrink. Thus n_0's for which $d\mathcal{R}(n_0)/dn$ is positive are "unstable" and therefore should be points of minimum likelihood. Another way of seeing this is that from Eq. (18) such unstable points are generalized free-energy maxima.

When $d\mathcal{R}(n_0)/dn$ is negative, by the same kind of argument, a droplet initially perturbed to a higher (or lower) n will shrink (or grow) back toward n_0. Thus n_0's for which $d\mathcal{R}(n_0)/dn$ is negative are "stable," are points of maximum likelihood, and are generalized free-energy minima.

At n large enough for the influence of the nucleation center and therefore $B(n)$ to be negligible, the behavior of $\mathcal{R}(n)$ is well understood. At very large n, $\mathcal{R}(n)$ becomes very negative because of the dominance of the recombination term. At small n, but not so small that $B(n)$ is important, the surface tension makes the evaporation term dominant and again $\mathcal{R}(n)$ is very negative. Between these limits, where neither the surface tension nor the recombination contributions are too strong, $\mathcal{R}(n)$ can have positive values if the exciton density ρ_{ex} is sufficiently large.

This behavior is illustrated schematically in Fig. 1. Ignore for the moment the low-n side of the figure. Curve (a) is $\mathcal{R}(n)$ for a value of the exciton concentration too low for electron-hole condensation to occur. Curve (b) is $\mathcal{R}(n)$ for an exciton concentration high enough for condensation. Point 2 is unstable and corresponds to a minimum in $P(n)$. This would be Landau's "critical droplet size" in the infinite-lifetime limit. Point 3 is stable and corresponds to a maximum in $P(n)$, as shown schematically in the lower part of Fig. 1. To a very good approximation electron-hole droplet sizes are Gaussian distributed, as given by Eq. (24), about stable point 3.

The behavior of $\mathcal{R}(n)$ at low n is determined by the nature of the nucleation center. The corre-

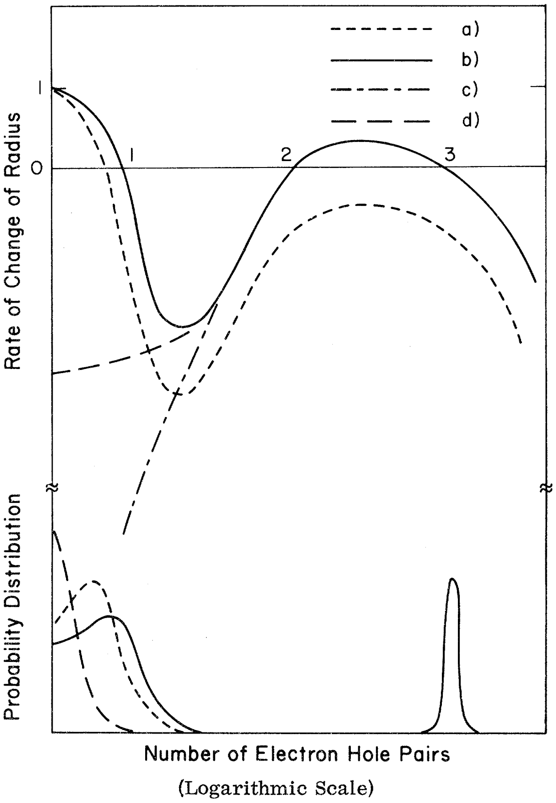

FIG. 1. Schematic illustration of possible behaviors of $\mathcal{R}(n)$ and corresponding probability distribution $P(n)$. Curve (a) exciton concentration too low for electron-hole condensation; curve (b), exciton concentration high enough for condensation; curve (c) $\mathcal{R}(n)$ without nucleation center contribution; curve (d) $\mathcal{R}(n)$ with a weak nucleation center contribution. Peaks in the probability distribution at low pair number correspond to "multiexciton complexes." Peak at high pair number corresponds to "electron-hole droplets."

sponding behavior of $P(n)$, as given by Eq. (22), is that negative $\mathcal{R}(n)$ means that $4\pi R_n^2 P(n)$ is decreasing with increasing n, and that positive $\mathcal{R}(n)$ means that $4\pi R_n^2 P(n)$ is increasing with increasing n. If there were no nucleation center term $B(n)$, as given by curve (c), $P(n)$ would be sharply peaked at low n. For a small nucleation center term, as given by curve (d), $P(n)$ would have a broader peak at low n but would continue to decrease monotonically with increasing but small n. For strong nucleation center binding of the first few excitons, as given by curve (b), point 1 is another stable point. However, since any point imperfection is not expected to bind strongly more than on the order of ten pairs, point 1 should occur at too small an n for the Gaussian approximation to be accurate. $P(n)$ may continue to decrease monotonically away from $n = 0$ or there may be a weak maximum at n_1.

Thus for any reasonable behavior of $\mathcal{R}(n)$ there is a peak in the probability distribution $P(n)$ at very low n. This is the "multiexciton complex" studied by Pokrovsky,[1] Sauer,[4] and Kosai and Gershenzon.[5] The sharp peak in $P(n)$ at n_3 is the "electron-hole droplet."

C. Condensation

Consider now the calculation of the relative probabilities of "multiexciton complexes" and "electron-hole droplets." If n_3 is the droplet size at a stable point 3, Eq. (22) may be rewritten for n near n_3 as

$$P(n) = \frac{R_0^2 P(0)}{R_n^2} \exp\left(-\int_0^{n_3} dn' \ln[1 - \mathcal{R}(n')]\right) \exp\left(\frac{1}{2}\,\frac{d\mathcal{R}(n_3)}{dn}\,(n - n_3)^2\right). \tag{25}$$

Without serious error R_n^2 may be set equal to $R_{n_3}^2$. The total probability of an electron-hole droplet is then obtained by integrating over the Gaussian which yields

$$P_{\text{droplet}} = \frac{R_0^2 P(0)}{R_{n_3}^2} \left(\frac{2\pi}{\dfrac{-d\mathcal{R}(n_3)}{dn}}\right)^{1/2} \exp\left(-\int_0^{n_3} dn' \ln[1 - \mathcal{R}(n')]\right). \tag{26}$$

In order to eliminate $R_0^2 P(0)$ from this expression an integral over $P(n)$ for small n must be evaluated. The unstable point 2 is a minimum in $P(n)$. Therefore, to a very good approximation, the normalization condition gives

$$\frac{1}{R_0^2 P(0)} = \int_0^{n_2} dn\, \frac{1}{R_n^2} \exp\left(-\int_0^{n} \ln[1 - \mathcal{R}(n')]\, dn'\right) + \frac{1}{R_{n_3}^2} \left(\frac{2\pi}{\dfrac{-d\mathcal{R}(n_3)}{dn}}\right)^{1/2} \exp\left(-\int_0^{n_3} dn \ln[1 - \mathcal{R}(n)]\right). \tag{27}$$

The first term on the right-hand side of (27) shall be called the "multiexciton complex" term, and the second the "electron-hole droplet" term.

The criterion for when electron-hole condensation occurs in determined by the noise level of the experiment which looks for some characteristic signal of the liquid phase. For most experiments this noise level corresponds to the droplet term being a few orders of magnitude smaller than the multiexciton complex term.

The magnitude of the droplet term is overwhelmingly determined by

$$\exp\left(-\int_0^{n_3} dn \ln[1 - \mathcal{R}(n)]\right). \tag{28}$$

The function $\ln[1 - \mathcal{R}(n)]$ is of order of magnitude 1, so that integrals over it from zero to n_3 are of order of magnitude n_3. This integral is exponentiated in Eq. (27). For germanium and silicon n_3 is typically several powers of ten. Therefore, a very small change in ρ_{ex} which changes $\mathcal{R}(n)$ only slightly will change the droplet term drastically. In contrast, most of the contribution to the multiexciton term occurs at very small n. Small changes in ρ_{ex} mean small changes in the multiexciton term. Hence, a very small change in ρ_{ex} can change the probability of a droplet from minus many many orders of magnitude to probability near 1.

Small increases in ρ_{ex} mean small increases in the droplet size n_3 but very large increases in the droplet number. Condensation occurs roughly at an exciton density where the integral in (28) is zero, i.e., when the generalized free-energy difference between gas and liquid phases is zero.

D. Lower bounds

These exciton densities differ significantly from what would be expected for infinite carrier lifetimes. A lower bound on the exciton density needed for condensation is given by the density at which the peak in $\mathcal{R}(n)$ first touches zero. With $B(n) = 0$ in the range of interest two equations must be solved,

$$\mathcal{R}(n) = 0 \tag{29}$$

and

$$\frac{d\mathcal{R}(n)}{dn}=0\,. \tag{30}$$

In the rest of this paper τ_n will be set independent of n, although this is probably in error at small n. Then (30) gives

$$\frac{2S}{R_n^2\rho k_B T}\,AT^2\exp\left[\left(-\Phi_\infty+\frac{2S}{R_n\rho}\right)\frac{1}{k_BT}\right]=\frac{\rho}{3\tau}\,. \tag{31}$$

To help see through this equation, let

$$x=2S/R_n\rho k_BT\ . \tag{32}$$

Then, (31) is the transcendental equation

$$x^2e^x=(2S/3\tau k_BT^3A)\,e^{\Phi_\infty/k_BT}\ , \tag{33}$$

and from (29)

$$\rho_{\text{ex}}\geqslant AT^2e^{-\Phi_\infty/k_BT}e^x/v_{\text{ex}}+2S/3v_{\text{ex}}\tau xk_BT\,. \tag{34}$$

First check that the correct limit is obtained as the carrier lifetime in droplets goes to infinity. At large τ,

$$x\sim(1/\tau^{1/2})R_n\sim\tau^{1/2}\,, \tag{35}$$

i.e., the droplet size goes toward infinity. Also,

$$\lim_{\tau\to\infty}\rho_{\text{ex}}=\frac{AT^2e^{-\Phi_\infty/k_BT}}{v_{\text{ex}}}\,, \tag{36}$$

as expected. The conditions of the usual liquid gas transition are recovered.

The exciton densities given by Eq. (34) for finite τ exceed the equilibrium thermodynamics values given by (36). The difference between them becomes very large in the limit of low temperatures. They approach one another in the limit of high temperatures. Therefore, the usual liquid-gas-phase diagram should be obtained only at high temperatures. The calculations of Sec. III suggest that for germanium significant deviations should occur for $T\lesssim 2\,^\circ\text{K}$.

It is interesting to note that in steady-excitation thermodynamics the true chemical potentials of gas and liquid phases are no longer equal to each other. Differentiating (16) with respect to n gives

$$\mu_G-\mu_L=-k_BT\ln(AT^2/v_{\text{ex}}\rho_{\text{ex}})+\Phi_n\,. \tag{37}$$

A lower bound on this chemical potential difference can be derived from Eqs. (29)–(34). This gives

$$\mu_G-\mu_L\geqslant kT\ln[1+(2S/3AT^2\tau k_B)^{1/2}\times e^{\Phi_\infty/2k_BT}]\,. \tag{38}$$

Obviously the chemical-potential difference increases as the temperature is lowered. This is of course only a reflection of the relatively increased exciton densities needed at low temperatures.

Note also that the lower bound on the droplet size as given by (32) and (33) increases with increasing temperature. This temperature dependence is also obtained from (26) and (27), and is true experimentally.

E. Nucleation center behavior

It seems logical to expect that at a given density the stronger the binding to a nucleation center the greater the probability of finding an electron-hole droplet. Stronger binding should mean a lower free energy of a droplet relative to the free energy of the gas.

It is possible to study how this comes about in Eq. (27). First note that for low n the recombination term in $\mathcal{R}(n)$ is unimportant and may be neglected. Second it is argued that the nucleation center can only be important for the binding of the first several electron hole pairs so that

$$B(n)\cong B_\infty\,,\quad n>n_0 \tag{39}$$

for some not very large n_0. Then the integral in (28) may be written as

$$-\int_0^{n_3}dn\ln[1-\mathcal{R}(n)]=-\int_0^{n_0}dn\ln[1-\mathcal{R}(n)]-\int_{n_0}^{n_3}dn\ln[1-\mathcal{R}(n)]\ , \tag{40}$$

which is approximately given by

$$-n_0\ln[(AT^2/v_{\text{ex}}\rho_{\text{ex}})\,e^{-\Phi_\infty/k_BT}]-(S/k_BT)\,4\pi R_n^2-B_\infty/k_BT-\int_{n_0}^{n_3}dn\ln[1-\mathcal{R}(n)]\,, \tag{41}$$

so that the electron-hole droplet term in (27) is proportional to

$$\text{droplet term}\propto e^{-B_\infty/k_BT}\ . \tag{42}$$

The more negative B_∞ the larger the droplet term.

Of course, it is the ratio of the droplet term to the multiexciton term in (27) that is important. Since the dominant contribution to the multiexciton term comes from small n the same approximation of neglecting the recombination term can be made. Then the multiexciton term is to a good approximation given by

$$\int_0^{n_2}dn\,\frac{1}{R_n^2}\exp\left\{-n\ln\left[\frac{AT^2}{v_{\text{ex}}\rho_{\text{ex}}}\,e^{-\Phi_\infty/k_BT}\right]-\frac{S}{k_BT}\,4\pi R_n^2-\frac{B(n)}{k_BT}\right\}\,. \tag{43}$$

Therefore, the ratio of multiexciton term to droplet term has the form

$$\int_0^{n_2}dn\,g(n)\,e^{B_\infty/k_BT-B(n)/k_BT}\,. \tag{44}$$

All that is required is the physically reasonable behavior

$$B(n) > B_\infty \tag{45}$$

for stronger nucleation center binding to mean more electron-hole condensation at a given exciton density and temperature.

Nucleation centers can be dislocations, other excitons, and point imperfections such as impurities. Little is known about the binding of excitons to dislocations. It is known from calculations[15, 16] that the binding energies of excitons to one another are very weak compared to the binding energy of an exciton to an impurity. In Sec. III "nucleation centers" refers only to impurities.

F. Concluding remarks

Thus the electron-hole liquid-gas transition can be described in terms of a steady excitation thermodynamics in which the finite carrier lifetimes makes the generalized Gibbs free energy rise toward positive infinity for very large droplets.

It should be straightforward to extend this theory to include a weak temperature dependence of parameters such as the work function, surface tension, and nucleation center term $B(n)$. Near the critical point, however, a more elaborate development will be needed. The calculations of Sec. III are confined to $T \lesssim 5\,^\circ\mathrm{K}$ in germanium, well below the critical temperature, and for simplicity the temperature dependence of the parameters is neglected.

III. NUMERICAL EXAMPLES AND COMPARISON WITH EXPERIMENT

In this section calculations will be carried out for electron-hole condensation in germanium. It is assumed for the sake of simplicity that (i) the exciton density is constant throughout the volume of the crystal; (ii) there are no temperature gradients; (iii) there is no generation of electron-hole pairs within droplets; and (iv) there is only one kind of nucleation center.

Comparison will be made with published data on laser-excitation experiments. It is important to keep in mind that these experiments always involve some transport effects such as exciton density gradients and temperature gradients. It will be pointed out where the differences between laser excitation and uniform excitation experiments complicate comparison with the calculations.

A. Parametrization

Some of the parameters needed for the calculation have been well established experimentally. There are pair lifetimes in droplets of $\tau = 40$ μsec,[17] exciton lifetimes of $\tau_{\mathrm{ex}} \cong 7.7$ μsec,[2, 9] and a work function of $\Phi_\infty \cong 17\,^\circ\mathrm{K}$ determined from threshold experiments studying cyclotron resonance,[12] luminescence,[1, 18] and shot noise.[19] This value is somewhat lower than Φ_∞'s determined from theoretical fits to the exciton and droplet recombination radiation.[20, 21] Contrary to some speculations,[11] it will be shown that surface energy does not account for the difference.

Very little information has, at the time of writing, been obtained about the evaporation constant A or the exciton velocity v_{ex}. The only experimental determination of A has given 8.82×10^{20} in cgs units.[9] This will be used with reservations since (a) sample heating was present in the experiment, and (b) the assumption made in their fit that a single droplet is formed is controversial. Theoretical values for A suffer from uncertainties about which effective mass to use or, more precisely, uncertainties about what exactly is evaporating.

The exciton velocity will be calculated from the often quoted but hardly justified value for the exciton mass $m_{\mathrm{exc}} = 0.33\, m_e$.[22] A calculation of the exciton band structure is needed. Fortunately, this uncertainty only affects the exciton density scale.

A new result of the present theory is that the surface tension can be determined by measuring the size distribution. Several calculations have suggested values around 10^{-4} in cgs units.[23–25] This value might well have been guessed by dimensional arguments which compare the electron-hole liquid-gas transition to the water-water vapor transition. Surface tension has dimensions energy/length^2. The only energy is the work function Φ_∞. The only length is $\rho^{-1/3}$, where ρ is the pair density in the liquid phase. The measured surface tension of water is about $\frac{1}{10}\Phi_\infty \rho^{2/3}$. The same calculation for the electron-hole liquid-gas transition gives 0.9×10^{-4} in cgs.

To the author's knowledge, the only published data on how droplet sizes vary as a function of temperature are the light-scattering experiments of Bagaev *et al.*[10] Sizes measured in shot-noise experiments clearly involve strong exciton density gradients.[26]

A lower bound on the size of electron-hole droplets is given by Eqs. (32) and (33). At high temperatures ($T > 2\,^\circ\mathrm{K}$) when x is small this lower bound on the size is proportional to

$$R \propto (SA\tau)^{1/2} . \tag{46}$$

That is, choosing different values for these parameters but leaving the product $SA\tau$ constant gives the same droplet size at a given temperature.

The author has found it possible to achieve an excellent fit to Bagaev's data by choosing a value for the surface tension S of 1.0×10^{-3} and the experimental value for A mentioned earlier. While these values for S and A will be used in all the calculations of this paper, clearly from (46) the theoretical value for S might have been used if A were larger by a factor of 10! With the experimental value for A and the theoretical value for S smaller droplets are obtained than in Bagaev *et al.*'s experiments, but the correct trend with temperature and droplet radii on the order of microns are still obtained.

Finally, the nucleation-center term $B(n)$ must be chosen. The important property is that it contribute to the work function only at small n. It is to be expected that eventually $B(n)$ will be determined from studies of recombination radiation from multiexciton complexes. For the present calculations, with little theoretical justification, the form used is

$$B(n) = S4\pi R_n^2\,(e^{-c/n^{2/3}} - 1)\,, \qquad (47)$$

where c is a positive constant. This has the advantage that at large n, $B(n)$ becomes constant and, calculationally, only a single parameter c determines the strength of binding to the nucleation center. The results discussed in this paper depend very weakly on the magnitude of c. For all the figures c is chosen to equal 10.

B. Size distribution

At the end of Sec. II it was argued that as the probability of an electron-hole droplet at an impurity varies from minus many orders of magnitude to near one, the droplet size and exciton density increase only infinitesimally. For an isolated impurity, a further increase in the exciton density beyond the condensation point will result in an increase in average droplet size. The exciton line intensity would increase as the one-third power of the droplet line intensity to a good approximation.

However, even the purest germanium available does not have what amounts to isolated impurities except at very low temperatures ($T \ll 2\,^\circ\mathrm{K}$). Suppose for example, that at a chosen temperature the droplet radius at condensation were as small as 1 μm ($T = 1.7\,^\circ\mathrm{K}$ in the present calculations). Then an impurity concentration of less than

$$N_i < 1/\tfrac{4}{3}\pi(1\ \mu\mathrm{m})^3 = 2.4\times 10^{11}\ \mathrm{cm}^{-3} \qquad (48)$$

would be needed to keep droplets from overlapping at "saturation." Saturation is defined as where the probability of a droplet at an impurity approaches one. At higher temperatures, since droplet radii are larger, even smaller impurity concentrations would be needed. About 10^{11} cm^{-3} impurities is the limit of what can be expected in available germanium.[27]

More importantly, with the experiments of the Berkeley[9] and Tokyo[28] groups as exceptions, most experiments employ much less excitation than would be needed to saturate impurities with electron-hole droplets. Therefore, a strong dependence of size on excitation level should not be expected.

In Bagaev *et al.*'s experiment[10] the pair-generation rate was such that the threshold for electron-hole condensation occurred at 3.5 °K. The generation rate is equal to

$$g = \rho_{\mathrm{ex}}/\tau_{\mathrm{ex}} + N_i\left[\int_0^\infty nP(n)\,dn/\tau\right]. \qquad (49)$$

One may readily calculate from (49) and the coexistence curve to be given in Sec. III C that the impurity concentration must be greater than only 10^7 cm^{-3} to prevent saturation at the lowest temperature measured by Bagaev, $T = 2.5\,^\circ\mathrm{K}$. Hence the size of droplets in Bagaev's *et al.*'s fixed-generation-rate experiment should be given by the size of droplets along the coexistence curve. This is shown in Fig. 2.

C. Phase diagram

As discussed in Sec. II, the liquid-gas phase diagram for electrons and holes in germanium is determined by $\mathcal{R}(n)$. The behavior of $\mathcal{R}(n)$ at various temperatures for an exciton density equal to

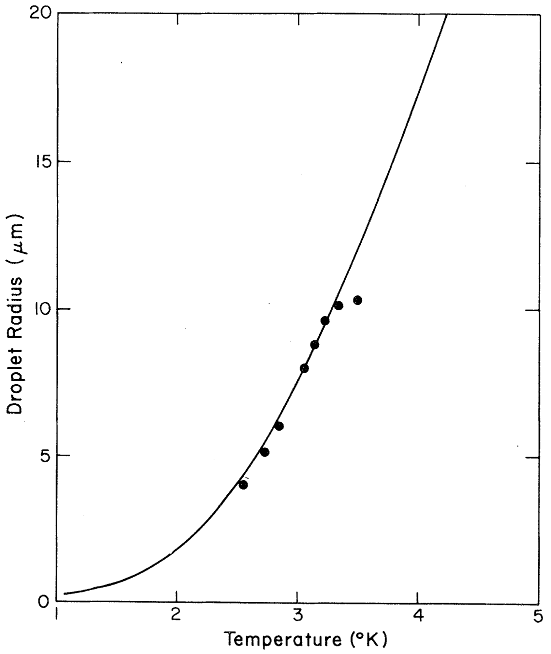

FIG. 2. Electron-hole droplet size vs temperature for germanium as calculated (solid line) and as measured in Ref. 10 (dots).

the infinite-lifetime condensation density, Eq. (36), is shown in Fig. 3. Notice that at high temperatures ($T > 2\,^\circ\mathrm{K}$) only a slightly higher exciton density is needed for the broad peak in $\mathcal{R}(n)$ to cross the zero axis and, therefore, for electron-hole condensation to occur. On the other hand, at low temperatures ($T \leqslant 2\,^\circ\mathrm{K}$) a considerably higher exciton density than Eq. (36) is needed for condensation. Thus deviations from the usual liquid-gas phase diagram should be expected at low temperatures.

Any real experiment looks for some characteristic signal of the liquid phase which must be strong enough to exceed a basic noise level. Hence the probability of electron-hole droplets given by Eqs. (26) and (27) must be significant. The solid black curve in Fig. 4 gives the exciton density at which

$$n_{\min} = \int_0^\infty nP(n)\,dn\,, \tag{50}$$

where $n_{\min}$ is chosen somewhat arbitrarily as 10^3. Explicit calculations show that, except at very low temperatures, the phase diagram is insensitive to orders-of-magnitude changes in $n_{\min}$.

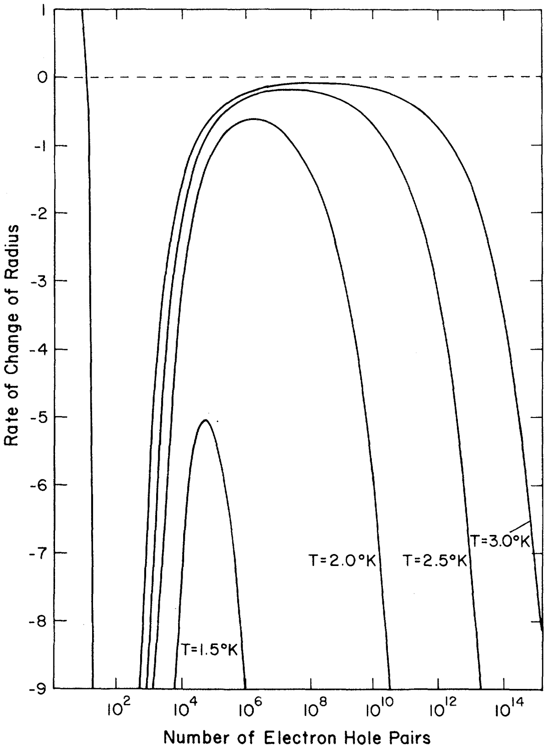

FIG. 3. $\mathcal{R}(n)$ vs pair number n at various temperatures for an exciton density equal to the coexistence curve for infinite carrier lifetime. At low n a possible form for the nucleation center contribution is shown.

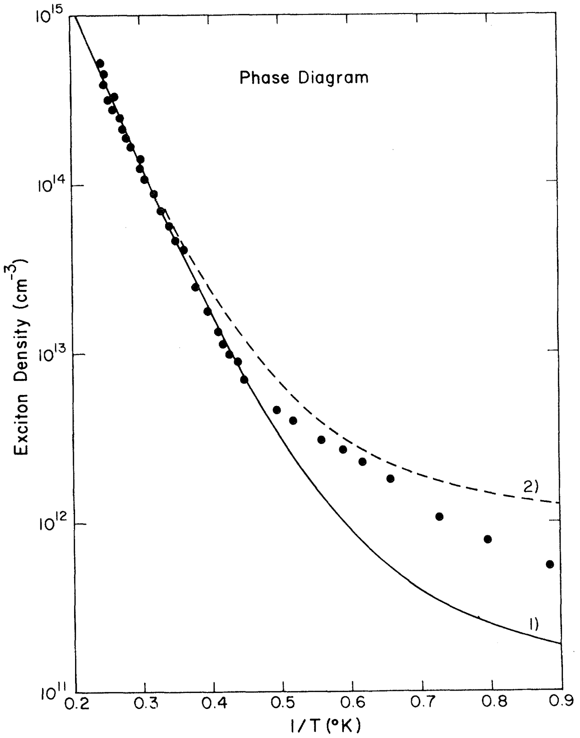

FIG. 4. Calculated coexistence curve for germanium. The dashed curve is calculated with the lifetime of electron-hole pairs in droplets reduced a factor of 10 to 4 μsec. The data points are taken from the cyclotron-resonance experiments of Ref. 12.

The phase diagram is also insensitive, except at very low temperatures, to the strength of the nucleation center parameter c. Varying c by an order of magnitude changes the number of pairs bound in multiexciton complexes considerably, but the exciton density along the coexistence curve changes at most by several percent for $T \gtrsim 1\,^\circ\mathrm{K}$.

The data points are taken from the cyclotron-resonance experiments of Hensel, Phillips, and Rice.[12] Notice that the agreement at high temperatures with a calculation using $\Phi_\infty = 17\,^\circ\mathrm{K}$ rules out a surface-energy contribution to the apparent phase diagram. At low temperatures the data indeed deviate from the usual liquid-gas phase diagram, but not in the way calculated with the form of $B(n)$ given by Eq. (47). This should not be taken as a disagreement between theory and experiment. The experimental curve at low T is a function of the noise level,[13] and the cyclotron-resonance signal is not a simple function of the amount of liquid phase present.

Further, in actual experiments it is not the exciton density but the generation rate which is controlled. When the temperature is low and the exciton density small, recombination in multiexciton complexes may dominate in Eq. (49). Thus, the uncertainties about nucleation-center behavior and impurity concentration are more important at low T.

The phase diagram which would be predicted if the electron-hole-pair lifetime inside droplets were 4 instead of 40 μsec is shown as the dashed curve in Fig. 4. The lack of agreement even at high temperatures rules out this pair lifetime.

Another measurement of the apparent phase diagram has been obtained from the shot-noise experiments of McGroddy *et al.*[19] These experiments measure the generation rate at which the noise power from droplets collected in a p-n junction exceeds some basic background level. To model this system, without getting involved in detailed transport questions, the generation rate at which

$$n_{\min}^2 = \int_0^\infty n^2 P(n)\, dn \qquad (51)$$

is calculated as shown in Fig. 5. There is quantitative agreement at high temperatures, and the correct qualitative behavior at low temperatures. This behavior may be simply understood as the result of (i) the decrease in droplet size as the temperature is lowered, and (ii) most of the pair-generation feeding recombination in droplets at low temperatures. Thus, at low temperatures,

$$g \cong \langle n \rangle / \tau \cong n_{\min}^2 / \tau \langle n \rangle , \qquad (52)$$

so that as droplet size decreases, the generation rate must increase.

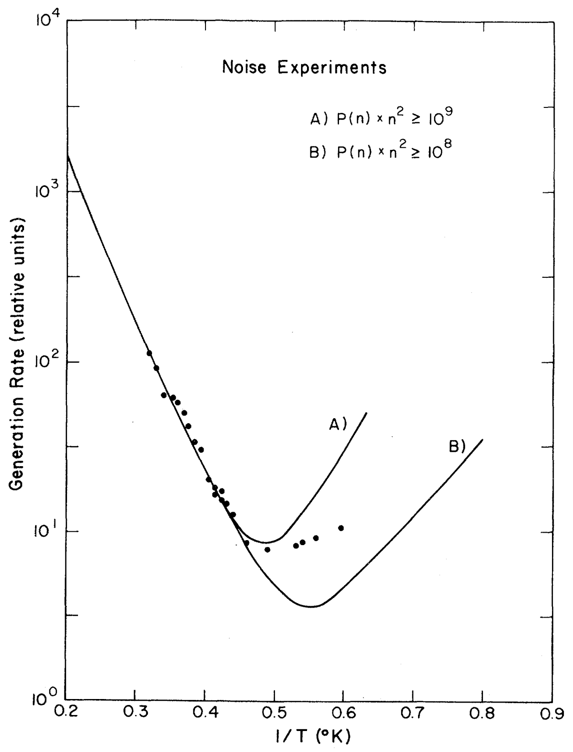

FIG. 5. Coexistence curves for germanium as measured by noise experiments. The solid lines are calculated for two different background-noise power levels. The data points are taken from the experiments of Ref. 19.

D. Evaporation and recombination

Several experiments[9,12] have studied the decay of the recombination radiation from electron-hole droplets and excitons after the source of excitation has been turned off. These data have been fit to rate equations governing evaporation and recombination which assume a single droplet size rather than a distribution. This assumption can be a good approximation in view of the narrowness of the Gaussian distribution given by Eq. (24).

In this section it will be argued that the surface-tension contribution to the work function is important to describing evaporation, at least for those experiments where the excitation level is not so high that huge droplets (~mm) are obtained.[9,28]

The time at which the characteristic signal of the electron-hole liquid disappears is referred to as the "cutoff time."[12] A lower bound on the cutoff time may be calculated by ignoring the backflow of excitons in Eq. (20). With ρ_{ex} set equal to zero, and also the surface tension set equal to zero, the solution of (20) may be obtained in closed form:

$$R_n(t) = e^{-t/3\tau} R_n(0) - 3\tau A T^2 e^{-\Phi_\infty / k_B T} (1 - e^{-t/3\tau}) / \rho . \qquad (53)$$

The lower bound on the cutoff time is given by $R_n(t_c) = 0$:

$$t_c = 3\tau \ln \left(1 + \frac{\rho R_n(0) e^{\Phi_\infty / k_B T}}{3\tau A T^2} \right). \qquad (54)$$

Even with the temperature-dependent radii of the present calculation, Eq. (54) seriously overestimates the cutoff time at low temperatures. The prediction of Eq. (54) is shown as the dashed curve in Fig. 6. The data are taken from the paper of Hensel, Phillips, and Rice.[12]

However, with finite surface-tension a lower bound on the data is indeed obtained. Numerical solutions of Eq. (20) for the cutoff time with surface tension included are shown as the solid black curve in Fig. 6.

E. Generation-rate experiments

In Fig. 7 the droplet line intensity is plotted versus generation rate, Eq. (49), for an assumed impurity concentration of 10^{11} cm^{-3}. Note that the relation is initially superlinear near threshold but

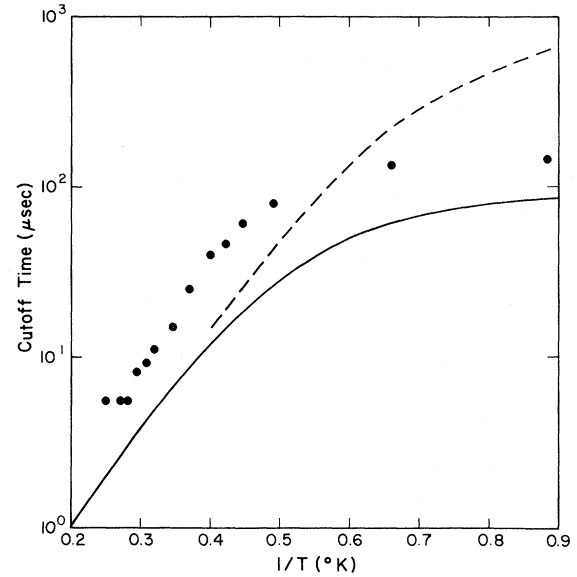

FIG. 6. Lower bounds on the cutoff time for electron-hole droplets in germanium calculated with sizes given in Fig. 2. The dashed line is calculated without surface tension. Data points are taken from the cyclotron-resonance experiments of Ref. 12.

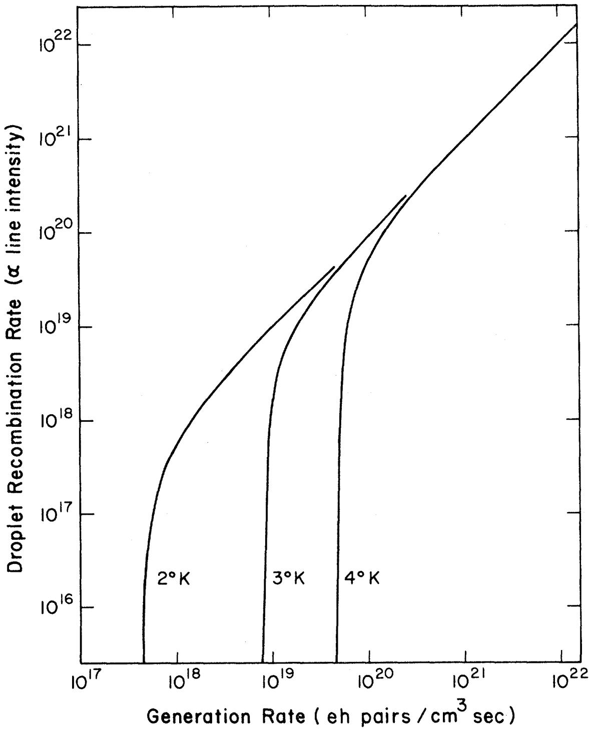

FIG. 7. Droplet recombination radiation intensity vs generation rate at various temperatures. Note that along an isotherm the droplet size is almost independent of generation rate.

becomes linear at high generation rates. However, in contrast to previous explanations of such behavior which required a strong dependence of droplet size on generation rate,[1] here the droplet size is changing only infinitesimally along the isotherms. What is happening is that in the superlinear region the recombination of excitons is the dominant term in (49). In the linear region the droplet number has increased to the point where recombination in droplets is dominant.

Some reported features of line-intensity-versus-generation-rate experiments are not explained by the calculations of this paper, in which uniform excitation of the semiconductor is assumed. In laser-excitation experiments the exciton line intensity is reported to increase as the one-third power of the droplet line intensity.[1] It has also been reported that an increase in impurity concentration lowers the threshold generation rate needed for electron-hole condensation.[29] The author believes that these features are a consequence of transport effects, specifically exciton density gradients in laser experiments, and will be understood by a calculation of how the "effective volume" occupied by excitons varies with generation rate and impurity concentration.

In Fig. 8 the droplet line intensity versus temperature is plotted for various fixed generation rates and an impurity concentration of 10^{11} cm^{-3}. Note that the droplet sizes are decreasing with decreasing temperature, but the droplet number is increasing. At low temperatures the total amount of electron-hole liquid approaches a constant value but the droplet size continues to fall. This behavior can and has been observed by Bagaev *et al.* in light scattering experiments. In Fig. 9 the intensity of scattered 3.3-μm light at 8° is calculated from Rayleigh-Gans theory[30] for the fixed-generation-rate experiments of Fig. 8. The initial rise in intensity as the temperature is lowered is due to the condensation of droplets. The fall at even lower temperatures is because the total amount of liquid approaches a constant but the droplet size continues to fall. While Bagaev *et al.* observed the same qualitative behavior in their experiments, the rise and fall in their data occurs over a somewhat smaller temperature range than the calculation of Fig. 9. Again, the author believes that calculation of the effects of exciton density gradients in laser excitation experiments will explain this difference.

IV. SUMMARY AND DISCUSSION

The essential step in the development of this new description of electron-hole condensation was the realization that evaporation, recombination, and exciton collection are random processes. Therefore, it is the "probability" of an *n*-pair complex

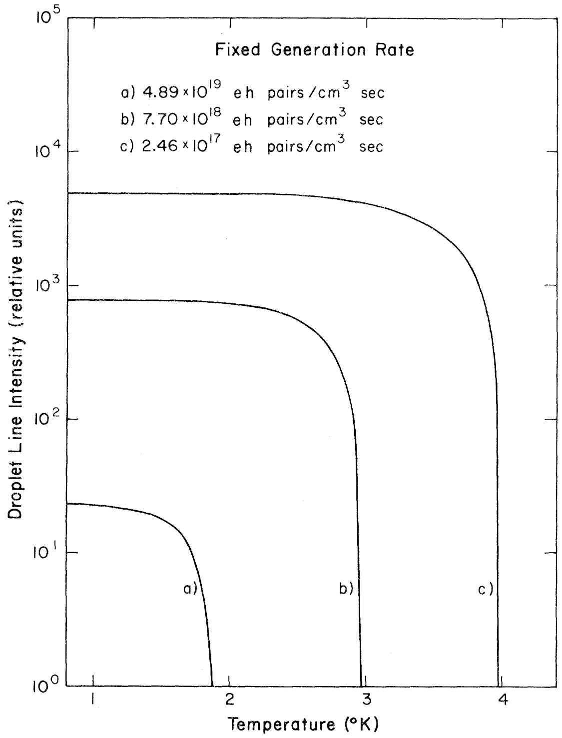

FIG. 8. Droplet recombination radiation intensity vs temperature at various fixed generation rates. Note that along each curve the droplet size decreases but the droplet number increases as the temperature is lowered.

which should be calculated. Section II was devoted to formulating equations governing this probability distribution $P(n, t)$ and exploring the steady-state solutions. It was shown that when proper account is taken of lifetime, surface tension, and nucleation-center effects, several new results are obtained: (a) The probability distribution in general has a diffuse peak at low n which corresponds to "multiexciton complexes"; (b) if the exciton density is high enough there is a sharp peak at high n which corresponds to "electron-hole droplets"; (c) the average droplet size increases with temperature; (d) the surface tension of the electron-hole liquid can be determined from droplet-size measurements under uniform excitation conditions; (e) in experiments at a fixed temperature it is the number of droplets, and not the droplet size, which varies strongly with generation rate; and (f) deviations from the usual liquid-gas phase diagram should be expected at low temperatures.

In Sec. III detailed calculations for uniform excitation of germanium were carried out with parameters determined where possible from available data on laser excitation experiments. The qualitative agreement of the present theory with experiment is excellent. The quantitative agreement is better at high temperatures (> 2 °K) than at low temperatures (< 2 °K). Among the successes of the theory are typical droplet radii on the order of many microns in experiments above 2 °K.[31]

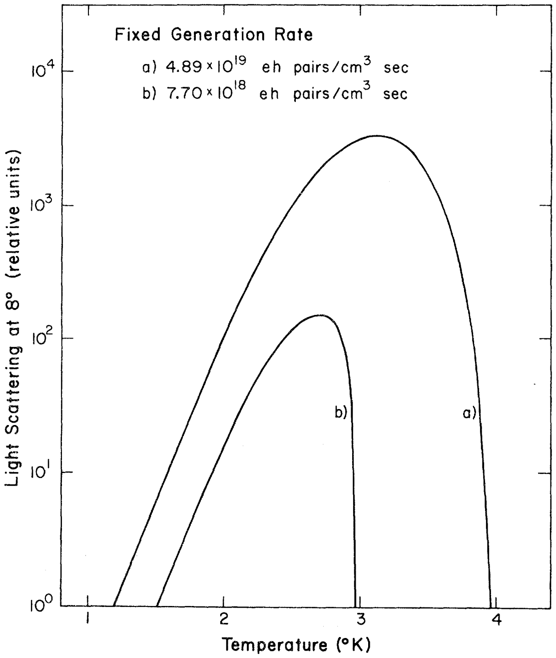

FIG. 9. Intensity of scattered 3.3-μm light at 8° vs temperature at the same fixed generation rates of Fig. 8.

The development of the preceding sections suggests a number of areas where more work is needed. First, more experiments on size distributions, evaporation phenomena, etc. are needed to verify the theory and pin down the parameters. Second, electron-hole condensation in silicon is in many ways even more interesting than in germanium because the much shorter carrier lifetime and larger work function mean more pronounced deviations from the usual liquid-gas phase diagram at higher temperatures. Third, the lifetime differences themselves need to be understood in terms of an understanding of Auger processes in germanium and silicon. Fourth, theoretical models of the energy-level structure and cross sections of multiexciton complexes, combined with more data on recombination radiation from complexes, would help in removing the present ambiguities about nucleation centers. They would also provide input needed to relate generation rate to exciton density in experiments at low temperatures (< 2 °K in germanium and < 7 °K in silicon). Fifth, more sophisticated calculations and independent experimental determinations of the parameters A and ν_{exc} are needed.

It should be possible to adapt the probabilistic ideas of this paper to situations where there are exciton density gradients. A calculation of the exciton diffusion constant would give an expression in terms of the cross sections for scattering from impurities. The theory of Sec. II says that these cross sections in turn depend strongly on exciton density. Thus, such transport situations should be terribly nonlinear but in a way predicted by this theory.

The motion of droplets should be rather sensitive to impurity effects, since, for even the best available material, typical droplet diameters are of the same magnitude as the distance between impurities. Another important effect follows from the usual ergodicity hypothesis, i.e., the ensemble average at a given time should equal the time average of an individual element of the ensemble. In the present context this means that in the usual situation where a small fraction of impurities have droplets on them an individual impurity has a droplet on it for the same small fraction of the time. The time scale of such fluctuations should be obtainable from the time-dependent equations for $P(n, t)$.

More experiments on transport effects would be a helpful guide to theory. Information gained from double injection experiments should compliment the results of laser excitation experiments.[32]

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Note added in proof. After the completion of this work the author learned of the extensive literature which exists on the application of stochastic rate equations similar to Eqs. (7) and (8) to the description of ordinary liquid gas transitions. This approach was first initiated by R. Becker and W. Doring [Ann. Phys. (Leip.) 24, 719 (1935)], and has been elaborated by many authors. An excellent review is the book by F. F. Abraham, *Homogeneous Nucleation Theory* (Academic, New York, 1974). The present paper shows the profound effects produced by the finite carrier lifetimes on electron hole condensation.

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[‡] Permanent address.

[1] Ya. Pokrovskii, Phys. Status Solidi 11a, 385 (1972). Pokrovskii correctly pointed out, based on studies of Eq. (20) with the surface tension set to zero, that the finite carrier lifetimes would limit the droplet size. With finite surface tension Eq. (20) would predict an initially negative rate of change of a droplet radius and hence no electron-hole condensation. Therefore, the stochastic treatment of the present paper is a necessity.

[2] L. V. Keldysh, Proceedings of the IX International Conference on the Physics of Semiconductors, Moscow, 1968 (unpublished), p. 1307.

[3] R. N. Silver, Phys. Rev. B 8, 2403 (1973).

[4] R. Sauer, Phys. Rev. Lett. 31, 376 (1973).

[5] K. Kosai and M. Gershenzon, Phys. Rev. B 9, 723 (1974).

[6] R. W. Martin, Solid State Commun. 14, 369 (1974).

[7] C. Benoît à la 'Guillaume, M. Voos. F. Salvan, J. M. Laurant, and A. Bonnot, Compt. Rend. 272 (1971).

[8] V. M. Asnin, A. A. Rogachev, and N. I. Sablina, Zh. Eksp. Teor. Fiz. Pis'ma Red. 11, 162 (1970) [JETP Lett. 11, 99 (1970)].

[9] V. S. Bagaev, N. A. Penin, N. N. Sibel'din, and V. A. Tsvetkov, Fiz. Tverd. Tela 15, 3269 (1973) [Sov. Phys.-Solid State 15, 2179 (1974)].

[10] J. C. McGroddy, Bull. Am. Phys. Soc. 19, 331 (1974).

[11] R. M. Westervelt, T. K. Lo, J. L. Staehli, and C. D. Jeffries, Phys. Rev. Lett. 32, 1051 (1974); R. S. Markiewicz, J. P. Wolfe, and C. D. Jeffries, *ibid.* 32, 1357 (1974); B. J. Feldman, *ibid.* 33, 359 (1974).

[12] J. C. Hensel, T. G. Phillips, and T. M. Rice, Phys. Rev. Lett. 30, 227 (1973).

[13] G. A. Thomas (private communication).

[14] R. B. Hammond, V. Marrello, R. N. Silver, T. C. McGill, and J. W. Mayer, Solid State Commun. 15, 251 (1974); V. Marrello, R. B. Hammond, R. N. Silver, T. C. McGill, and J. W. Mayer, Phys. Lett. A 47, 237 (1974).

[15] W. F. Brinkman, T. M. Rice, B. Bell, Phys. Rev. B 8, 1570 (1973).

[16] O. Akimoto, E. Hanamura, Solid State Commun. 10, 253 (1972).

[17] Reference 12; C. Benoît à la Guillaume, M. Voos, and F. Salvan, Phys. Rev. B 5, 3079 (1972); 7, 1723 (1973); and V. Marrello (private communication).

[18] T. K. Lo, B. J. Feldman, and C. D. Jeffries, Phys. Rev. Lett. 31, 224 (1973).

[19] J. C. McGroddy, M. Voos, and O. Christensen, Solid State Commun. 13, 1801 (1974).

[20] C. Benoît à la Guillaume and M. Voos, Solid State Commun. 12, 1257 (1973).

[21] G. A. Thomas, T. G. Phillips, T. M. Rice, J. C. Hensel, Phys. Rev. Lett. 31, 386 (1973).

[22] Ascribed originally to W. F. Brinkman (unpublished).

[23] L. M. Sander, H. B. Shore, and L. J. Sham, Phys. Rev. Lett. 31, 533 (1973).

[24] T. L. Reinecke and S. C. Ying, Solid State Commun. 14, 381 (1974).

[25] T. M. Rice, Phys. Rev. B 9, 1570 (1974).

[26] O. Christensen and J. M. Hvam, in Proceedings of the XII International Conference on the Physics of Semiconductors, Stuttgart, 1974 (unpublished).

[27] R. N. Hall, IEEE 1, 260 (1974); and in Proceedings

of the XII International Conference on the Physics of Semiconductors, Stuttgart, 1974 (unpublished).

[28] A. Nakamura and K. Morigaki, Solid State Commun. 14, 1213 (1974).

[29] A. S. Alekseev, V. S. Bagaev, T. I. Galkina, O. V. Gogolin, and N. A. Penin, Fiz. Tverd. Tela 12, 3516 (1970) [Sov. Phys.-Solid State 12, 2855 (1971)].

[30] M. Kerker, *The Scattering of Light* (Academic, New York, 1968).

[31] The effects of a possible charge on electron-hole droplets will be considered elsewhere. A general remark, however, is that the screening of this charge by the metallic electron-hole liquid would reduce considerably its effects compared to the effects of charge in a dielectric medium such as water.

[32] V. Marrello, T. F. Lee, R. N. Silver, T. C. McGill, and J. W. Mayer, Phys. Rev. Lett. 31, 593 (1973).