

## Time-dependent behavior in electron-hole condensation\*

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The dominant relaxation rates in electron-hole condensation are calculated from the stochastic rate equations proposed in a previous paper. These govern the time scale for the nucleation of electron-hole droplets and for fluctuations in the number of electron-hole pairs bound to a nucleation center. The calculational procedure makes use of exact recursion relations for the temporal moments of the probability distribution. It is found that metastable states of electrons and holes can exist at high temperatures ( $T \gtrsim 2^\circ\text{K}$  in Ge), for a limited range of exciton densities. At low temperatures the finite carrier lifetimes lead to measurably short relaxation times. The importance of the time dependence of the exciton density in experiments at fixed generation rates is stressed. Some of the reported discrepancy between spectroscopic and thermodynamic values of the work function may be ascribed to supersaturation effects.

### I. INTRODUCTION

The gain or loss of an electron-hole pair by an electron-hole droplet is a random event. The sequence of pair collections, evaporations, and recombinations make up the stochastic process which governs the time evolution of droplets in an exciton vapor. In a previous paper,<sup>1</sup> the author proposed stochastic rate equations for the probability distribution of the number of electrons and holes bound to a nucleation center.<sup>2</sup> The properties of the steady-state probability distribution, to which the system must eventually relax after sufficient time, were studied in detail. The present paper examines the rate of relaxation to the steady state and the related question of metastable states of electrons and holes in highly excited semiconductors.

The principal feature, which distinguishes the nucleation kinetics of the electron-hole liquid-gas transition<sup>3-5</sup> from that of ordinary liquid-gas transitions, is the finite lifetime of the electrons and holes.<sup>1</sup> Large electron-hole droplets, where the surface-to-volume ratio is too small for pair collection to make up for recombination, are unstable and will decay. Small electron-hole droplets are also unstable, since the surface free energy significantly enhances the evaporation rate. Thus, gas-phase densities higher than the equilibrium thermodynamics coexistence curve are needed to give a high enough pair collection rate so that the condensate exists. At densities above this minimum, stable droplet sizes may be found above a minimum value that is a strong function of temperature. The change in the measured coexistence curve is small at high temperatures ( $T \gtrsim 2^\circ\text{K}$  in Ge) where previous studies of the electron-hole phase diagram have been made.<sup>6-9</sup> Since evaporation rates and pair collection rates decrease strongly

with temperature, whereas recombination rates are almost temperature independent, the finite lifetime effects become very important at low temperatures.

The finite lifetimes also affect calculation of the nucleation rate of electron-hole droplets, since the conventional assumption owing to Becker and Doring<sup>10</sup> that the nucleation rate is time independent can no longer be made. Rather, in Sec. II a phenomenological model will be proposed in which a nucleation center can exist in only two states, either with a multiexciton complex,<sup>4,11,12</sup> or with an electron-hole droplet bound to it. A simple pair of stochastic rate equations describes this system, and may be solved trivially for the time dependence. In the Appendix the parameters of this two-state model will be derived by a moment technique from the complete time-dependent rate equations of the previous paper. The relaxation time calculated in this way governs both condensation rates and the time scale for fluctuations in droplet size at constant gas-phase density. For readers not interested in the calculational method, the results are summarized in Sec. II C.

In Sec. III the question of metastable states will be discussed. If, at fixed exciton density and temperature, the relaxation time is astronomically long, a metastable state of the electron-hole system can exist where equilibrium between complexes and droplets is not achieved on a measurable time scale.<sup>8</sup> The size of droplets in a metastable state can differ from the steady-state value. The range of density and temperature where this can occur will be calculated. At low temperatures, because of the finite lifetimes, metastability cannot occur.

In Sec. IV a discussion will be given of the time evolution of the electron-hole system after an excitation source such as a laser is turned on. Since

considerable supersaturation may be required at high temperatures for nucleation rates to be appreciable, a correct theory of the nucleation of droplets must take into account the time dependence of the gas-phase density. This problem will be addressed, but not completely resolved since a numerical or Monte Carlo solution of nonlinear stochastic rate equations is required.

## II. TWO-STATE MODEL

### A. Properties of the steady-state probability distribution

In the previous paper,<sup>1</sup> it was argued that if  $P(n, t)$  is the probability distribution of the number of electron-hole pairs bound to a nucleation center, then

$$\frac{dP(n, t)}{dt} = l_{n+1}P(n+1, t) - l_nP(n, t) - g_nP(n, t) + g_{n-1}P(n-1, t), \quad (1)$$

where  $l_n$  is the rate of loss of excitons by an  $n$ -pair complex and  $g_n$  is the rate of gain of excitons by an  $n$ -pair complex. The rate of loss includes contributions from both evaporation and recombination

$$l_n = l_n^E + l_n^R, \quad (2)$$

where

$$l_n^E = 4\pi R_n^2 A T^2 e^{-\Phi_n/k_B T}, \quad l_n^R = n/\tau \quad (3)$$

and

$$\Phi_n = \Phi_\infty - (2S/R_n\rho), \quad (4)$$

where the parameters are:  $A$ , the thermionic emission constant;  $R_n$ , the radius of an  $n$ -pair complex;  $\tau$ , the lifetime of electron-hole pairs in droplets;  $S$ , the surface tension;  $\rho$ , the pair density of the liquid phase; and  $\Phi_\infty$ , the chemical potential of the infinite liquid. The rate of gain is given by

$$g_n = 4\pi R_n^2 \nu_{ex} \rho_{ex}, \quad (5)$$

where  $\nu_{ex}$  is the exciton velocity and  $\rho_{ex}$  is the exciton density.

The steady-state solutions of Eq. (1) are

$$P(n) = (1/g_n) e^{-G(n)/k_B T}, \quad (6)$$

where  $G(n)$  is a generalized Gibbs potential given by

$$G(n) = k_B T \int_1^n \ln \left( \frac{l_n}{g_n} \right). \quad (7)$$

The schematic behavior of  $G(n)$  is illustrated in Fig. 1. There is a local minimum for very small  $n$  labeled as point 1. The Gibbs potential increases for increasing  $n$  until an "unstable" point 2 is reached where

$$l_{n_2} = g_{n_2} \quad \text{and} \quad \left. \frac{d}{dn} \left( \frac{l_n}{g_n} \right) \right|_{n_2} < 0. \quad (8)$$

Then the Gibbs potential falls with increasing  $n$  until a second minimum, or "stable" point, labeled 3 is reached where

$$l_{n_3} = g_{n_3} \quad \text{and} \quad \left. \frac{d}{dn} \left( \frac{l_n}{g_n} \right) \right|_{n_3} > 0. \quad (9)$$

For  $n$  larger than  $n_3$  the Gibbs potential rises monotonically with increasing  $n$ . For comparison,

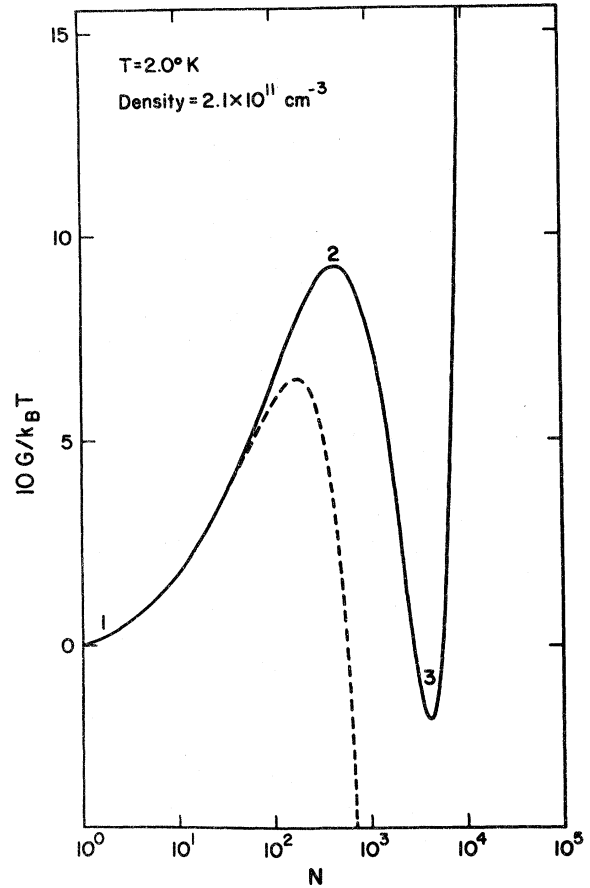


FIG. 1. The solid line gives the generalized Gibbs potential as a function of pair number for the finite lifetimes characteristic of electron-hole condensation. The potential rises toward positive infinity for very large droplets. There are two minima in the potential at the "stable" points labeled 1 and 3. The most probable number of electron-hole pairs bound to a nucleation center are values near the minima. Pair numbers near point 1 correspond to multiexciton complexes, those near point 3 to electron-hole droplets. Equilibrium between multiexciton complexes and droplets is controlled by the magnitude of the potential barrier at "unstable" point 2. For comparison, the dashed line gives the ordinary Gibbs potential for infinite carrier lifetime.

shown as the dashed curve is the Gibbs potential for infinite lifetime. The potential falls monotonically for  $n > n_2$  and there is no "stable" point.

At the two local minima in the generalized Gibbs potential at points 1 and 3, there are peaks in the steady-state probability distribution. The peak centered around point 1 corresponds to "multiexciton complexes," while the peak centered about point 3 corresponds to "electron-hole droplets." The Gibbs potential barrier at point 2 controls the rate at which equilibrium is established between complexes and droplets.

### B. Time-dependent probability distribution

A brute force method, which might be employed to solve for the time evolution of the probability distribution starting from some initial condition, is as follows. One would rewrite Eq. (1) as an eigenvalue problem substituting

$$P(n, t) = P^\lambda(n) e^{-\lambda t} \quad (10)$$

and solve for the eigenvalues  $\lambda$  and the eigenvectors  $P^\lambda(n)$ . The initial conditions could be matched by a suitable linear combination of eigenvectors and the time evolution studied. One can prove on general grounds that there is only one zero eigenvalue corresponding to the steady state and that all the remaining  $\lambda$  are positive so that relaxation to the steady state must eventually occur. These statements follow from the properties of tridiagonal matrices.

In practice, such a procedure is to be avoided for two reasons. First, since  $n_3$  is typically several powers of ten, matrices at least of that dimension must be considered and the calculation would be prohibitively difficult. Second, and more important, little physical insight would be gained by such a brute force procedure.

The simplified approach adopted in this paper follows from noting that most of the probability distribution is centered either in a narrow region about "multiexciton complex" point 1 or in a narrow region about "electron-hole droplet" point 3. The unstable point 2 is a minimum in the steady-state probability distribution. Then the probability of being in a "multiexciton" complex state might conveniently be defined by

$$P_C(t) = \int_0^{n_2} dn P(n, t). \quad (11)$$

The probability of being in an "electron-hole droplet" state is similarly defined by

$$P_D(t) = \int_{n_2}^{\infty} dn P(n, t). \quad (12)$$

Then a simple pair of stochastic rate equations

may be written which has as parameters the rate,  $g$ , of transition from complexes to droplets and the rate,  $l$ , of loss of droplets back to complexes. We write

$$\frac{dP_C(t)}{dt} = -gP_C(t) + lP_D(t), \quad (13)$$

$$\frac{dP_D(t)}{dt} = gP_C(t) - lP_D(t). \quad (14)$$

The condition for the validity of this two-state model is that relaxation to the steady-state probability distribution for sizes in the separate regions  $n < n_2$  and  $n > n_2$  must occur much more rapidly than the establishment of the steady-state relative probability of being in either of the two regions. A simple physical rationale for this is that the peak in the Gibbs potential at point 2 presents a barrier through which a cluster of electrons and holes must, in effect, tunnel by fluctuations from one side to the other. This process is certainly slow if the barrier height  $G(n_2)$  is sufficiently large.

It is trivial to solve Eqs. (13) and (14) for the time dependence of electron-hole condensation. The method of solution using eigenvectors will be useful in motivating the derivation of the parameters  $l$  and  $g$  given in the Appendix. We write

$$P_C(t) = P_C^\lambda e^{-\lambda t} \quad \text{and} \quad P_D(t) = P_D^\lambda e^{-\lambda t}. \quad (15)$$

Then the eigenvalues and eigenvectors are

$$\lambda = 0, \quad P_C^0 = l/(l+g), \quad P_D^0 = g/(l+g) \quad (16)$$

and

$$\lambda = l+g, \quad P_C^{l+g} = +1, \quad P_D^{l+g} = -1. \quad (17)$$

Suppose, for example, that the system started out with no electron-hole droplets. Then the time evolution is given by

$$P_C(t) = \frac{l+ge^{-(l+g)t}}{l+g}, \quad P_D(t) = \frac{g-ge^{-(l+g)t}}{l+g}, \quad (18)$$

which starts with zero probability of finding electron-hole droplets at  $t=0$  and evolves toward the steady-state probability at  $t=\infty$ .

As another example consider fluctuations in the number of pairs bound to a nucleation center. Suppose a center starts with a droplet on it at time  $t=0$ . Then at a later time  $t$  the probability of finding a droplet on it is given by

$$P_D(t) = (g+le^{-(l+g)t})/(l+g). \quad (19)$$

Clearly, relaxation to the steady state of an ensemble of nucleation centers is related to the fluctuations in the number of electron-hole pairs bound to an individual center. This is simply another manifestation of the fluctuation dissipation theorem.

### C. Rate parameters

The utility of this two-state model of course requires knowledge of the rate of gain  $g$  and rate of loss  $l$  as a function of density, temperature, and the other parameters of the system. These must be determined from the complete set of equations (1). A procedure for doing this will be given in the Appendix. Here, we will only state the answers which, to a good approximation, are given by

$$\frac{1}{g} = \int_0^{n_2} \frac{1}{g_n} e^{-G(n)/k_B T} \int_0^{n_3} e^{G(n)/k_B T} \quad (20)$$

and

$$\frac{1}{l} = \int_{n_2}^{\infty} \frac{1}{g_n} e^{-G(n)/k_B T} \int_0^{n_3} e^{G(n)/k_B T} \quad (21)$$

First, it should be noted that these expressions give the correct answer for the relative probabilities of multiexciton complexes and electron-hole droplets in the steady state. Second, the dominant contribution to the second integral in these two expressions comes from  $G(n)$  near its maximum at  $n_2$ , so that as expected the height of the Gibbs potential barrier controls the relaxation rate to the steady state.

Third, in the limit of infinite carrier lifetimes, as in an ordinary liquid-gas transition,  $n_3$  goes to  $\infty$  and  $G(n)$  goes toward  $-\infty$  for very large  $n$ . The rate of gain  $g$  goes to the expression for the rate of nucleation calculated by Becker and Döring.<sup>10</sup> The rate of loss  $l$  goes to zero so that there is no normalizable steady-state probability distribution in an ordinary liquid-gas transition.

### III. METASTABLE STATES IN ELECTRON-HOLE CONDENSATION

In the previous sections, expressions have been given for the rate  $g$  at which because of statistical fluctuations multiexciton complexes convert to electron-hole droplets, and the rate  $l$  of the reverse process in which droplets convert to complexes. In the steady state the distribution of droplets and complexes will be such that

$$lP_D = gP_C \quad (22)$$

However, if the rates  $l$  and  $g$  are astronomically slow, relaxation to the steady state may not be achieved within the duration of the excitation. Instead of a steady state, the measured distribution of droplets and complexes, as well as the size of droplets, will depend on the history of the excitation process.

In this section calculations will be presented for the dependence of  $l$  and  $g$  on exciton density and temperature. The range of density and tempera-

ture where both  $l$  and  $g$  are negligibly slow, and therefore metastability can occur, will be given. The relation of spectroscopic determinations of the work function to "thermodynamic" determinations, which measure the threshold excitation level for observable condensation, will also be considered.

### A. Parameters

Some significant changes are made in the parameters of this paper compared to those of the previous paper. The work function  $\Phi_\infty$  is changed to its spectroscopic value  $\Phi_\infty = 23$  eV, and the surface tension  $S$  is taken to be  $1.5 \times 10^{-4}$  erg/cm<sup>2</sup>. This corresponds to

$$S \cong \frac{1}{9} \Phi_\infty (\rho)^{2/3}, \quad (23)$$

typical of liquid metals.

The high value of  $S$  used in the previous paper can be ruled out because it produces a Gibbs potential barrier to condensation so large that densities higher than the liquid-phase density would be needed for measurable droplet nucleation rates. The new value of  $S$  might have been used to fit droplet size measurements if a correspondingly larger  $A$  were chosen. However, this would assume that the steady state had been reached in these experiments. Rather, the parameters are chosen to be close to theoretical values. It is emphasized that the present paper is not a determination of the parameters of the electron-hole liquid-gas transition.

### B. Study of relaxation rates

The controlling variable in the calculation of rate,  $l$ , of conversion of droplets to complexes is the height of the Gibbs potential barrier  $G(n_2) - G(n_3)$ . This barrier goes to zero at densities below

$$\rho_{\text{ex}} = \frac{AT^2 e^{-\Phi_\infty/k_B T} e^x}{\nu_{\text{ex}}} + \frac{2S}{3\nu_{\text{ex}} \tau k_B T}, \quad (24)$$

where  $x$  is the solution of

$$x^2 e^x = (2S/3\tau k_B T^3 A) e^{\Phi_\infty/k_B T} \quad (25)$$

and

$$x = 2S/R_n \rho k_B T. \quad (26)$$

These lower bound expressions were given in the previous paper<sup>1</sup> and correspond to the density at which  $n_2$  equals  $n_3$ . As the density is increased beyond these values the rate  $l$  drops dramatically and electron-hole droplets become stable.

In Fig. 2 the logarithm of  $l$ , calculated in the Gaussian approximation, is plotted versus exciton density for  $\rho_{\text{ex}}$  greater than Eq. (24) and  $T = 2.0$  eV. It is seen that the relaxation time  $1/l$  is quite ob-

servable at sufficiently low densities, but it increases to astronomical size with a small increase in density.

The controlling variable in the calculation of the rate,  $g$ , of nucleation of electron-hole droplets is the height of the Gibbs potential barrier  $G(n_2)$ . If the lifetime were infinite, it is readily proved that

$$\frac{G(n_2)}{k_B T} = \frac{16\pi S^3}{3\rho^2(k_B T)^3 \ln^2(AT^2 e^{-\phi_{\infty}/k_B T}/\nu_{ex} \rho_{ex})} \quad (27)$$

This is a good approximation at high levels of supersaturation, and is always a lower bound to the actual barrier for finite lifetimes as seen in Fig. 1. Since this is in turn exponentiated in the Gaussian approximation to  $g$ ,

$$g = \left( \int_0^{n_2} \frac{1}{g_n} e^{-G(n)/k_B T} \right)^{-1} e^{-G(n_2)/k_B T} \times \left( \frac{1}{\pi} \frac{d^2 G}{dn^2} \frac{1}{K_B T} \right)^{1/2}, \quad (28)$$

small changes in the value of surface tension  $S$ , or the degree of supersaturation, can change  $g$  by orders of magnitude.

Also plotted in Fig. 2 is the logarithm of  $g$  versus exciton density at  $T=2.0^\circ\text{K}$ . It is seen that the nucleation time  $1/g$  is astronomically large at

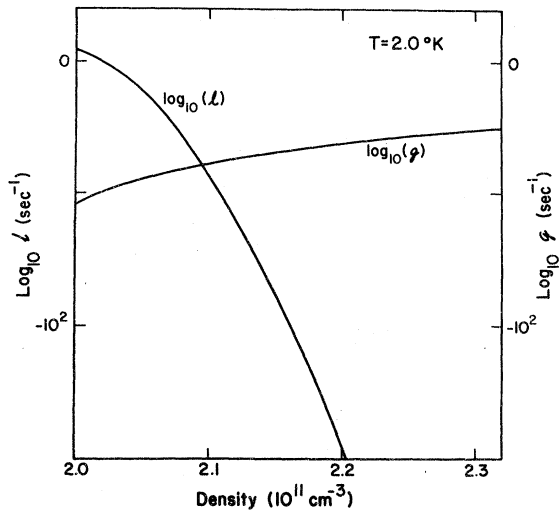


FIG. 2. Logarithms of the rate of nucleation, or gain  $g$ , of electron-hole droplets from multiexciton complexes, and the rate of decay, or loss  $l$ , of droplets back to complexes are plotted vs exciton density for densities near the condensation point. A logarithm of zero corresponds to a relaxation time of 1 sec. In the steady state, condensation occurs near the density where the nucleation and decay curves cross. However, if the rates of nucleation and decay are astronomically slow, as in Fig. 2, then metastable states are possible where the steady-state distribution of complexes and droplets is not achieved on a measurable time scale.

densities near Eq. (24). As the density is increased the nucleation time drops until, as shown in Fig. 3, the nucleation time becomes sufficiently short to be observable. (Shown for comparison as the dashed line is a  $g$  of  $1/\tau$ .) This is the well-known phenomenon of "supersaturation," where a density considerably higher than the coexistence curve is needed for nucleation to proceed at a measurable rate. The actual densities needed depend strongly on the strength of binding to nucleation centers. The stronger the binding the faster the nucleation rate  $g$ .

### C. Metastable states

In the previous paper, a detailed study was made of the properties of the steady-state probability distribution. The relative probabilities of multiexciton complexes and droplets in the steady state changed rapidly over the small density range near where the curves for  $l$  and  $g$  cross in Fig. 2. How-

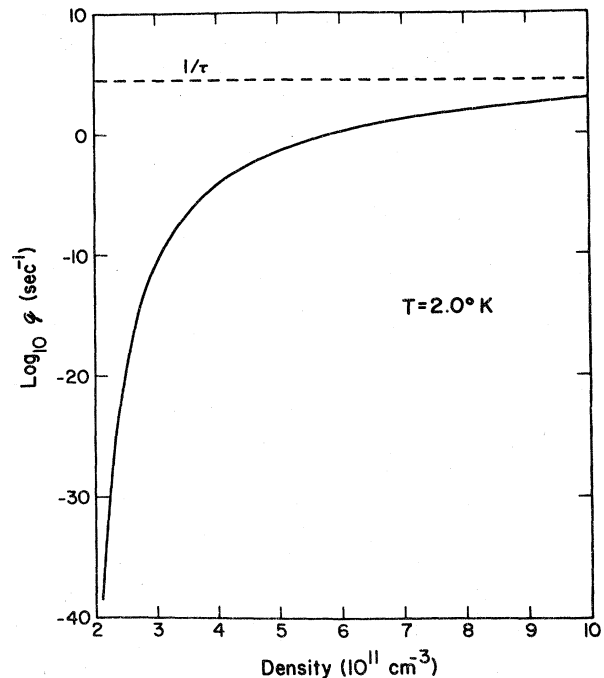


FIG. 3. Logarithm of the rate of nucleation, or gain  $g$ , of electron-hole droplets is plotted vs exciton density for densities higher than the condensation point. In order for measurable condensation to occur, the inverse of the product of  $g$  and the number of nucleation centers must be comparable to the duration of the excitation. As shown in Fig. 3, this may require densities considerably higher than the steady-state condensation density. This is the well-known supersaturation phenomenon in phase transitions. For comparison the dashed line corresponds to  $g=1/\tau$  where  $\tau=40 \mu\text{sec}$ . The actual values of  $g$  may be increased significantly by strong binding to the nucleation center.

ever, as is clear from the figure, the relaxation rates are negligibly small at high temperatures. Relaxation to the steady state may not occur within the time scale of the typical experiment. The attempts at comparison with experiment made in the previous paper may be criticized, aside from the question of transport effects, because it is questionable whether the steady state had been achieved in these experiments.

Rather, we consider the possibility that there is a range of exciton densities at a given temperature where metastability can occur. This is a range where the number of droplets changes astronomically slowly with time. Clearly, a lower bound on this range is given by Eq. (24) since  $1/l$  is measurably short at this density. As Fig. 2 shows, a small increase in density increases  $1/l$  to astronomical values. The upper bound to this range is given by the densities where  $1/g$  becomes measurably short.

The solid line in Fig. 4 gives the exciton densities at which  $l=g$ . Except at low temperatures ( $T < 2^\circ\text{K}$ ) these densities are only slightly larger than Eq. (24). The dotted line gives the exciton densities at which the relaxation time  $1/g$  is 10 sec. The dashed line gives the densities at which the relaxation time is  $10^{-3}$  sec, the excitation pulse length of typical experiments.

The first lesson of Fig. 4 is that experiments which attempt to determine the work function by measuring the threshold for observable electron-hole condensation in a short pulse length will underestimate the work function. Exciton densities considerably larger than the coexistence curve are needed to reduce nucleation times to, say,  $10^{-3}$  sec. In practice nucleation times do not have to be this short since the number of nucleation centers may be large, e.g.,  $\sim 10^{11}$   $\text{cm}^{-3}$  in the purest Ge. Nevertheless, even in this case there exists a considerable difference between the density at which nucleation becomes observable and the coexistence curve. This may account for some of the reported discrepancy between spectroscopic and so called "thermodynamic" values of the work function.

The second lesson of Fig. 4 is that metastability can occur only at high temperature ( $T \gtrsim 2^\circ\text{K}$ ). The 10 sec and  $10^{-3}$  sec curves cross the  $l=g$  curve at temperatures less than  $2^\circ\text{K}$ . The finite lifetimes of electrons and holes in droplets require densities increasingly greater than the equilibrium thermodynamics coexistence curve at low temperatures. Hence, the Gibbs barrier is smaller and relaxation faster at low temperatures.

#### IV. TIME DEPENDENCE OF EXCITON DENSITY

The calculations of the preceding sections have considered the relaxation rates  $l$  and  $g$  when the

exciton density is held constant. In laser experiments it is the total generation rate of electrons and holes, rather than the exciton density, which is constant. However, the present calculations may be applied to laser excitation experiments if it is assumed that the instantaneous values of  $l$  and  $g$  are determined by the instantaneous value of the exciton density.

One can speculate on the sequence of events which occur after the source of excitation, a laser, is turned on. Assume for simplicity that the excitation is uniform throughout the crystal. The exciton density will begin to rise. Measureable condensation will occur if the density rises to a high enough level that the nucleation rate  $g$  is significant. A number of embryonic electron-hole drop-

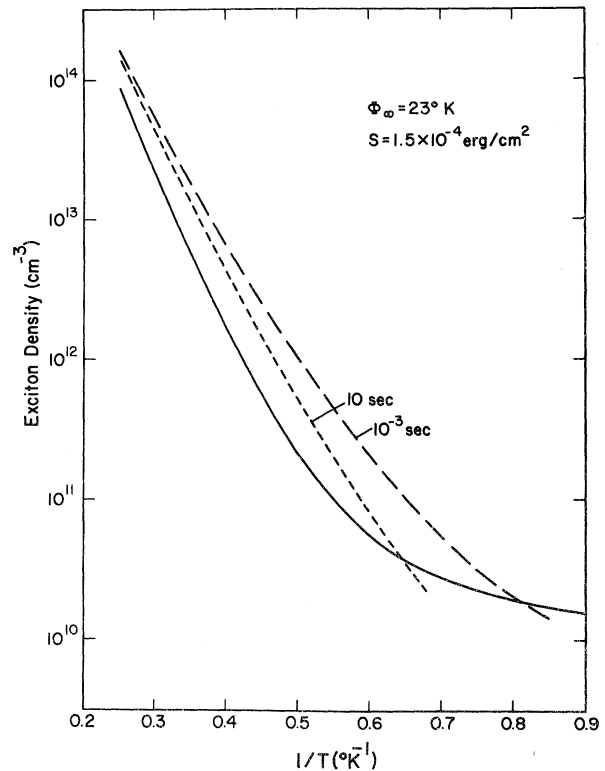


FIG. 4. Solid line: exciton densities at which the rate of gain  $g$  equals the rate of loss  $l$  as a function of temperature; dotted line: exciton densities at which the relaxation time  $1/g$  is 10 sec; dashed line: exciton densities at which  $1/g = 10^{-3}$  sec. Since typical phase-diagram experiments employ pulsed excitation at  $\sim 1$  kHz, Fig. 4 shows that some of the reported discrepancy between spectroscopic and thermodynamic values of the work function may be ascribed to supersaturation effects. At low temperatures, the solid line deviates strongly from the usual liquid-gas coexistence curve. The rates of gain and loss become measurably fast and metastability phenomena such as supersaturation cannot occur.

lets of size greater than the critical size  $n_2$  will be formed. The embryonic droplets grow at the expense of the excitons in the gas phase. If the temperature is high enough for metastability, the fall in the exciton density as the droplets grow will shut off the nucleation of more droplets.

Eventually, a state should be reached where the droplet size is at a "stable" point,  $n_3$ , a minimum in the generalized Gibbs potential, and the exciton density is high enough to provide a strong Gibbs barrier,  $G(n_2) - G(n_3)$ , to the decay of droplets. However, we know that there is a minimum stable droplet size given by Eqs. (25) and (26). The number of embryonic droplets formed initially may be too large for the generation rate to make up for recombination of excitons and electron-hole pairs in that number of droplets at the minimum stable size. The exciton density will have to fall to a level where the decay rate  $l$  is appreciable so that some droplets decay. Then the exciton density may rise again as the remaining droplets reach a stable size. This should yield values of droplet size and exciton density close to steady-state values.

If the number of embryonic droplets initially formed is small enough, a metastable state should be reached where the droplet size and exciton density are higher than steady state. Relaxation to the steady state may occur at an astronomically slow rate.

At low temperatures, where metastability cannot occur, the steady state should be reached within the measurable relaxation times. Furthermore, fluctuations in cluster size between complexes and droplets should be observable.<sup>13</sup>

These speculations could be given more weight by a solution of Eq. (1) with the exciton density allowed to be a function of time. The equation for the exciton density in the case of uniform excitation is

$$\frac{d\rho_{\text{ex}}}{dt} = G - \frac{\rho_{\text{ex}}}{\tau_{\text{ex}}} - N_i \sum_n (g_n - l_n^E) P(n, t), \quad (29)$$

where  $N_i$  are the number of nucleation centers and  $G$  is the generation rate. A time-dependent solution of these equations is beyond the scope of the present paper. We note that the steady-state solution for the probability distribution is the same as discussed in the previous paper.<sup>1</sup>

Finally, we emphasize two areas where outstanding theoretical problems remain. The first is the nucleation kinetics near the critical temperature where the interaction of clusters with one another is undoubtedly important. The second is transport effects in single-photon laser excitation experiments where the electrons and holes must migrate inward from the crystal surface.

#### ACKNOWLEDGMENTS

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#### APPENDIX: DERIVATION OF THE RELAXATION RATES

##### A. Method of temporal moments

The procedure to be followed in deriving the relaxation rates was deduced from the remark of Goodrich<sup>14</sup> that for birth and death stochastic processes an exact recursion relation for the temporal moments of the probability distribution,

$$\mu_m(n) = \int_0^\infty t^m P(n, t), \quad (A1)$$

can be derived from equations such as Eq. (1) provided  $P(n, t)$  tends to zero for long times.

For electron-hole condensation, in contrast to ordinary liquid-gas transitions,  $P(n, t)$  tends to a steady-state value at long times. Instead of dealing with Eq. (A1), a new temporal moment is defined,

$$\mu_m(n) = \int_0^\infty t^m [P(n, t) - \bar{P}(n)], \quad (A2)$$

where  $\bar{P}(n)$  is the steady-state probability distribution.

Then from Eq. (1) and

$$0 = l_{n+1} \bar{P}(n+1) - l_n \bar{P}(n) - g_n \bar{P}(n) + g_{n-1} \bar{P}(n-1) \quad (A3)$$

one may readily derive that

$$g_{n+1} \mu_0(n+1) = \left( \prod_{m=0}^n \frac{g_{1+m}}{l_{1+m}} \right) \times \left[ g_0 \mu_0(0) - \sum_{l=0}^n \left( \prod_{j=1}^l \frac{l_j}{g_j} \right) \sum_{k=0}^l [P(k, 0) - \bar{P}(k)] \right], \quad (A4)$$

which is an exact expression for the zeroth temporal moment in terms of the initial probability distribution. As in the previous paper, this is readily converted to an expression for continuous  $n$  by introducing the generalized Gibbs potential  $G(n)$ . One finds

$$g_n \mu_0(n) = e^{-G(n)/k_B T} \left( g_0 \mu_0(0) - \int_0^n dn' e^{G(n')/k_B T} \int_0^{n'} dk [P(k, 0) - \bar{P}(k)] \right). \quad (A5)$$

One can eliminate  $\mu_0(0)$  from this expression with the normalization requirement

$$\int_0^\infty [P(n, t) - \bar{P}(n)] dn = 0. \quad (A6)$$

This gives

$$g_n \mu_0(n) = \frac{e^{-G(n)/k_B T}}{\int_0^\infty (1/g_n) e^{-G(n)/k_B T}} \left( \int_0^\infty dn' \frac{1}{g_n'} e^{-G(n')/k_B T} \right. \\ \left. \times \int_n^{n'} dn'' e^{G(n'')/k_B T} \int_0^{n''} dk [P(k, 0) - \bar{P}(k)] \right). \quad (\text{A7})$$

One may derive in similar fashion for the higher-order moments that

$$g_n \mu_m(n) = m \frac{e^{-G(n)/k_B T}}{\int_0^\infty (1/g_n) e^{-G(n)/k_B T}} \left( \int_0^\infty dn' \frac{1}{g_n'} e^{-G(n')/k_B T} \right. \\ \left. \times \int_n^{n'} dn'' e^{G(n'')/k_B T} \int_0^{n''} \mu_{m-1}(k) dk \right). \quad (\text{A8})$$

It is clear from Eqs. (A7) and (A8) that the temporal moments to all orders may be calculated from a given initial distribution. These rather formidable exact relations are the starting point of the calculations to follow.

#### B. Initial probability distribution

The purpose of the two-state model is to describe the relaxation of the electron-hole system after the initial transients have died out. A probability distribution in which relaxation to the steady state has already occurred in the separate regions  $n < n_2$  and  $n > n_2$  but not between those two regions would have

$$P(n, 0) - \bar{P}(n) = C \left( \frac{\theta(n_2 - n)(1/g_n) e^{-G(n)/k_B T}}{\int_0^{n_2} (1/g_n) e^{-G(n)/k_B T}} \right. \\ \left. - \frac{\theta(n - n_2)(1/g_n) e^{-G(n)/k_B T}}{\int_{n_2}^\infty (1/g_n) e^{-G(n)/k_B T}} \right), \quad (\text{A9})$$

where  $C$  is some constant.

By comparing with Eq. (17), one sees that Eq. (A9) is similar to the eigenvector of the two-state model which has a nonzero eigenvalue. Therefore, if the two-state model is correct, it should be possible to prove from the exact relations Eqs. (A7) and (A8) that  $P(n, t) - \bar{P}(n)$  decays exponentially in time. The exponential decay constant should provide the quantity  $l+g$ . Since  $l/g$  is already known from the steady-state distribution, the parameters  $l$  and  $g$  can be separately determined in this way.

Since the mathematics is a bit tricky, we will outline the procedure here. Consider the integral in Eq. (A7)

$$I = \int_n^{n'} dn'' e^{G(n'')/k_B T} \int_0^{n''} dk [P(k, 0) - \bar{P}(k)] \quad (\text{A10})$$

with the initial guess of Eq. (A9). The principal contributions to the  $n''$  integral comes from the regions where  $G(n'')$  is large. This occurs for  $n''$  near  $n_2$  and for  $n''$  larger than  $n_3$ . However, for our initial guess

$$J(n'') = \int_0^{n''} dk [P(k, 0) - \bar{P}(k)] \quad (\text{A11})$$

is very close to 1 for  $n''$  near  $n_2$  and is very close to 0 for  $n''$  larger than  $n_3$ . Hence, only the  $n''$  integral around  $n_2$  need be considered.

Break up the integral over  $n''$  as follows:

$$I = \int_n^{n'} dn'' e^{G(n'')/k_B T} J(n'') \\ = \int_{n_2}^{n'} dn'' e^{G(n'')/k_B T} J(n'') - \int_{n_2}^n e^{G(n'')/k_B T} J(n''). \quad (\text{A12})$$

Since the principle contribution comes for  $n''$  near  $n_2$  (including the properties of  $J$  discussed above) this integral is to a good approximation

$$I = \theta(n' - n_2) \theta(n_2 - n) \int_0^{n_3} dn'' e^{G(n'')/k_B T} \\ - \theta(n_2 - n') \theta(n - n_2) \int_0^{n_3} dn'' e^{G(n'')/k_B T}, \quad (\text{A13})$$

except for  $n'$  and  $n$  very close to  $n_2$ . Divide the integral over  $n'$  into two parts from 0 to  $n_2$  and from  $n_2$  to  $\infty$ . Then it is readily seen that

$$\mu_0(n) = (1/\lambda) [P(n, 0) - \bar{P}(n)], \quad (\text{A14})$$

where

$$\frac{1}{\lambda} = \frac{\int_0^{n_3} dn'' e^{G(n'')/k_B T}}{\int_0^\infty (1/g_n) e^{-G(n)/k_B T}} \int_0^{n_2} dn' \frac{1}{g_n'} e^{-G(n')/k_B T} \\ \times \int_{n_2}^\infty dn'' \frac{1}{g_n''} e^{-G(n'')/k_B T}. \quad (\text{A15})$$

Since the structure of Eq. (A8) is similar to that of Eq. (A7) the same mathematics can be applied to the higher-order moments. In this way it may be proved that

$$\mu_m(n) = + (m/\lambda) \mu_{m-1}(n) = (m!/\lambda^m) \mu_0(n). \quad (\text{A16})$$

This behavior is consistent with

$$P(n, t) - \bar{P}(n) = [P(n, 0) - \bar{P}(n)] e^{-\lambda t}, \quad (\text{A17})$$

i.e., an exponential decay. Q. E. D.

Now we make identification with the two-state model in order to identify the parameters  $l$  and  $g$ . We have

$$l + g = \lambda \quad (\text{A18})$$

and

$$\frac{l}{g} = \frac{\int_0^{n_2} \frac{1}{g_n} e^{-G(n)/k_B T}}{\int_{n_2}^\infty \frac{1}{g_n} e^{-G(n)/k_B T}}, \quad (\text{A19})$$

which reduces to Eqs. (20) and (21) for  $g$  and  $l$ .

It should be apparent that this method could be adapted to nucleation kinetics problems where there are more than two minima in the Gibbs potential.



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- <sup>13</sup>At extremely low temperatures, the theory would predict a very small minimum stable size and a very small Gibbs barrier. However, this would involve extrapolating the concept of surface tension to a non-macroscopic regime where its application is doubtful. What should be true at very low temperatures is that the nature of the nucleation center will be very important and a division of electron-hole cluster sizes into multiexciton complexes and droplets may not be a useful concept. There may be an experimental lower limit to the temperatures at which high excitation may be studied, determined by the heating associated with the relaxation of excited electrons and holes to the band edges.
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