NUCLEATION PHENOMENA IN ELECTRON-HOLE DROP CONDENSATION IN ULTRA-PURE Ge[†]

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ABSTRACT

By careful measurements and appropriate theory, we are able to observe and explain quantitatively for the first time major aspects of electron-hole drop nucleation phenomena in ultra-pure Ge. The free exciton-drop system above 1.3 K is shown to be always in a metastable state, i.e. dependent upon the history of optical excitation. We quantitatively explain the observed luminescence hysteresis and measure the drop surface tension, $\sigma = 2.6 \times 10^{-4}$ erg cm^2 at 2 K. The metastability lifetime is experimentally found to be $\sim 8 \times 10^6$ sec. The gas-liquid up-going and down-going threshold curves are measured and explained using an exciton condensation energy $\phi \cong 2$ meV. The theory also predicts the drop radius and drop concentration as a function of temperature and excitation history.

I. NUCLEATION PHENOMENA: EXPERIMENTAL

Optical hysteresis in the luminescence of electron-hole drops (EHD)[1] in Ge was first reported by Lo *et al.*[2] The relative intensities I_{709} of the drop luminescence and I_{714} of the free exciton (FE) luminescence were found to depend on the history of optical excitation. This was interpreted as a gas-liquid supersaturation phenomenon providing direct evidence for the existence of the surface energy of EHD. In this paper we present fuller experimental and theoretical details of

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hysteresis and other nucleation phenomena in ultra-pure Ge.[3,4] The experiments are done as follows: Single crystals of polished and etched ultra-pure Ge of size $3 \times 4 \times 9$ mm^3 are mounted without stress and without metallic contacts over a 2×8 mm^2 hole in a copper plate, and immersed in liquid He in an optical dewar. One surface is uniformly illuminated with the light from a highly stabilized electronically controlled incandescent lamp, using a beam splitter to accurately monitor the absolute power flux P absorbed by the Ge surface. Both surface excitation ($0.5 < \lambda < 1.4$ μm, $\lambda_{ave} \simeq 0.9$ μm) and volume excitation ($\lambda \simeq 1.52$ μm) are used. The luminescence is collected from the opposite crystal face, analysed by a spectrometer and recorded by a sensitive Ge detector using lock-in techniques. We are able to observe direct thresholds down to 1.3 K where P is only a few microwatts/mm^2. A variety of crystal samples were used, both n and p type, with net impurity density in the range 3×10^9 to 4×10^{12} cm^{-3}, some dislocation-free with vacancy clusters, and some with dislocations and no vacancies. The crystals were grown in the ⟨100⟩ or ⟨111⟩ direction in H_2 gas.

Figure 1 shows the observed luminescence I_{709} and I_{714} as functions of excitation power flux P for both "up-going" and "down-going" excitation. The pronounced hysteresis near threshold is always observed and is accurately reproducible when the data are taken in the following pattern: First, $P \rightarrow 0$ for 5 sec, then the power is switched smoothly and monotonically to a low value for 50 sec at which I_{709} and I_{714} are recorded. Then $P \rightarrow 0$ for 5 sec, and is then switched to a slightly higher value, *etc.*, thereby obtaining the points on the up-going excitation curve. At the up-going threshold, $P_+ \simeq 4.4$ mW cm^{-2}, I_{709} rises sharply while I_{714} breaks downward as expected, because the e-h pairs produced by increased excitation go largely into the liquid phase once drop nucleation has begun. In Fig. 1 the down-going excitation data are taken in a similar pattern: $P \rightarrow 0$ for 5 sec, then P

$\rightarrow$ 100 mW cm^{-2}, *i.e.* far above threshold, for 5 sec, then P $\rightarrow$ 3.4 mW cm^{-2} for 50 sec, at which I_{709} and I_{714} are recorded; then P $\rightarrow$ 0, P $\rightarrow$ 100 mW cm^{-2}, P $\rightarrow$ 3.2 mW cm^{-2}, *etc.* A very sharp down-going threshold at $P_- \simeq 1.4$ mW cm^{-2} is quite evident, as well as a corresponding break in I_{714}. The fact that the up-going threshold P_+ is considerably larger than the down-going one P_- has a simple explanation: It is necessary to supersaturate the exciton gas density to initiate nucleation because the surface tension of embryonic droplets tends to reduce them to zero size. A measurement of P_+ and P_- is the most direct way to experimentally determine the surface tension, as discussed below. The hysteresis is an intrinsic and invariant feature of drop nucleation in ultra-pure Ge, observed in all samples between $1.3 < T < 4.2$ K, for both surface and volume excitation. The persistence of the hysteresis shows that the

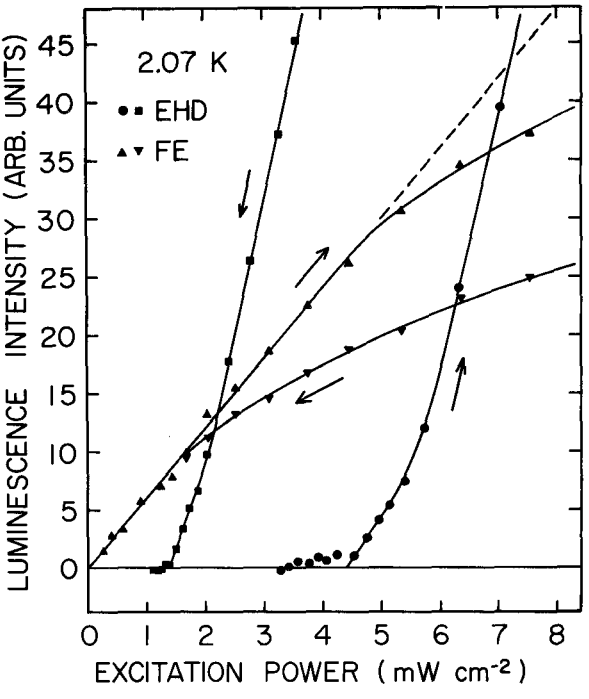

Fig.1. Luminescence intensity of free excitons (FE) in ultra-pure Ge at 714 meV and of electron-hole drops (EHD) at 709 meV, as a function of calibrated excitation power absorbed in the crystal at $\lambda_{ave} \simeq 0.9$ μm. The crystal has a net impurity concentration $N_A \simeq 5 \times 10^{10}$ cm^{-3}, and dislocation density ~10^2 cm^{-2}. The data points are taken by increasing (up arrows) and by decreasing (down arrows) the excitation, and display a large hysteresis owing to the droplet surface tension.

free exciton-drop system is in a long-lived metastable state, not in thermodynamic equilibrium. Failure to observe hysteresis may be due to insufficient detector sensitivity, excess impurities, or a number of mechanisms which destroy drops, such as unstable excitation, sample strains, and electrical contacts. If the lifetime of drops against destruction is very short, the observed state of the system is determined by these external mechanisms.

How long is the metastability lifetime in pure crystals? We have measured this, Fig. 2, by switching from P = 0 to a power P = 25 mW cm^{-2} on an up-going excitation curve, then recording $I_{709}(t)$ while P is accurately held constant; a very slow increase in drop luminescence is observed. Similarly, in the down-going case we reduced the excitation from P = 140 mW cm^{-2} to P = 25 mW cm^{-2}, the same level, then recorded $I_{709}(t)$ while holding P constant; a slow

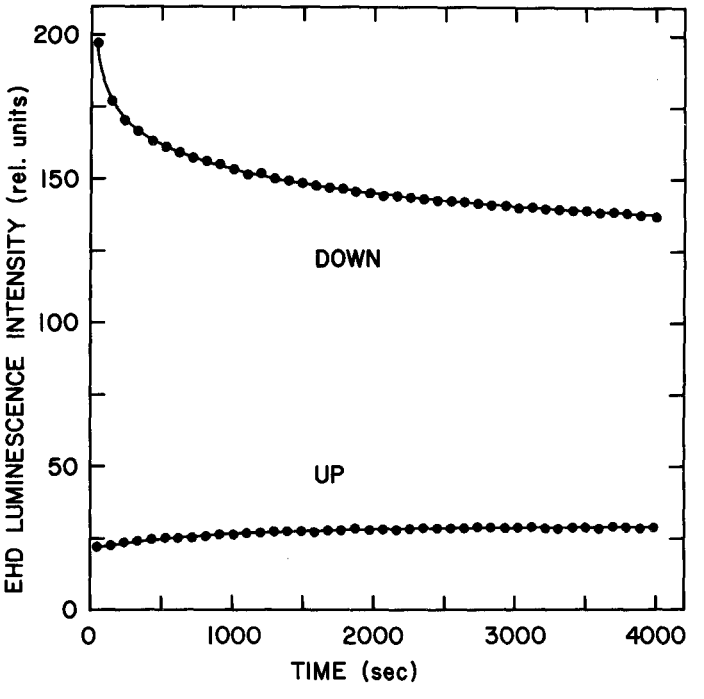

Fig.2. Slow time behavior of drop luminescence following an up-going and a down-going step in excitation (see text) at T = 2.01 K in ultra-pure Ge, net $N_D \simeq 3\times10^9$ cm^{-3}, dislocation density ~10^4 cm^{-2}. These data clearly show that the exciton-drop system is in a long-lived metastable state, dependent on the excitation history.

decrease is observed. As detailed below, the luminescence varies logarithmically with time, in excellent agreement with our theory—this allows us to predict that, barring external destruction of drops, the two curves will cross, *i.e.* the hysteresis would be naturally quenched, after a time of $\gtrsim 8 \times 10^6$ sec. Thus the exciton gas and drops, even though excited states of the Ge crystal, can be conveniently conceptualized as stable components of a quasi-thermodynamic system —as long as the excitation is uniform and stably maintained.

The magnitude of the hysteresis, *i.e.* the ratio P_+/P_-, is observed to depend on the temperature, Fig. 3, where it is evident that the hysteresis vanishes at temperatures below 1.3 K, a fact quantitatively explained by the theory below. As shown in Fig. 3, we observe sharp thresholds at all temperatures down to the lower limit of our apparatus, $T \simeq 1.25$ K. At temperatures above the λ point of liquid He, the hysteresis is found to be smaller and more difficult to measure, but non-vanishing. By measuring the up-going and down-going thresholds at various temperatures, we obtain the data of Fig. 4 showing that the surface energy and finite drop size give two

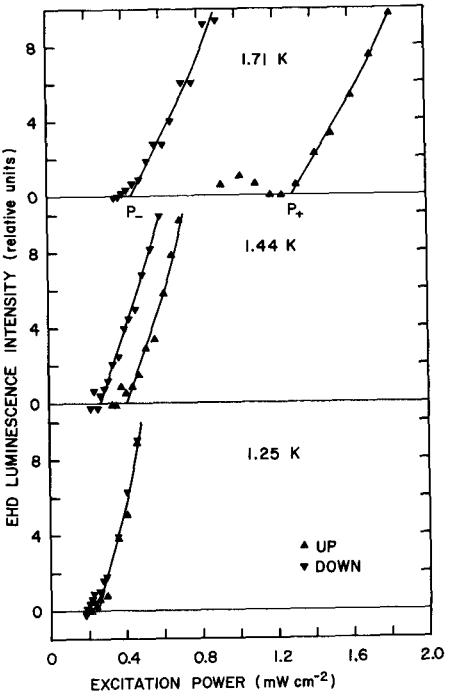

Fig.3. Drop luminescence for up-going and down-going excitation showing that below $T \simeq 1.3$ K the hysteresis vanishes. The sample is the same as Fig. 2. The ratio of the up-going threshold power P_+ to the down-going threshold power P_- experimentally determines the surface tension.

branches of the gas-liquid coexistence curve. Below 2 K both branches roll upward, away from the exponential dependence on 1/T usually assumed. Previous threshold experiments were performed in such a way that only the up-going curve was measured.

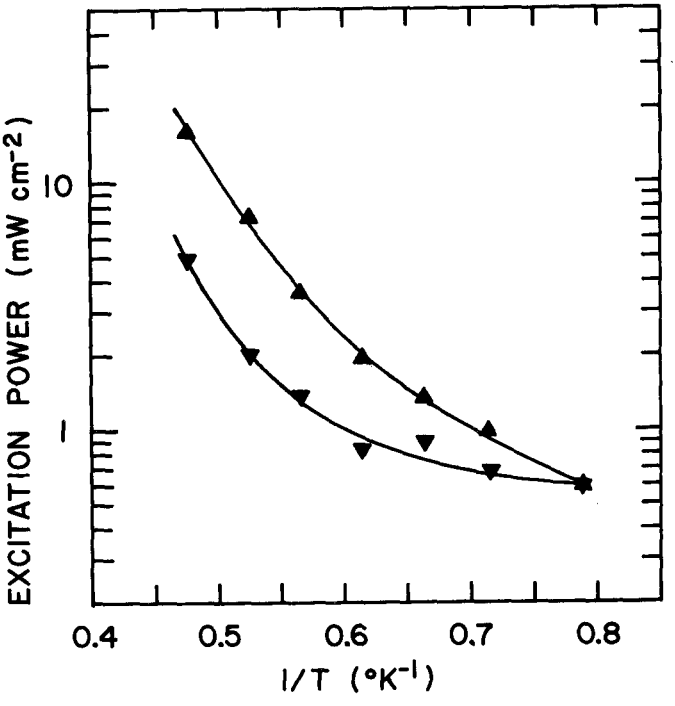

Fig.4. Observed up-going (△) and down-going (▽) thresholds versus reciprocal temperature for ultrapure Ge, net $N_D \simeq 6\times10^{10}$ cm^{-3}, dislocation density ~10^4 cm^{-2}. The power is not absolutely calibrated (in contrast to Figs. 1 and 3).

Figures 1 to 4 can be considered to represent intrinsic nucleation phenomena of EHD, to be explained through an adequate theoretical model possessing these features: 1) quantitative prediction of hysteresis (Figs. 1 and 3) providing a procedure for data reduction to obtain the drop surface tension; 2) quantitative explanation of coexistence curves (Fig. 4) to be used to extract the exciton condensation energy ϕ; 3) quantitative explanation of metastable time behavior (Fig. 2); 4) prediction of drop radius near both up-going and down-going thresholds, as a function of temperature; 5) prediction of drop radius and concentration, and free-exciton density in time evolution for arbitrary excitation P(t); 6) applicability to drop formation both on and free of

nucleation centers. Such a model has been developed.[3,4]

II. OUTLINE OF NUCLEATION THEORY

The point of departure is the classical theory of vapor condensation in a spatially uniform system.[5] Fluctuations in the exciton gas density, or impurities, will nucleate embryonic droplets; those smaller than a critical radius R_c are unstable because surface tension quickly reduces them to zero size. Embryos with $R > R_c$ quickly grow into observable macroscopic drops. Lord Kelvin showed that $R_c = (2\sigma/n_o kTx)$, where σ is the surface tension, n_o is the particle density in the drop and $x = \ln (n/n^s)$ is the degree of gas supersaturation. For the exciton gas the saturated density can be found approximately by setting the chemical potential of an ideal gas equal to the condensation energy:[6]

$$n_s = \gamma \left[\frac{m^* kT}{2\pi\hbar^2}\right]^{3/2} e^{-\phi/kT} \tag{1}$$

The rate of macroscopic drop formation J_+ (drops cm^{-3} sec^{-1}), is determined by the density of drops of critical size, which can be estimated from the entropy decrease ΔS in forming a critical drop from free particles, *i.e.* $J_+ \propto \exp(\Delta S/k) = \exp(-16\pi\sigma^3/3k^3T^3n_o^2x^2)$. Because J_+ is extremely sensitive to the degree of supersaturation, this theoretical model yields sharp thresholds.

However, because the classical theory does not include the effects of the finite pair lifetime τ_o within drops, it does not yield a finite drop size, and cannot be used to calculate the rate of breakup J_-(drops cm^{-3} sec^{-1}) of macroscopic drops. It therefore cannot explain central features of hysteresis and metastability and provides no adequate procedure for measuring the surface energy. Similarly, an equilibrium model[7] including τ_o, but neglecting the time required to reach the steady state, does not predict hysteresis and is inapplicable above

1.3 K. It is in fact necessary to calculate the separate non-equilibrium rates of drop formation J_+ and breakup J_- including the lifetime τ_0. We have done this by extending the classical nucleation theory of Becker and Döring:[8] to their rate equations we add the volume decay rate of drops.

An important parameter is ϕ_ν, the difference in free energy between ν e-h pairs condensed in a drop and the same number of free excitons:

$$\phi_\nu = 4\pi R_o^2 \nu^{2/3} \sigma - xkT\nu + f_\nu \tau \qquad (2)$$

The first term is the surface free energy. The second is the chemical potential difference, and the third is a new effective free energy due to the finite pair lifetime. This function is plotted in Fig. 5 *versus* the drop radius $R = R_o \nu^{1/3}$, for various values of the supersaturation ratio $S = (n/n^s)$. For ratios larger than a minimum value S_M, below which no drop size is stable, there is a minimum in ϕ_ν at the stable radius R_s which can be populated by macroscopic drops, and a maximum ϕ_c at the critical radius R_c. For $R > R_s$, ϕ_ν turns up sharply due to the finite lifetime term, limiting the drop size to a finite value with a

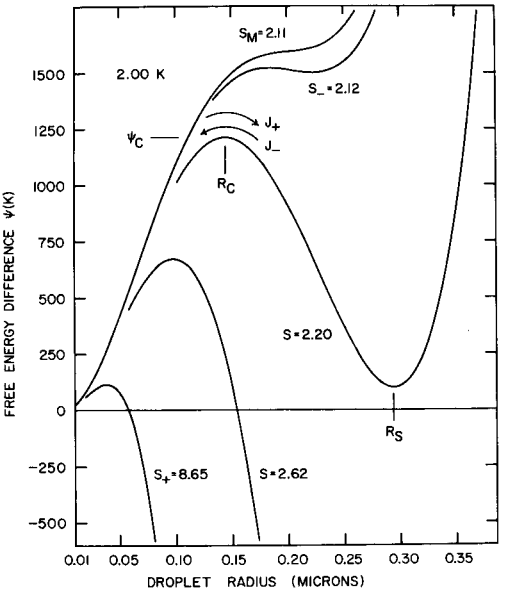

Fig.5. Effective free energy difference ϕ_ν, eq. (2), for EHD in Ge versus droplet radius. The curves are calculated assuming T = 2.0 K, ϕ = 2.03 meV and $\sigma = 2.6 \times 10^{-4}$ erg cm^{-2}. [From the nucleation theory of Westervelt[4]]

sharply peaked distribution. We see that the maximum ψ_c due to the surface energy, acts as a "barrier" to the drop formation rate J_+; an excitation P_+ that can produce a supersaturation ratio $S_+ = 8.65$ at 2 K is necessary to reduce the barrier sufficiently to allow J_+ to become significant, *i.e.* to "turn on." Similarly the "barrier" $(\psi_c - \psi_s)$ limits the rate of breakup J_- at 2 K until the supersaturation ratio is reduced to $S_- = 2.12$. A plot of J_+ and J_- *versus* ln S, Fig. 6, shows the sharp dependence on the degree of supersaturation. The minimum in ψ_v for S = 8.65 lies offscale at $R_s \simeq 2.5$ μm, the stable drop size produced at up-going threshold. If the excitation is increased, a larger number of identical drops are formed. If the excitation is now decreased, the nucleated drops continue to be maintained by condensation of excitons on their surface, but the stable drop size R_s, Fig. 5, decreases steadily until the supersaturation ratio $S_- = 2.12$ is reached, where the breakup current J_- "turns on", Fig. 6, and the down-going threshold is reached, at $R \simeq 0.22$ μm. The nucleation currents are found to be[4]:

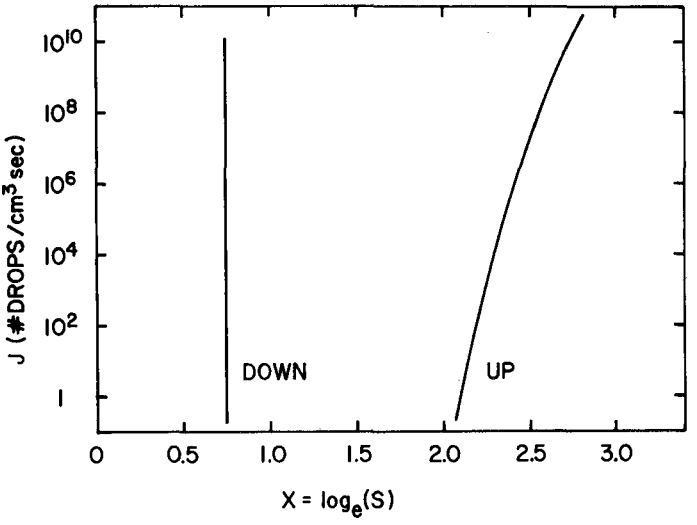

Fig.6. Up-going (J_+) and down-going (J_-) homogeneous nucleation rates for EHD in Ge, eq. 3, versus the degree of exciton gas supersaturation $x = \log_e(n/n^s)$. Calculated from nucleation theory [Westervelt[4]], using the parameters of Fig. 5.

$$J_+ = \beta n \nu_c^{2/3} \, h_c / \Delta\nu_c \; ; \; J_- = J_+ \, N/h_s \Delta\nu_s \; . \qquad (3)$$

Here $\beta = 4\pi R_o^2 v_x$, where v_x is the FE mean speed, the subscripts c and s refer to the critical and stable sizes ν_c and ν_s, $\Delta\nu$ is the Gaussian width of the appropriate extremum in ψ_ν, N is the drop concentration (drops cm^{-3}) in the well about R_s, and h_c and h_s are the densities (cm^{-3}) of drops of size ν_c and ν_s. It is clear from Fig. 6 that for values of S between S_+ and S_- both J_+ and J_- are vanishingly small and thus N must remain constant. In fact, for $T \gtrsim 1.3$ K we find no value of S for which J_+ and J_- are simultaneously appreciable. This predicts that the system will always be in a metastable state, *i.e.* $J_+ \neq J_-$.

By incorporating eq. 3 into a set of rate equations somewhat like those of Pokrovskii,[1] it is possible to include a treatment of nucleation in the time evolution of the EHD-FE system

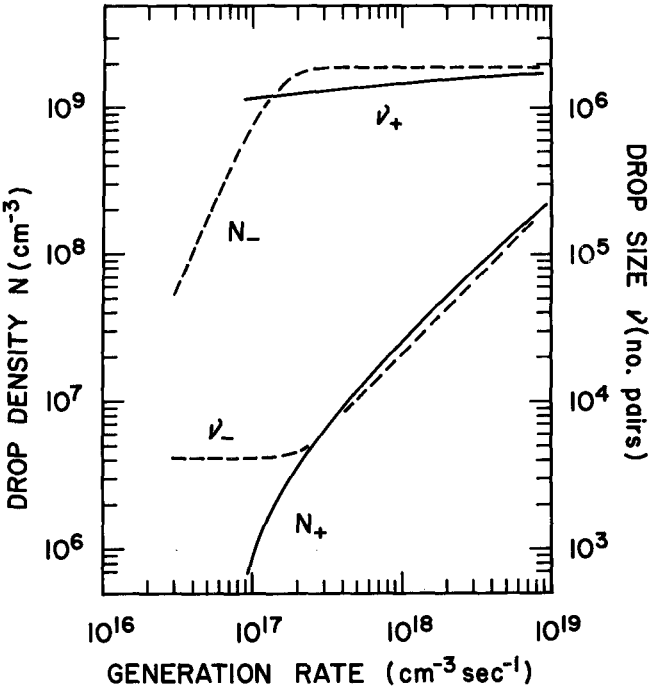

Fig.7. Drop concentration N (cm^{-3}) and number of pairs per drop ν versus e-h pair generation rate, computed from exciton-drop rate equations including non-equilibrium homogeneous nucleation currents J_+ and J_-, eq. (3). Results are given for both up-going and down-going exponential step excitation, (τ_{on} = 0.1 sec), and show a marked dependence on excitation history. The computations assume T = 2.1 K, $\sigma = 2.5 \times 10^{-4}$ erg cm^{-2} and ϕ = 2.04 meV. [Staehli[9]]

subject to an arbitrary exciton generation rate.[9] Figure 7 shows the computed solutions for the up-going drop concentration N_+ and number of pairs per drop ν_+ at 10 sec following excitation switch-on to the value shown on the abscissa. It turns out that the solutions depend markedly on the rate of turn-on of the excitation; the calculations shown are for a step with an exponential time constant 0.1 sec. Figure 7 also shows N_- and ν_- at 10 sec following a step down from a high generation rate of 10^{20} excitons cm^{-3} sec^{-1} to the values on the abscissa. Noteworthy is the prediction that for up-going excitation the drop size remains nearly constant while the drop concentration increases. For down-going excitation the drop concentration remains nearly constant while the drop size decreases until threshold is approached. The predicted total EHD up-going luminescence intensity $I^+_{709} \propto N_+\nu_+$ and down-going intensity $I^-_{709} \propto N_-\nu_-$ calculated from Fig. 7 are in reasonable agreement with our data.

III. COMPARISON OF THEORY AND EXPERIMENT

To extract the value of the surface tension σ from the hysteresis data, the drop luminescence intensity *versus* generation rate has been computed from the theory; representative results for up-going and down-going excitation are shown in Fig. 8. The indicated thresholds G_+ and G_- are linear continuations of the curves to the axis; they are well-defined theoretically and correspond exactly to the measured thresholds P_+ and P_- shown in Fig. 3. Because the threshold ratio G_+/G_- is a monotonic function of the surface tension, linearly extrapolated threshold ratios P_+/P_- from data such as that in Figs. 1 and 3 can be fit to the theory with only σ as an adjustable parameter. The only other important parameters are the temperature and the pair density in the drop n_o, both well known. Since no measurement of σ could be considered reliable unless a large number of different crystal samples were investigated, we have taken threshold data on seven

crystals in the temperature range $1.3 < T < 2.1$ K. We have shown that dislocation densities in the range 0 to 10^4 cm^{-2} have no discernible effect on P_+/P_-. This ratio was found to decrease somewhat at 2.1 K as the net impurity concentration varied from 3×10^9 to 4×10^{12}. Since *a priori* we do not know whether nucleation is homogeneous or inhomogeneous, we reduced all the data for both cases. Assuming homogeneous nucleation, we find $\sigma = (2.4 \pm 0.2) \times 10^{-4}$ erg cm^{-2} at the mean temperature T = 2 K. Assuming inhomogeneous nucleation we find values $\sigma = (2.4 \pm 0.2) \times 10^{-4}$ erg cm^{-2} and $(2.8 \pm 0.3) \times 10^{-4}$ erg cm^{-2} assuming representative values[10] of 4.3 meV and 8.6 meV for the barrier lowering due to neutral impurities. Thus we can conclude that the surface tension at 2 K lies in the range

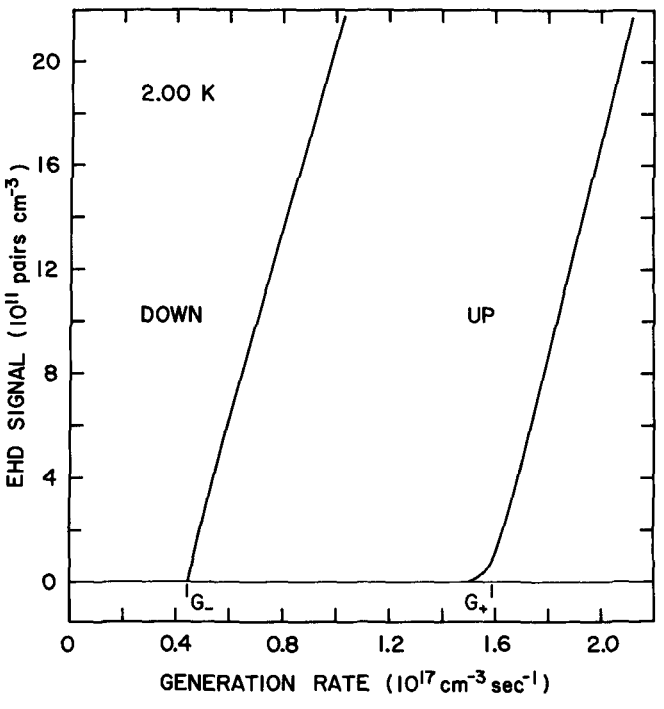

Fig.8. Predicted up-going and down-going drop luminescence intensity for pure Ge versus e-h pair generation rate. The scales have been chosen to correspond approximately to those of Fig. 1. This computation assumes $\sigma = 2.4 \times 10^{-4}$ erg cm^{-2} and $\phi = 2.03$ meV. [Westervelt[4]]

$$\sigma = (2.4 \text{ to } 2.8) \times 10^{-4} \text{ erg cm}^{-2} \qquad (4)$$

regardless of the role of impurities in our samples. The surface tension at T = 0, denoted as the surface energy w, is found using the approximate expression $w \simeq \sigma \left[1 - (T/T_c)^2\right]^{-1}$ to be

$$w = (2.7 \text{ to } 3.1) \times 10^{-4} \text{ erg cm}^{-2} , \qquad (5)$$

which agrees well with the recent theoretical prediction of Vashishta *et al.*,[11] who, by including the exchange correlation gradient correction, find $w \simeq 3.5 \times 10^{-4}$ erg cm^{-2}. Earlier theoretical estimates yielded $w \simeq 10^{-4}$ erg cm^{-2}.[12] To our knowledge our value, eq. 5, is the first and only accurate measurement of the surface energy.[13]

The detailed theory[4] also predicts the slow time behavior of the EHD luminescence under the experimental conditions described above for Fig. 2. Under up-going excitation the prediction is that, near threshold, $I^+_{709} = I^+_o + I^+_1 \ln(Dt)$ where D depends only on fundamental drop parameters and the excitation level. Similarly $I^-_{709} = I^-_o - I^-_1 \ln(Et)$. The data of Fig. 2 fit these forms very well, as shown in Fig. 9, in the range $100 < t < 4000$ sec. If extrapolated, the curves will cross at $t = 8 \times 10^6$ sec, which represents a lower limit to the time it takes to reach the equilibrium state, $J_+ = J_-$. The fact that the drop signals obey these expressions for a time exceeding 1 hour suggests that the droplets in our samples, once formed, are not subject to significant external destruction mechanisms. It is likely that the droplets nucleate or become trapped on impurities and remain virtually fixed in the crystal, the decaying pairs being replenished by exciton condensation. Momentum transferred from an exciton density gradient is far too small to dislodge the drops.

The theory also predicts the up-going threshold curve, Fig. 10(a), and the down-going threshold, Fig. 10(b), including the effects of hysteresis and surface tension.[4] The coexistence curve for the ideal exciton gas, eq. 1, is also shown, Fig. 10(c). The data, Fig. 4, show the predicted behavior, in particular that the hysteresis vanishes at

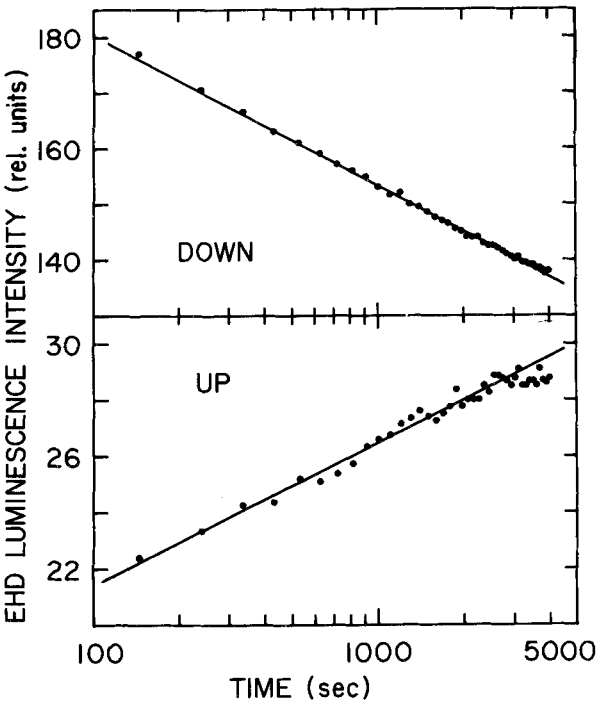

Fig.9. Semilogarithmic replot of the data of Fig. 2; the solid lines are I^{-}_{709} = 235 - 11.9 $\times \log_e t(\text{sec})$ and I^{+}_{709} = 11.2 + 2.22 $\log_e t$ (sec). These forms are expected theoretically [Westervelt[4]]. The lines would cross at t = 8 $\times 10^6$ sec.

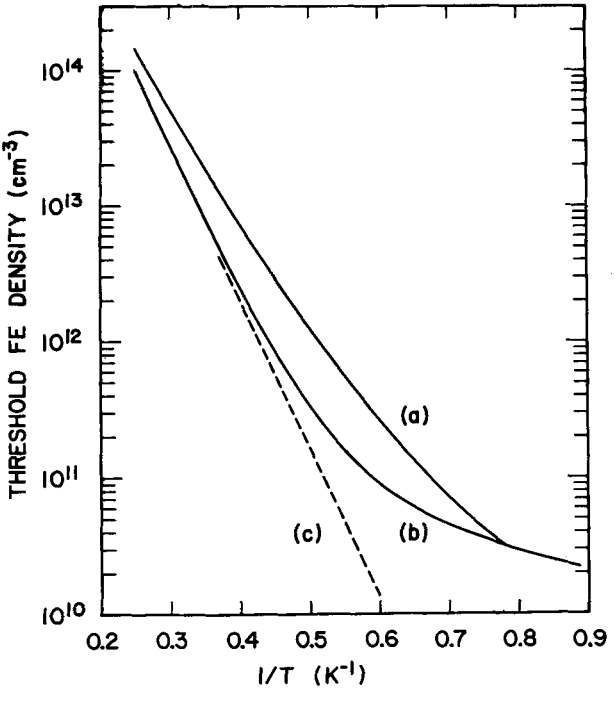

Fig.10. Threshold curves for (a) up-going excitation, and (b) down-going excitation for EHD in pure Ge, from homogeneous non-equilibrium nucleation theory [Westervelt[4]]. Curve (c) is the saturated density of an ideal exciton gas, eq. (1). Values assumed are $\sigma = 2.7 \times 10^{-4}\ [1 - (T/6.5)^2]$ erg cm^{-2} and $\phi = (1.97 + 0.016\ T^2)$ meV. The predicted vanishing of the hysteresis at $T \gtrsim 1.3$ K is observed, Fig. 4.

$T \simeq 1.25$ K; the homogeneous nucleation theory predicts this at $T \simeq 1.3$ K, and the inhomogeneous theory at $T \simeq 1.4$ K. What has happened physically below 1.3 K is that the barrier ϕ_c to nucleation has lowered sufficiently that J_+ and J_- are simultaneously large, and the system rapidly reaches thermal equilibrium.

Previous threshold measurements of the condensation energy, typically $\phi \simeq 1.5$ meV, were made by fitting data apparently taken on the up-going curve, Fig. 10(a), to the saturated exciton density, eq. 1. The apparent value deduced in this way from Fig. 10(a) between 2 K and 4 K is $\phi \simeq 1.3$ meV. As pointed out earlier,[3] this seems to explain the apparent discrepancy between threshold and spectroscopic measurements of ϕ. Furthermore, from the absolute value of threshold measurements at 2 K, Fig. 1, calibrated in FE density, we find $\phi = 2.1 \pm 0.2$ meV in good agreement with the spectroscopic value at 2 K, $\phi = 2.03$ meV.[1] (The error in ϕ quoted above corresponds to an uncertainty of a factor ~3 in FE

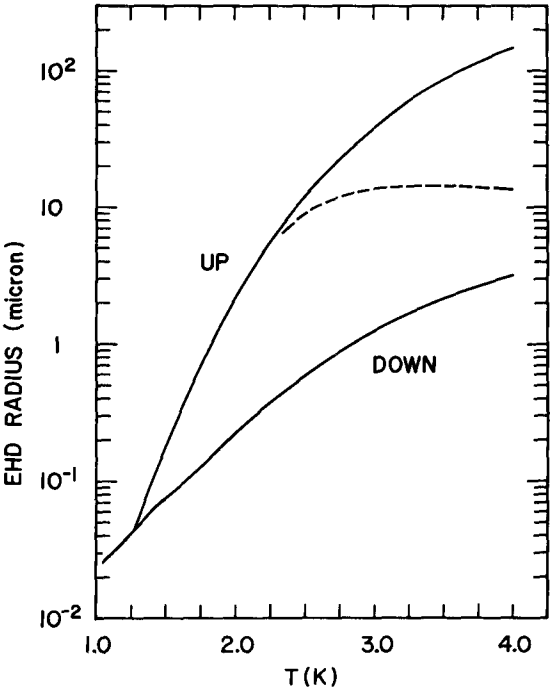

Fig.11. Predicted EHD radius near up-going and down-going thresholds versus temperature in pure Ge from homogeneous non-equilibrium nucleation theory [Westervelt[4]], with the parameters of Fig. 10. The dashed curve shows the reduced up-going radius predicted when local diffusive exciton depletion is also take into account.

density).

The stable drop radius R_s near threshold can be predicted from the theory for both up- and down-going excitation, and these results are shown in Fig. 11 as a function of the temperature. This plot explicitly illustrates the point discussed earlier, that the down-going radius is much smaller than the up-going radius, except below T $\simeq$ 1.3 K, where they are equal. The predicted large radii, R ~ 100 μm, near the up-going threshold at higher temperatures have never been observed. It is possible to add to the theoretical model the effects of local diffusive exciton density depletion, shown as the dashed line, to account for the reported drop radii R ~ 10 μm from light scattering experiments.[14)]

In summary, careful measurements on ultra-pure Ge crystals reveal a number of intrinsic nucleation phenomena of EHD arising from the surface energy of drops and their finite pair lifetime. Above T ~ 1.3 K the system is always in a long-lived metastable state which depends on the history of optical excitation; equilibrium nucleation theory is invalid. An adequate theory has been developed that quantitatively explains the observed phenomena and yields an accurate measurement of the surface energy, eq. 5. We acknowledge valuable discussions with C. Kittel, and thank W. L. Hansen for providing Ge crystals.

REFERENCES

1) For a review of electron-hole drops see Ya Pokrovskii: Phys. Stat. solidi (a) 11 (1972) 385; for a recent review see C. D. Jeffries: Science 189 (1975) 955.

2) T. K. Lo, B. J. Feldman and C. D. Jeffries: Phys. Rev. Letters 31 (1973) 224.

3) Some results of this paper have been briefly published by R. M. Westervelt, J. L. Staehli and E. E. Haller: Bull. Am. Phys. Soc. 20 (1975) 471; J. L. Staehli, R. M. Westervelt and E. E. Haller:

Bull. Am. Phys. Soc. 20 (1975) 471.

4) A detailed nucleation theory is given by R. M. Westervelt: Part I, Phys. Stat. sol. (b) 74 (1976) 727; and Part II, Phys. Stat. sol. (b), in press.

5) For a clear review of homogeneous nucleation theory see J. E. McDonald: Am. J. Phys. 30 (1962) 870; also see J. Frenkel: *Kinetic Theory of Liquids* (Oxford Press, Oxford, 1946).

6) See, *e.g.* C. Kittel: *Thermal Physics* (John Wiley, New York, 1969) p.163. For Ge we use the effective mass $m^* = 0.335\ m_o$ and degeneracy $\gamma = 16$, from ref. 2. At temperatures above ~3 K, corrections to eq. 1 become significant, A. Frova, G. A. Thomas, R. E. Miller and E. O. Kane: Phys. Rev. Letters 34 (1975) 1572.

7) An equilibrium treatment of the effects of surface tension has been given by R. N. Silver: Phys. Rev. B11 (1975) 1569.

8) R. Becker and W. Döring: Ann. Physik 24 (1935) 719; R. Becker: *Theory of Heat* (Springer-Verlag, New York, 1967), 2nd Edition, p.239.

9) J. L. Staehli: Phys. Stat. sol. (b) 75, issue 2 (June 1, 1976).

10) R. W. Martin: Solid State Comm. 14 (1974) 369.

11) P. Vashishta: Private communication; P. Vashishta, R. Kalia and K. S. Singwi: *Proc. of the Oji Seminar.*

12) L. M. Sander, H. B. Shore and L. J. Sham: Phys. Rev. Letters 31 (1973) 533; H. Büttner and E. Gerlach: J. Phys. C6 (1973) L433; T. M. Rice: Phys. Rev. B9 (1974) 1540; T. L. Reinecke and S. C. Ying: Solid State Comm. 14 (1974) 381.

13) The value $\sigma = 1.6 \times 10^{-4}$ erg cm^{-2} is estimated by V. S. Bagaev, N. N. Sibeldin, and V. A. Tsvetkov: J.E.T.P. Letters 21 (1975) 80, by measuring the temperature dependence of the concentration of drops by light scattering. However, this paper uses an inaccurate equation (their eq. (2)) and classical nucleation theory. The paper of B. Etienne, C. Benoit à la Guillaume and M. Voos: Phys.

Rev. Letters 35 (1975) 536 uses equilibrium theory to estimate an empirical value of (A/σ), where A is the Richardson-Dushman constant, not known for EHD.

14) A. S. Alekseev, T. A. Astemirov, V. S. Bagaev, T. I. Galkina, N. A. Penin, N. N. Sybeldin, V. A. Tsvetkov: *Proc. of 12th Intern. Conf. on Physics of Semiconductors, Stuttgart* (Teubner, Stuttgart, 1974) p.91.