uc-34

LBL-6619

c.1

NUCLEATION PHENOMENA IN THE FORMATION OF
ELECTRON-HOLE DROPS IN Ge

Robert Moore Westervelt
(Ph. D. thesis)

September 1977

RECEIVED
LAWRENCE
BERKELEY LABORATORY

DEC 1 1977

LIBRARY AND
DOCUMENTS SECTION

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

For Reference

Not to be taken from this room

LBL-6619

c.1

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

NUCLEATION PHENOMENA IN THE
FORMATION OF ELECTRON-HOLE DROPS

Table of Contents

1	INTRODUCTION	1
11	Properties of the FE-EHD System	5
12	Classical Nucleation Theory	11
13	Application of Nucleation Theory to EHD	17
2	NUCLEATION THEORY FOR ELECTRON-HOLE DROPS	21
21	Rate Equations	21
22	Size Distribution in Dynamic Equilibrium	24
23	Free Energy Difference	29
24	Calculation of Nucleation Rates	32
25	Inhomogeneous Nucleation	37
3	APPLICATION OF NUCLEATION THEORY TO OBSERVABLE PHENOMENA	41
31	Conservation Equation	43
32	Metastable Time Development	46
33	Hysteresis and Thresholds	50
34	Determination of the Surface Tension	53
35	Modified Phase Diagram	55
36	Drop Radius	59
4	EXPERIMENTAL APPARATUS	63
41	Optical Excitation	64
42	Germanium Samples	77
43	Signal Detection Apparatus	84

5	EXPERIMENTAL RESULTS AND ANALYSIS	90
51	Hysteresis Curves	91
52	Metastable Time Development	104
53	Effect of Impurities and Dislocations on Nucleation; Surface Tension Measurement	111
54	Free-Exciton-Electron-Hole Drop Phase Diagram	119
6	CONCLUSIONS	139
	ACKNOWLEDGEMENTS	143
	REFERENCES	144
	TABLES	158
	FIGURE CAPTIONS	163
	FIGURES	176

NUCLEATION PHENOMENA
IN THE FORMATION OF ELECTRON-HOLE DROPS IN Ge

Robert Moore Westervelt

Materials and Molecular Research Division, Lawrence Berkeley Laboratory
and Department of Physics, University of California
Berkeley, California 94720

ABSTRACT

A detailed theory of the nucleation of electron-hole drops (EHD) from a gas of free excitons (FE) in Ge is presented, together with a systematic experimental study of hysteresis and threshold phenomena in the luminescence of optically excited crystals of ultrapure Ge. The non-equilibrium rates of EHD formation and breakup and the concentration of EHD in dynamic equilibrium with the FE gas are calculated including the effects of the EHD surface energy w and the EHD lifetime τ_0 . Large metastable and non-equilibrium effects are found. These results are used to quantitatively predict for Ge under continuous excitation 1) the EHD concentration and size vs. excitation level and history of excitation, 2) the metastable time development of the EHD concentration, 3) mathematically well-defined FE density thresholds n_+ and n_- for the formation and destruction of EHD and thus the FE-EHD phase diagram including the effects of metastability and the EHD lifetime, 4) a procedure to accurately determine the EHD surface energy w from threshold data, and 5) limits to the steady-state EHD radius vs. temperature. Results for the calculated FE-EHD phase diagram for Si are also presented. Each calculation is made for two separate

assumptions: homogeneous nucleation, and inhomogeneous nucleation of EHD on neutral impurity atoms. An experimental apparatus specially constructed to measure hysteresis and threshold phenomena in the luminescence of EHD and FE in Ge is described, including 1) a feedback-stabilized source of optical volume excitation for Ge, which can be accurately and reproducibly cycled, and 2) a sensitive automated luminescence detection and signal averaging system. Experimental data obtained from ultrapure Ge are presented for 1) hysteresis curves for the EHD and FE luminescence intensity obtained by cycling the excitation at various temperatures between 1.2K and 2.1K, including a procedure to accurately extrapolate the excitation thresholds 2) various experimental tests of the validity of EHD nucleation theory 3) the metastable time development of the EHD signal for very long times $\sim 4 \times 10^3$ sec at temperatures between 1.25K and 1.8K, 4) the effect of dislocations and shallow electrically active impurities on the excitation thresholds, and 5) a carefully calibrated phase diagram for the measured FE density thresholds n_+ and n_- vs. T between 1.2K and 2.0K. Excellent agreement between these data and nucleation theory is found. The principal experimental results and conclusions are 1) an estimate $\rho \sim 4.4$ for the EHD radiative enhancement factor, the ratio of the electron density at the position of a hole to the mean density, 2) logarithmic variation of the EHD signal with time and direct evidence that luminescence hysteresis can exist for times as long as 6×10^4 sec, suggesting that EHD can be practically immobile under suitable circumstances, 3) the ineffectiveness of dislocations

as nucleation centers for EHD in Ge and evidence for inhomogeneous nucleation on impurity atoms, 4) the first correct measurement

$\phi_0 = 1.9 \pm 0.2$ meV of the EHD condensation energy from threshold data, resolving the previous discrepancy with spectroscopic measurements,

and 5) an accurate measurement of the EHD surface energy,

$$w = (2.6 \pm 0.3) \times 10^{-4} \text{ erg cm}^{-2}.$$

CHAPTER 1. INTRODUCTION

Normally a crystal of Ge held at liquid helium temperatures is practically devoid of free carriers. However, when the crystal is excited by light, electrons and holes are created: the holes relax to the top of the valence band at the (0,0,0) point in the Brillouin zone, and the electrons rapidly ($\lesssim 1$ nsec) relax to the indirect minimum in the conduction band at the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ point as shown in Fig. 1.1. The coulomb attraction of these carriers leads to the formation of a mobile bound state of an electron and a hole known as the Mott-Wannier free exciton (FE), analogous to a positronium atom. For low FE densities n , the free excitons are well separated, do not interact appreciably, and behave somewhat like an ideal gas. However, when a certain threshold value of n is exceeded (analogous to a saturated vapor pressure), drops of metallic electron-hole liquid (EHL) form. The existence of this novel state of matter was first suggested by Keldysh in 1968.^{1.1} Since that time, the properties of electron-hole drops (EHD) have been extensively studied, both experimentally and theoretically. This work has been the subject of a number of review articles,^{1.2-1.7} notably those by Hensel et al.,^{1.6} and by Rice.^{1.7}

The simplest and most direct method of experimentally investigating the properties of electron-hole drops in Ge is to study the recombination luminescence emitted by EHD and FE. Using the sensitive apparatus described in chapter 4 we obtained the luminescence spectrum shown in

Fig. 1.2 from highly excited ultra-pure Ge at 2.00K. The signal-to-noise ratio of the largest peak in Fig. 1.2 is larger than 10^5 . Because the bandgap in Ge is indirect, radiative recombination at low temperatures must involve the emission of a phonon at the Brillouin zone edge to conserve crystal momentum. The principal features in Fig. 1.2 are three replicas of the EHD luminescence line at 729 meV, 709 meV, and 701 meV due to the emission of TA, LA and TO phonons as indicated. The LA phonon replica is used throughout this thesis both because it is the strongest, and because it is allowed by group theory.^{1.8} As indicated in Fig. 1.2, the LA phonon replica of the FE luminescence is also visible in the spectrum. Additional unresolved structure thought to be due to the emission of two phonons^{1.9} is also present in Fig. 1.2 for photon energies between 710 and 730 meV and energies less than 700 meV. At lower energies the spectrum in Fig. 1.2 must be corrected for the response of the Ge photodetector used for the measurement (see Fig. 4.7).

The luminescence spectrum near 710 meV obtained from the same Ge sample at 2.10K for a much lower level of optical excitation is shown in Fig. 1.3. At this excitation level the EHD signal is entirely absent, and the only features visible in the spectrum are the LA and TO phonon replicas of the FE luminescence as indicated. When the excitation level is increased by a factor of 2.2, the broad luminescence line near 709 meV characteristic of EHD abruptly appears, as shown in Fig. 1.4. Thus there exists an excitation threshold for the creation of EHD.

The line shapes and positions of the FE and EHD signals contain a good deal of information about the system. As indicated in Fig. 1.4, the lower energy edge of the FE line corresponds to the ground state energy $-E_x$ in Fig. 1.1, where E_x is the FE binding energy. The intrinsic FE linewidth, unresolved in Fig. 1.4, is due to the thermal motion of excitons and is roughly proportional to the temperature. At temperatures below $\sim 3K$, the split-off FE ground state, which lies ≈ 1 meV above the lowest ground state, is not appreciably populated and does not contribute to the lineshape (see section 11). For EHD the ground state energy $-(\phi_e + \phi_h)$ in Fig. 1.1 corresponds to the upper energy edge of the line; thus luminescence spectra can be used to measure the condensation energy $\phi = (\phi_e + \phi_h) - E_x$ of an e-h pair relative to the FE ground state as indicated in Fig. 1.4. The linewidth for EHD is equal to the sum of the electron and hole Fermi energies $E_F = E_F^e + E_F^h$ as indicated in Fig. 1.4, and can be used to determine the EHL liquid density. The spectral characteristic most important to the work presented in this thesis is that the lineshapes and positions for both FE and EHD are practically independent of the excitation level, and vary only slowly with temperature below $T \sim 4K$. Therefore the signals obtained with broad spectrometer slits (≈ 2 meV resolution) centered about 709 meV and 714 meV are accurately proportional to the average concentrations of e-h pairs in the sample condensed as EHD and FE respectively, and can be used to study the variation of these concentrations with excitation level and temperature.

While performing such an experiment in 1973, Lo, Feldman and Jeffries discovered that the EHD signals obtained by increasing and by decreasing the excitation to the same level were different, and that these signals displayed separate excitation thresholds.^{1.10,1.11} They immediately realized that this hysteresis was clear evidence for gas-liquid supersaturation effects such as those observed in cloud chambers, for example, but did not make a detailed comparison of their data with theory. A careful study of such phenomena can yield a great deal of information about the EHD-FE system. Supersaturation caused by the finite surface tension σ of ordinary liquids is known to have a profound effect on the apparent gas-liquid phase diagram, particularly at low temperatures, and theoretical analysis of threshold data yields measurements of σ and the condensation energy ϕ . The e-h liquid, unlike ordinary liquids, is characterized by a finite lifetime which adds interesting and novel complexity to the system.

The work contained in this thesis constitutes a systematic experimental and theoretical study of supersaturation effects for the EHD-FE system in ultrapure Ge. We find excellent quantitative agreement between hysteresis and threshold data and nucleation theory, presented in chapters 2 and 3, which includes the effects of the finite EHL lifetime, and we are able to deduce accurate values for several important parameters, notably the surface tension σ and the condensation energy ϕ .

11 Properties of the FE-EHD System

The simplest electronic complex present in excited crystals of Ge at low temperatures is the free exciton. Each exciton consists of an e-h pair bound by the Coulomb interaction. If the electron and hole bands were spherically symmetric, the binding energy E_x of the ground state would be given by the simple hydrogenic expression

$$E_x = \mu e^4 / 2\kappa^2 h^2$$

where μ is the reduced mass, and κ is the dielectric constant. The exciton mass would be the sum of the electron and hole masses and the degeneracy for Ge would be 32, the product of the electron and hole degeneracies. Unfortunately, both the electron and hole bands in Ge are highly anisotropic. This anisotropy greatly complicates the theory, and leads to the creation of two types of excitons with different symmetry. Thus the ground state is split into two levels, separated by ≈ 1 meV, each with a degeneracy of 16.

The most careful theoretical treatment of free excitons in Ge to date is that by Altarelli and Lipari.^{1.12} They find values of the ground state energy $E_x = 4.18$ meV for the lower exciton and $E_x - \Delta = 3.17$ meV for the upper exciton, where $\Delta = 1.01$ meV

is the ground state splitting. This calculation compares very well with the recent experimental values $E_x = 4.15$ meV from far-IR photo-conductivity^{1.13} and $\Delta = 1.01 \pm 0.03$ meV from absorption spectra.^{1.14} Altarelli and Lipari also calculate the energy dispersion relation for the motion of entire free excitons and find that the variation of exciton energy with wavevector is strongly non-parabolic,^{1.12} as originally suggested by Kane.^{1.15} Their calculated FE density of states is in excellent agreement with the measurements of Frova et al.^{1.14} and yields values of the FE density-of-states effective masses near the energy minima of $m^* = 0.436 m_0$ for the lower exciton and $m^* = 0.555 m_0$ for the upper one. These parameters are of importance in the analysis of threshold data presented in chapter 5.

Excitons at high density in Ge can conceivably condense in a number of ways other than the formation of electron-hole drops. The most important of these is probably the formation of multi-exciton (ME) complexes (excitonic molecules); the density threshold for Bose condensation lies above that for the formation of EHD. Each ME complex consists of two or more excitons bound together by Coulomb forces; for example, a biexciton is analogous to a H_2 molecule. Because the degeneracy of the bands is so large, the formation of complexes of more than two excitons should be possible before the exclusion principle becomes active, unlike the case for H. The stability of ME complexes, either free or bound to centers, is an important assumption in EHD nucleation theory, as discussed in chapter 2.

The first evidence for ME complexes was the observation of a series of sharp luminescence lines at lower energies than the FE line in lightly doped Si^{1.16,1.17,1.18} and Ge,^{1.19} which were attributed to ME complexes bound to impurity atoms. Subsequently this interpretation has been placed in doubt by the stress and Zeeman splitting measurements of Sauer^{1.20} and recently resurrected theoretically by Morgan^{1.21} and by Kirczenow et al.^{1.22} At this time the question of the existence of bound ME complexes is unresolved. However, Thomas et al.^{1.23} have very recently reported experimental evidence for free biexcitons in ultrapure Ge with the binding energy ~ 0.2 meV relative to two FE.

The various properties of electron-hole drops in Ge have been extensively studied for nine years. Rather than attempt to summarize all of this work here, we shall describe only the intrinsic characteristics of EHD in unstressed ultrapure Ge, free of externally applied magnetic or electric fields.

The EHL in Ge is a highly-degenerate ($E_F^e, E_F^h \gg kT$) Fermi liquid composed of both electrons and holes, which can move freely through the crystal lattice. Because the pressure exerted on the liquid by the FE gas at temperatures below $\sim 3K$ is negligible, the density n_0 of e-h pairs in the liquid at a given temperature is a constant characteristic of the EHL. At $T=0$, the liquid density is determined by minimizing the energy $-E_g$ per e-h pair with respect to n_0 , where E_g is the binding energy relative to free carriers.

Applying the usual argument (see Ref. 1.7, for example) that the recombination of an electron and hole, each at the Fermi level, takes an e-h drop from ground state to ground state (i.e., the EHD is not left in an excited state), we find that both the energy $-E_g$ and the chemical potential are given by the sum of the electron and hole work functions, i.e., $\mu = -E_g = -(\phi_e + \phi_h)$ at $T=0$ as shown in Fig. 1.1. The condensation energy ϕ (FE work function) is defined as the difference between the chemical potential of the liquid and the lower FE ground state and is given by $\phi = \phi_e + \phi_h - E_x$. Thus the binding energy E_g is measured from the high energy edge of the EHL luminescence line. This situation is in contrast to that in simple metals, where the electron gas is confined under pressure, and the energies $-E_g$ and μ differ by $(2/5) E_F$, where E_F is the Fermi energy. At finite temperatures, small T^2 corrections to μ and E_g can be calculated in a straightforward manner using Fermi gas theory.^{1.7}

Thus the electrons and holes in a Ge crystal excited above threshold separate into two phases, the FE gas and the constant density e-h liquid. Because the EHL possesses a finite surface tension σ , the liquid forms drops, presumed to be spherical, similar to those found in rainclouds, for example. However, unlike ordinary liquids the EHL has a finite lifetime τ_o , so that the drop radius R is limited by the rate of collection of FE at the surface.^{1.2} Measured values of R are typically several μm at 2K.^{1.6} Thus we can picture the FE-EHD system in Ge under relatively low excitation as a fog of tiny spherical EHD surrounded by FE "vapor". Under much higher

excitation other regimes analogous to the spray from a nozzle are possible,^{1.6} but will not be considered here.

Reliable values for most of the parameters of the EHL have been determined by careful analysis of luminescence spectra; we shall discuss only the most recent work. Thomas et al.^{1.24} find for the condensation energy

$$\phi = (1.8 \pm 0.2) + (2.2 \pm 0.9)(kT)^2, \quad (1.1)$$

where ϕ and kT are in meV, and for the liquid density

$$n_o = (2.38 \pm 0.05)[1 - (0.94 \pm 0.10)(kT)^2] \quad (1.2)$$

where kT is in meV and n_o is in units of 10^{17} cm^{-3} . These values agree with the earlier measurements of Lo.^{1.25} Using the value^{1.13}

$E_x = 4.15 \text{ meV}$ for the FE binding energy Eq. (1.1) yields

$E_g = 5.95 \pm 0.2 \text{ meV}$ for the e-h pair binding energy, which agrees

very well with the most recent theoretical value^{1.26} $E_g = 5.9 \text{ meV}$.

The density n_o from Eq. (1.2) also agrees with the calculated value^{1.26}

$n_o(T=0) = 2.2 \times 10^{17} \text{ cm}^{-3}$. Equations (1.1) and (1.2) are only valid

well away from the critical point of the EHL, given by the measured

values^{1.27} $n_c = (0.8 \pm 0.2) \times 10^{17} \text{ cm}^{-3}$ for the critical density and

$T_c = (6.5 \pm 0.1) \text{ K}$ for the critical temperature. The EHL lifetime is

apparently an intrinsic property of the liquid and is found to be^{1.3, 1.28}

$\tau_o \approx 40 \text{ } \mu\text{sec}$ from luminescence decay data in ultrapure Ge. One

fundamental parameter of the EHL which had not been reliably measured

before the work reported in this thesis is the EHL surface tension σ .

In chapter 5 we present an accurate measurement $\sigma = (2.6 \pm 0.3) \times 10^{-4}$ erg cm⁻² from threshold data. Preliminary accounts of this measurement were given in Refs. 1.29 and 1.30. The calculation of σ for EHD is an important test of the surface theory of metals; the most careful theoretical treatments to date are those of Rose et al.^{1.31} and of Vashishta et al.^{1.32} who find respectively at T=0, $\sigma = (2.4 \pm 0.5) \times 10^{-4}$ erg cm⁻² and $\sigma = (3.5 \text{ to } 4) \times 10^{-4}$ erg cm⁻².

A second and equally important way to study the e-h liquid is to investigate the FE-EHD phase diagram obtained from measurements of the thresholds for drop formation vs. temperature. If one assumes that EHD and FE behave like simple classical fluids, the threshold for drop formation is determined by the saturated vapor density:

$$n_s = D_x \exp(-\phi/kT) \quad (1.3)$$

where $D_x = \gamma_x (m^* kT / 2\pi \hbar^2)^{3/2}$ is the effective density of states with γ_x the FE degeneracy. Equation (1.3) is obtained by simply setting the chemical potential of an ideal FE gas equal to that for the liquid.^{1.33} Using expressions similar to Eq. (1.3) to analyze onset threshold data between 2K and 4K, several authors^{1.2,1.10,1.34,1.35} have obtained measurements of the condensation energy, typically $\phi \approx 1.5$ meV, which disagree with the more reliable spectroscopic value. Furthermore, the thresholds measured below 2K increasingly deviate from Eq. (1.3) as T is decreased and appear to approach a temperature independent value. Neither of these effects was understood at the time of these experiments; the discrepancy between spectroscopic and threshold

measurements of ϕ in particular was the subject of much speculation. The first proper explanation of this discrepancy as an effect of EHD nucleation was given by Westervelt, Staehli, and Haller.^{1.36}

At the same time, in 1973, Lo et al.^{1.10} discovered the existence of hysteresis and metastable behavior in the luminescence of EHD in Ge. As discussed previously, they found that the EHD luminescence signal at a given excitation depended on the history of excitation of the sample, and that the apparent time for the system to reach equilibrium was very long (≥ 300 sec). Furthermore, their observation that the thresholds for the formation and breakup of EHD differed by a factor of 2 to 3 indicated that the analysis of onset threshold data in terms of Eq. (1.3) was questionable. These observations motivated the experimental and theoretical analysis of supersaturation effects of the FE-EHD system presented in this thesis. We start with a discussion of classical nucleation theory for ordinary liquids such as water in the following section.

12 Classical Nucleation Theory

The theory of the nucleation of drops of ordinary liquids has been developed over the past 60 years. Classic treatments of nucleation theory have been given by Volmer,^{1.37} by Becker and Doring^{1.38} and by Zeldovich.^{1.39} The subject has also been reviewed by McDonald^{1.40} and by Abraham^{1.41} among others.

The basic physical process which causes metastability and supersaturation effects in the gas to liquid phase transition is the

nucleation and growth of small embryonic liquid drops from the vapor. A macroscopic body of liquid is in equilibrium with its vapor at the saturated vapor density determined by equating the chemical potentials of the liquid and vapor, given by Eq. (1.3). However, such a body of liquid can only form by the growth of small clusters of vapor molecules. This growth is inhibited by the contribution to the total energy of a small drop due to the liquid surface tension σ . In order to maintain a drop of radius R in equilibrium with the vapor, the chemical potential of the vapor must be increased above the saturated value by the amount $\Delta\mu$ determined by equating the Gibbs free energies per particle of the drop and the vapor.

$$\Delta\mu = \Delta p/n_o = 2\sigma/n_o R \quad (1.4)$$

where $\Delta p = 2\sigma/R$ is the additional pressure inside the drop due to the surface tension, and n_o is the liquid density. Equation (1.4) implies that for a given supersaturated value of $\Delta\mu$, drops of a certain critical radius

$$R_c = 2\sigma/n_o \Delta\mu \quad (1.5)$$

will be in unstable equilibrium with the vapor. Drops of radius smaller than R_c tend to shrink and disappear, whereas drops larger than R_c tend to grow. Drops of radius $R > R_c$ can in principle grow to infinite radius; in practice either a macroscopic body of liquid is formed, or the final drop radius is limited by external mechanisms. Statistical fluctuations in the system lead to the formation of a finite number of

embryonic drops of radius R_c . The fundamental problem of nucleation theory is the calculation of the concentration of embryos at the critical radius and thus the rate of formation of macroscopic drops.

We shall describe here a simple thermodynamic approach to this problem which contains most of the physical principles involved in more detailed calculations. We assume an ideal system free of contamination or external surfaces. The total difference in Helmholtz free energy between a drop of radius R and an equivalent number of vapor molecules is

$$\Delta f = 4\pi R^2 \sigma - (4\pi/3) R^3 n_o \Delta \mu \quad (1.6)$$

For an ideal gas $\Delta \mu = kT \ln(n/n_s)$ where n is the vapor density and n_s is the saturated density from Eq. (1.3). This free energy difference is plotted for water at 300K for several values of the supersaturation ratio n/n_s in Fig. 1.5. As indicated in Fig. 1.5, the quantity Δf has a maximum Δf_c at the critical radius R_c given by Eq. (1.5). As the supersaturation ratio n/n_s increases, both Δf_c and R_c decrease. Drops smaller or larger than the critical radius R_c respectively tend to shrink or grow in order to minimize the free energy of the system. Thus one can make an analogy between changes in drop radius subject to the potential Δf and the motion of particles in a potential well.

The concentration $h(R)$ of drops of radius R is given in thermodynamic equilibrium by

$$h(R) = D \exp(-\Delta f/kT) \quad (1.7)$$

where D is an effective density of states for drops (because R is quantized by the number of molecules in a drop, we need not use distributions for D and h). Obviously Eq. (1.7) cannot hold for arbitrarily large radii, because Δf decreases monotonically for $R > R_c$. However, inspection of Fig. 1.5 indicates that the free energy Δf_c required to form a drop of critical size is very much greater than kT for small supersaturation ratios. Thus the population of drops at R_c from Eq. (1.7) is insignificant, and the collection of drops of radius $R < R_c$ is thermodynamically isolated from those of larger radii. Therefore the system is in a metastable state in which thermodynamic equilibrium holds for $R < R_c$ but not for $R > R_c$. As the supersaturation ratio n/n_s increases from one, the concentration of embryos of less than critical size increases until the rate at which embryos grow past the potential barrier Δf_c at R_c eventually becomes appreciable.

With these assumptions, the estimation of the formation rate J of macroscopic drops is straightforward. The rate J is simply given by the product of $h(R_c)$, the equilibrium concentration of embryos at R_c , and $(\pi R_c^2) n \bar{v}$, the collision rate of vapor molecules with a drop of critical size, where $\bar{v}$ is the mean speed. Thus

$$J = \pi R_c^2 n \bar{v} D \exp\left(-\frac{16\pi\sigma^3}{3(n_0 \Delta\mu)^2 kT}\right) \quad (1.8)$$

where the argument of the exponential is equal to $\Delta f_c/kT$. The most striking feature of Eq. (1.8) is that the formation rate J is an

extremely sensitive function of the supersaturation ratio n/n_s . Assuming $D \sim n$, we can calculate J from Eq. (1.8) for water at 300K as shown in Fig. 1.5. The results are $J=0$ for $n/n_s = 1$, Fig. 1.5a; $J = 5 \times 10^{-41} \text{ cm}^{-3} \text{ sec}^{-1}$ for $n/n_s = 2$, Fig. 1.5b; $J = 5 \times 10^{13} \text{ cm}^{-3} \text{ sec}^{-1}$ for $n/n_s = 5$, Fig. 1.5c; and $J = 8 \times 10^{19} \text{ cm}^{-3} \text{ sec}^{-1}$ for $n/n_s = 10$, Fig. 1.5d; note that J increases by sixty orders of magnitude as n/n_s increases from 2 to 10. The variation of the drop formation rate with n is so rapid that one can speak of a threshold vapor density n_t at which J suddenly "turns on". For water vapor at 300K, the threshold supersaturation ratio is $n_t/n_s \sim 5$. Thus measurements of the onsets n_t for vapor condensation can differ greatly from the saturated density n_s for ordinary liquids. Also, because the ratio n_t/n_s decreases with increasing T , the apparent value of the condensation energy obtained by applying Eq. (1.3) to the slope of n_t vs. T is smaller than the actual value.

The discussion above applies only to an ideal system free of impurities or external surfaces; this case is commonly referred to as homogeneous nucleation. In practice, the condensation of ordinary liquids is usually dominated by inhomogeneous nucleation, i.e. the formation of drops on various impurities or surfaces. Effects often associated with the inhomogeneous nucleation of ordinary liquids are the destruction of metastability and other supersaturation phenomena, and the limitation of the drop concentration by the density of nucleation centers. However, as we show in chapters 2 and 3, these qualitative effects are not expected for the case of EHD in ultrapure Ge, and the

differences between the results of homogeneous and inhomogeneous nucleation theory are primarily quantitative and surprisingly small.

Finally, we discuss some modern developments in nucleation theory. The fundamental problem with the theoretical approach of Becker and Döring^{1.38} and of Zeldovich^{1.39} is that near threshold, the size of an embryo at the critical radius is so small that one questions whether this embryo can be treated as a drop of liquid; for water at 300K the number of molecules in a drop of radius $R_c = 0.61$ nm, Fig. 1.5c, is only 32. If such an embryo behaves more like a molecular complex than a liquid, Eq. (1.6) for the free energy is inapplicable. Lothe and Pound^{1.42} addressed this problem by making a detailed calculation of the free energy of small molecular complexes. Briefly, they found that the entropy associated with such complexes was expected to be much larger than for a liquid drop of the same size. Correspondingly, the formation rate J is much larger, and the calculated formation threshold n_t for water decreases by roughly 30%.^{1.41} However, the thresholds n_t calculated for water from Becker and Döring theory agree quite well with the measured values, whereas those calculated with the Lothe-Pound theory do not. Empirically, most ordinary liquids seem to fall in classes which agree with one theoretical approach or the other. Abraham^{1.41} has suggested that the difference between these classes is caused by molecular ordering in the liquid. In this case, we expect electron-hole drops to more nearly obey the Becker and Döring theory, because the e-h liquid itself is a degenerate Fermi system, highly ordered in momentum space, rather than a molecular liquid.

13 Application of Nucleation Theory to EHD

In the preceding section we have shown how classical nucleation theory can qualitatively explain some of the threshold phenomena experimentally observed for EHD in Ge. Namely, the finite surface tension of drop embryos results in metastable states of the liquid-vapor system in which the threshold n_t for drop formation is several times the saturated value, and the apparent value of ϕ the condensation energy is smaller than the actual value. Because macroscopic drops of ordinary liquid are stable for vapor densities as small as n_g , the saturated value, classical nucleation theory also predicts hysteresis and separate thresholds for the creation and destruction of drops. However, because the lifetime τ_0 of EHD is not infinite, the quantitative application of the theory for ordinary liquids to EHD is not justified a priori. In fact, classical nucleation theory cannot explain the large deviations from simple behavior observed in the FE-EHD phase diagram below 2K, nor does it predict the finite stable radius which is observed for EHD. In order to quantitatively analyze threshold data for EHD we have developed a theory of EHD nucleation, presented in chapters 2 and 3, incorporating the e-h liquid lifetime, which predicts these phenomena among others.

To gain an understanding of the effect of the lifetime τ_0 on nucleation theory, we consider the rate equation^{1,2} for the number of e-h pairs in a single electron-hole drop:

$$\frac{d}{dt} \left(\frac{4}{3} \pi R^3 n_o \right) = (\pi R^2) (n\bar{v} - a) - \left(\frac{4}{3} \pi R^3 n_o \right) / \tau_o \quad (1.9)$$

Here n_o is the density of e-h pairs in the EHL, $n\bar{v}$ and a are the coefficients of the rates of collection and evaporation of FE from EHD, with $\bar{v}$ the mean FE speed, and the last term is the rate of volume decay. As we show in Chapter 2, the evaporation coefficient is given by

$$a = n_s \bar{v} \exp(2\sigma/Rn_o kT) \quad (1.10)$$

where n_s is the saturated density from Eq. (1.3), and the argument of the exponential contains the correction to the work function ϕ due to the surface tension. Equation (1.9) is easily solved in the steady state to yield the FE density n in dynamic equilibrium with an EHD of radius R :

$$n = n_s \exp(2\sigma/Rn_o kT) + (4n_o R/3\bar{v}\tau_o) \quad (1.11)$$

For a given value of n , Eq. (1.11) is an implicit expression for the drop radius R . If n is sufficiently large Eq. (1.11) has two solutions: the smaller one is approximately equal to the critical radius R_c from Eq. (1.5), and the larger one is approximately

$$R_s \approx (3\bar{v}\tau_o/4n_o) (n - n_s) \quad (1.12)$$

Inspection of Eq. (1.9) indicates that the solution near R_c is unstable as for ordinary liquids whereas that near R_s is stable. Thus this analysis reproduces the result of classical nucleation theory, but also predicts a stable radius R_s determined by the EHL lifetime. The stable radius R_s is simply a result of the balance of the net rate of FE collection of the drop surface and the rate of volume decay.

Another new result predicted by Eq. (1.11) (independently obtained by Silver^{1.43}) is the existence of a minimum value n_m of the FE density greater than n_s for the existence of drops. At relatively high temperatures ($T \gtrsim 2K$) the first term in Eq. (1.11) is much greater than the second, and the minimum density n_m is approximately equal to n_s for macroscopic drops, as for ordinary liquids. However, n_s decreases exponentially with temperature, and for $T < 2K$, the second term in Eq. (1.11), due to the lifetime τ_0 , dominates and leads to hugely supersaturated values of n_m , which vary only slowly with temperature. The origin of this effect can be clarified by solving Eq. (1.12) for n , assuming $n \gg n_s$; we find

$$n = n_o R_s / 3\bar{v}\tau_0 \quad (1.13)$$

which is just the second term in Eq. (1.11). Thus, if the EHD stable radius possesses a minimum value, the FE density for which drops are stable also has a minimum value, given by Eq. (1.13). The minimum value of R_s is in turn determined by the effect of the surface tension σ on the drop radius in dynamic equilibrium, as for the critical radius R_c . The interplay of these effects is considered in detail in chapter 2.

Again, this analysis reproduces the result of classical nucleation theory at high T , but also predicts new phenomena below $T \sim 2\text{K}$ caused by the EHL lifetime.

The full theory of the nucleation of EHD in ultrapure Ge is developed in chapters 2 and 3 for both the homogeneous and inhomogeneous cases. The calculated thresholds n_+ and n_- for the creation and destruction of EHD increasingly deviate from the saturated density n_s at temperatures below 2K as described above, but join at $T \approx 1.3\text{K}$. Below this temperature hysteresis and metastability in the FE-EHD system are predicted to vanish. Threshold curves for the EHD signal vs. excitation are also calculated, as is the metastable time development of the EHD concentration and the variation of the EHD stable radius with temperature and history of excitation.

In chapter 5 we present the results of a systematic study of nucleation phenomena manifested in the luminescence of EHD and FE in ultrapure Ge. Hysteresis curves for the EHD and FE signals vs. excitation are measured for temperatures between 1.2K and 2.1K, and are used to determine the threshold phase diagram (n_+ and n_- vs. T) and the metastable time development of the EHD signal for times $\sim 4 \times 10^3$ sec. In addition, an investigation is made of the effects of impurity type and concentration and of dislocation density on the thresholds n_+ and n_- , in order to determine the effectiveness of these defects as nucleation centers. All of the data obtained are in good quantitative agreement with the predictions of EHD nucleation theory. A careful fit of the phase diagram measured below 2K to theory yields accurate values of the EHD surface tension σ and the condensation energy ϕ .

CHAPTER 2. NUCLEATION THEORY FOR ELECTRON-HOLE DROPS

In chapters 2 and 3 we present a general theory of EHD nucleation for a spatially uniform system, with the following features:

- 1) quantitative prediction of hysteresis providing a procedure for data reduction to accurately determine the surface tension;
- 2) quantitative explanation of metastable time behavior; 3) quantitative explanation of the FE-EHD phase diagram which can be used to extract the condensation energy ϕ ; 4) prediction of EHD radii near both thresholds as functions of the temperature; and 5) calculation of the above results for drop formation in the pure FE gas (homogeneous case) and on impurity atoms (inhomogeneous case). In this chapter we derive explicit expressions for the non-equilibrium rates of formation J_+ and breakup J_- of drops, and for the size distribution of drops in dynamic equilibrium. In chapter 3 we apply these results to experimentally measurable phenomena in Ge and Si. The contents of this chapter have been previously published.^{2.1}

21 Rate Equations

The basis of our calculation of the rates of EHD formation and breakup, J_+ and J_- , is the kinetic approach of Becker and Döring.^{2.2} Rather than using the thermodynamic approach to find the density of critical embryos (see Chapter 1), they solved rate equations describing the collisions between vapor molecules and drops. The physical situation we assume is the following: Within a spatially uniform

FE gas, drops containing ν e-h pairs are formed from free or bound excitons by successive collisions of the type

We assume that "drops" of all sizes $\nu > 1$ are energetically stable and are therefore able to participate in the chain of collisions leading to larger drops. Because the concentration of embryos and small complexes is usually quite low, we ignore collisions in which two or more embryos coalesce. (At temperatures $\lesssim 1\text{K}$ for Ge and $\lesssim 3\text{K}$ for Si, the predicted drop size becomes quite small and this need no longer be true, see chapter 3.) For the inverse reaction

drops release free excitons by thermionic emission ("evaporation"). In contrast to classical liquids, the EHD size ν can also be reduced by the recombination of an e-h pair within a drop.

The rates of these three processes determine in general the time evolution of both the size distribution g_ν (drops cm^{-3}) and the net rate J_ν (drops $\text{cm}^{-3} \text{sec}^{-1}$) at which drops grow from size $(\nu - 1)$ to ν . By adding the volume decay rate ν/τ_0 of an EHD of size ν to the rates of FE collection $\beta n \nu^{2/3}$ and evaporation $\alpha_\nu \nu^{2/3}$, we construct a set of rate equations similar to those of Becker and Döring:^{2,2}

$$J_\nu = g_{\nu-1} \beta n (\nu - 1)^{2/3} - g_\nu (\alpha_\nu \nu^{2/3} + \nu/\tau_0) ; \quad (2.1)$$

$$dg_\nu/dt = J_\nu - J_{\nu+1} . \quad (2.2)$$

In Eq. (2.1) we have $\beta \equiv \pi r_o^2 (8kT/\pi m^*)^{1/2}$, where $r_o \equiv (3/4\pi n_o)^{1/3}$ is the Wigner-Seitz radius, n_o is the density of e-h pairs within the liquid, and m^* is the FE effective mass; n is the FE density; τ_o is the total EHD lifetime; and the temperature-dependent evaporation coefficient α_v will be derived below. Hensel and Phillips^{2,3} have reported evidence for an additional temperature-independent evaporation rate $cv^{2/3}$ which should be added to $\alpha_v v^{2/3}$ in Eq. (2.1). The most probable origin of this effect is emission of FE by excitations created by the volume decay of e-h pairs in a layer near the surface of a drop. Because the measured value $c \sim 10^5 \text{ sec}^{-1}$ (see chapter 5) corresponds to a surface layer only $\sim 15 \text{ nm}$ thick, this term is proportional to the surface area even for small EHD embryos.

Although Eqs. (2.1) and (2.2) could in principle provide a detailed description of the time development of drop nucleation and growth, their general solution is impractical. We shall consider only the steady state, defined by $dg_v/dt = 0$, where the net rate of drop formation $J_v = J = J_+ - J_-$ is constant in time and size independent. Dynamic equilibrium is defined by the additional condition $J_+ = J_-$. As we shall see, steady-state solutions for J_+ and J_- can be applied to time dependent problems if the size distribution g_v satisfies the above restrictions for only a limited range of v about the critical size.

The arguments presented above and the rate Eqs. (2.1) and (2.2) apply equally well to both homogeneous and inhomogeneous nucleation. The difference between the two cases arises in the effect of a nucleation center on the thermodynamic potential of a drop. In section 22

through 24 we calculate the nucleation rates J_+ and J_- , and the size distribution in dynamic equilibrium for homogeneous nucleation, then in section 25 modify the calculation where necessary to describe the inhomogeneous case.

22 Size Distribution in Dynamic Equilibrium

For the model of homogeneous nucleation, drops of e-h liquid nucleate in a FE gas free of nucleation centers and can rotate and move about within the crystal. Because the radii of embryos are much smaller than the FE mean free path, it is permissible to treat the drops of a given size v as an ideal gas. We can thus picture the FE-EHD system as a collection of interpenetrating ideal gases identified by their sizes v , which interact with each other via e-h recombination and by the absorption and emission of excitons.

In order to calculate the EHD size distribution in dynamic equilibrium, denoted by h_v , for this system, we first need to find an expression for the thermionic emission coefficient α_v . This coefficient in turn is determined by the thermodynamic potentials of the system. The application of thermodynamics to EHD is legitimate, because the internal relaxation time of the e-h liquid is^{2.4} $\lesssim 1$ nsec, much shorter than the lifetimes $\tau_o = 40$ μ sec for Ge^{2.5} and $\tau_o \approx 0.2$ μ sec for Si.^{2.6} By solving the rate equations, Eqs. (2.1) and (2.2), we find that h_v is determined by an effective free energy difference ψ_v which includes the effects of the EHD lifetime τ_o . This free energy difference is analogous to the free energy Δf_v required to create a

drop of classical ($\tau_o \rightarrow \infty$) liquid from v vapor molecules discussed in chapter 1, and can be written in the form $\psi_v = \Delta f_v + f_v^T$, where f_v^T is the contribution from τ_o .

The total Helmholtz free energy f_v of a freely moving drop of v e-h pairs is the sum of the translational, rotational, and internal contributions:

$$f_v = f_v^{\text{trans}} + f_v^{\text{rot}} + f_v^{\text{int}} . \quad (2.3)$$

Assuming an ideal gas of rigidly rotating drops, we have

$$f_v^{\text{trans}} = kT \ln(g_v / eD_v) , \quad (2.4)$$

where $D_v \equiv (vm^*kT/2\pi\hbar^2)^{3/2}$ is the effective density of states for drops of mass vm^* ; and

$$f_v^{\text{rot}} = kT \ln[(\pi/8)^{1/2} (\hbar^2/IkT)^{3/2}] , \quad (2.5)$$

where $I = (2/5)m^*r_o^2 v^{5/3}$ is the EHD moment of inertia. The internal Helmholtz free energy f_v^{int} is given by

$$f_v^{\text{int}} = 4\pi r_o^2 \sigma v^{2/3} - v\phi , \quad (2.6)$$

where σ is the surface tension, and ϕ is the condensation energy of an e-h pair relative to FE. The surface tension is approximately related to the surface energy w by $\sigma \simeq w[1 - (T/T_c)^2]$, where T_c is the critical temperature (see for example Ref. 2.7). Equations (2.3) to (2.6) are strictly valid only for macroscopic drops, but should be

reasonably accurate for complexes of size greater than $v \sim 10$.

The chemical potential of an ideal FE gas of density n is given by

$$\mu_x = kT \ln(n/D_x) , \quad (2.7)$$

where $D_x \equiv \gamma_x (m^* kT / 2\pi \hbar^2)^{3/2}$ is the effective density of states, and γ_x is the degeneracy of the FE ground state. By equating μ_x with the condensation energy $-\phi$ we obtain the saturated FE density,

$$n_s = D_x \exp(-\phi/kT) . \quad (2.8)$$

Were it not for the existence of the surface tension σ and the lifetime τ_0 , condensation would occur whenever the FE density n reaches n_s . The change in the bulk Helmholtz free energy of the FE-EHD system when an e-h pair is transferred from an EHD to a FE neglecting drop translation and rotation is $\mu_x + \phi = xkT$, where we define

$$x \equiv \ln(n/n_s) , \quad (2.9)$$

the degree of supersaturation. It is this free energy difference which provides the driving force for the nucleation and growth of drops. The total internal free energy difference Δf_v is then given by

$$\Delta f_v = f_v^{\text{int}} - v\mu_x = 4\pi r_0^2 \sigma v^{2/3} - xkTv , \quad (2.10)$$

the expression which enters into classical nucleation theory, as discussed in chapter 1.

With this information we can derive the evaporation coefficient α_v from Eq. (2.1) by using the principle of detailed balance. Because each droplet very rapidly establishes internal thermodynamic equilibrium, α_v must be independent of the EHD lifetime. Therefore we can treat EHD as drops of classical fluid for the purpose of deriving α_v and ignore the last term in Eq. (2.1). In dynamic equilibrium ($dg_v/dt = 0$, $J_v = 0$) we have

$$d_{v-1} \beta n (v-1)^{2/3} = d_v \alpha_v v^{2/3} , \quad (2.11)$$

where we use d_v to denote the classical ($\tau_0 \rightarrow \infty$) equilibrium size distribution. We can obtain an expression for d_v by equating μ_x with $d(d_v f_v)/dd_v$, the chemical potential of the gas of drops of size v . We find

$$d_v = H_v \exp(-\Delta f_v/kT) , \quad (2.12)$$

where Δf_v is given by Eq. (2.10), and the slow v dependence of f_v^{rot} has been included in the new effective density of states $H_v \equiv D_v \exp(-f_v^{\text{rot}}/kT)$. By using Eq. (2.12) for d_v in Eq. (2.11), and by assuming $v \gg 1$, we find the evaporation coefficient,

$$\alpha_v = (H_{v-1}/H_v) \beta n_s \exp(8\pi r_o^2 \sigma / 3v^{1/3} kT) , \quad (2.13)$$

where $(H_{v-1}/H_v) \approx 1$. The argument of the exponential in Eq. (2.13) is just the difference in surface free energy between a drop of size v

and one of size $v - 1$ divided by kT . Thus the surface tension increases the evaporation rate of small drops. For large drops α_v reduces to the Richardson expression βn_s .

Returning to the original rate equations, Eqs. (2.1) and (2.2), we are now in a position to calculate the EHD size distribution in dynamic equilibrium h_v , including the effect of the EHD lifetime. Setting $dg_v/dt = 0$ and $J_v = 0$, Eqs. (2.1) and (2.2) reduce to the following recursion relation:

$$h_v/h_{v-1} = (d_v/d_{v-1}) / (1 + v^{1/3}/\alpha_v \tau_o) . \quad (2.14)$$

Because an EHD as formulated is indistinguishable from a FE for $v = 1$, we have the boundary condition $h_1 = d_1 = n$. By using Eq. (2.14) repeatedly we find

$$h_v = d_v \exp \left[- \sum_{j=2}^v \ln \left(1 + \frac{j^{1/3}}{\alpha_j \tau_o} \right) \right] . \quad (2.15)$$

From Eq. (2.12) for d_v it is apparent we can put h_v in a similar form by defining the quasi free energy f_v^τ so that the contents of the square brackets in Eq. (2.15) are equal to f_v^τ/kT . We have finally:

$$h_v = H_v \exp(-\psi_v/kT) , \quad (2.16)$$

where the effective free energy difference ψ_v is given by $\psi_v = \Delta f_v + f_v^\tau$. Although the size distribution in dynamic equilibrium given by Eq. (2.16) is inapplicable above $T \sim 1.3K$, where the FE-EHD system is characterized

by metastable states^{2.8,2.9,2.10} (see chapter 5), it is useful in analyzing the actual process of nucleation.

23 Free Energy Difference

An understanding of the origins of metastability in the FE-EHD system is aided by detailed consideration of the potential ψ_v . Explicitly written out, it is

$$\psi_v = 4\pi r_o^2 \sigma v^{2/3} - xkTv + kT \sum_{j=2}^v \ln \left(1 + \frac{j^{1/3}}{\alpha_j \tau_o} \right) . \quad (2.17)$$

The three terms in Eq. (2.17) are respectively contributions from surface, bulk, and lifetime effects. The free energy difference ψ_v from Eq. (2.17) is plotted for Ge at 2K in Figs. 2.1 and 2.2 for various values of the degree of supersaturation x . For small drop radii $R = r_o v^{1/3}$ the surface contribution always dominates ψ_v . If x is larger than a minimum value x_m , Figs. 2.1(a) and 2.2(a), the negative bulk free energy difference $-xkTv$ drives ψ_v downward, creating a maximum ψ_c at the critical radius R_c , indicated in Fig. 2.1. For greater radii the positive lifetime term f_v^τ becomes large, creating a very sharp minimum ψ_s at the stable radius R_s . Although R_c , R_s , ψ_c , and ψ_s must in general be calculated numerically from Eq. (2.17), the following expressions are valid if $R_s \gg R_c$:

$$R_c \simeq 2\sigma/n_o xkT ; \quad (2.18)$$

$$R_s \simeq r_o \beta \tau_o (n - n_s) ; \quad (2.19)$$

$$\psi_c \approx [16\pi\sigma^3/3(n_0 x kT)^2] . \quad (2.20)$$

Here Eqs. (2.18) and (2.20) are identical to the expressions obtained in classical nucleation theory,^{2,2,2.11} and Eq. (2.19) is the same as the result found from the EHD rate equations developed by Pokrovskii.^{2.6}

As shown in Figs. 2.1 and 2.2, there exist two wells in ψ_v : one about $v = 1$ populated by FE and multiexciton (ME) complexes, and one about R_s populated by macroscopic drops. Within each well local equilibrium is rapidly established, and the density of ME of less than critical size is given by the equilibrium expression Eq. (2.16). If this expression were also valid for macroscopic drops at 2K, the "equilibrium" threshold $x_e = 0.771$, Figs. 2.1(c) and 2.2(c), would be observed when the concentration of drops rapidly became significant. However, the drop well is isolated from free and multiexcitons by the large potential barrier ψ_c ; as a result the concentration of drops in the well is not fixed by Eq. (2.16) but depends upon the history of the system. The degree of supersaturation must be increased to the "up-going" threshold value $x_+ = 2.01$ (or $n/n_s = 7.46$), Figs. 2.1(e) and 2.2(e), before ψ_c is small enough to permit the nucleation of new drops. Similarly, x must be reduced to the "down-going" threshold $x_- = 0.734$ (or $n/n_s = 2.08$), Fig. 2.1(b), before drops already present can "escape" over the potential barrier and break up into FE. The appropriate formation and breakup "currents", J_+ and J_- , are indicated in Fig. 2.1. As we show in the next section, both thresholds are very sharp.

As also shown in Figs. 2.1 and 2.2, the well about R_s disappears for values of x less than the minimum value $x_m = 0.728$ (or $n/n_s = 2.07$) defined by the condition that the first and second derivatives of ψ_v from Eq. 2.17 are simultaneously zero. Consequently, macroscopic drops cannot exist in Ge at 2K for supersaturation ratios less than $n/n_s = 2.07$, or with stable radii less than the value at x_m , $R_m \approx 0.19 \mu\text{m}$ from Fig. 2.1(a). These effects follow from the inclusion of the EHD lifetime in Eqs. (2.1) and (2.2) and were first reported by Silver^{2.12}. However, his prediction that actual drop radii in Ge above 1.3K are determined by the value of R_s at the equilibrium threshold x_e cannot be accurate.

When the temperature-independent evaporation rate $cv^{2/3}$ is included in the calculation of h_v , the same result is obtained except f_v^τ from Eq. (2.15) is replaced by the expression

$$f_v^\tau = kT \sum_{j=2}^v \ln \left(1 + \frac{j^{1/3} + c\tau_o}{\alpha_j \tau_o} \right), \quad (2.21)$$

which also replaces the last term in Eq. (2.17) for ψ_v . From Eq. (2.21), we find that the effect of the coefficient c is to increase the size of the lifetime term in ψ_v , and therefore to increase the expected deviations from classical nucleation theory (see chapter 3).

A point we have previously neglected is that the lifetimes τ_v of small ME complexes ($v \lesssim 10$) certainly differ from the bulk value τ_o . If these lifetimes were known, we could use them in Eq. (2.17), where an unusually short τ_v causes a positive step in f_v^τ and ψ_v . As long

as $\alpha_v \tau_v > 1$ (or $\tau_v \gtrsim 30$ nsec for Ge at 2K), the potential ψ_v , and therefore h_v and the formation rate J_+ , are insensitive to the values of τ_v . However if $\alpha_v \tau_v \ll 1$ for any small value of v , then many body collisions are required to bridge the gap between long-lived sizes, lowering the distribution h_v for larger v , and decreasing the formation rate J_+ . Bearing this possible complication in mind, we shall use $\tau_v = \tau_0$ for the remainder of this paper.

24 Calculation of Nucleation Rates

With knowledge of the dynamic equilibrium size distribution h_v and the potential ψ_v , we can now calculate the rates of formation J_+ and breakup J_- of macroscopic drops in the steady state ($dg_v/dt = 0$). Returning to the rate equations, Eqs. (2.1) and (2.2), we divide through by h_{v-1} and use Eq. (2.13) to obtain

$$g_{v-1}/h_{v-1} - g_v/h_v = J/h_{v-1} \beta n(v-1)^{2/3}, \quad (2.22)$$

where $J = J_v$ is the size-independent net formation rate in the steady state. Of course J cannot truly be positive for arbitrarily large v ; mathematical solutions of Eq. (2.22) for g_v pass through zero at a finite drop size and become unphysically negative beyond. It is interesting to note that Eq. (2.22) is a diffusion equation for the function g_v/h_v with the diffusion coefficient $h_{v-1} \beta n(v-1)^{2/3}$. The boundary conditions for this difference equation are appropriately made at the FE and stable sizes $v = 1$ and v_s . Summing Eq. (2.22)

between $v = 2$ and v_s and approximating the sum by an integral we have

$$(g_1/h_1) - (g_s/h_s) = (J/\beta n) \int_1^{v_s} dv (h_v v^{2/3})^{-1}. \quad (2.23)$$

For the formation rate J_+ the appropriate boundary conditions are $g_1/h_1 = 1$ and $g_s/h_s = 0$, i.e. no macroscopic drops are initially present. We define the breakup rate J_- by the boundary conditions $g_1/h_1 = 0$ and $g_s/h_s = N/h_s \Delta v_s$, where N is the actual non-equilibrium concentration of drops in the well about v_s , and $\Delta v_s \equiv [(d^2\psi_v/dv^2)_{v_s}/2vkT]^{-1/2}$ is the Gaussian width of the well. With this definition the net formation rate is given by $J = J_+ - J_-$. Because $1/h_v$ has a very sharp maximum at $v = v_c$ (see Figs. 2.1 and 2.2), we can perform the integral in Eq. (2.23) by expanding ψ_v about v_c to second order, setting $v = v_c$ outside the exponential, and extending the limits of integration to $\pm \infty$. In this way we obtain the final results:

$$J_+ = \beta n v_c^{2/3} h_c / \Delta v_c; \quad (2.24)$$

$$J_- = J_+ N / h_s \Delta v_s. \quad (2.25)$$

The subscripts c and s refer to the critical and stable sizes v_c and v_s , and Δv_c is defined in the same way as Δv_s . The form of Eq. (2.24) for J_+ can be easily understood as the product of the FE collision rate $\beta n v_c^{2/3}$ with the concentration gradient $h_c / \Delta v_c$ at the critical size driving the diffusion of droplets over the potential barrier ψ_c to larger sizes. The expression Eq. (2.25) for J_- is similar except the

breakup rate is weighted by the ratio of the actual concentration of drops N to the concentration $h_s \Delta v_s$ in dynamic equilibrium. Therefore the potential barrier to be surmounted is the difference $\psi_c - \psi_s$ between ψ_v at the critical and stable sizes, rather than ψ_c (see Figs. 2.1 and 2.2). In order for these solutions, Eqs. (2.24) and (2.25) to be valid when the FE density changes with time, it is only necessary that the size distribution have the steady-state value near the critical radius. For the formation rate the time required for this to happen is roughly $v_c^{1/3}/\beta n$, which is $\lesssim 1$ μsec for Ge at 2K. For J_- this time is roughly $v_s^{1/3}/\beta n \sim \tau_o$, which is ≈ 40 μsec for Ge. Therefore these solutions can be applied to situations where the rise and fall times of the excitation are moderately fast.

Semilogarithmic plots of J_+ and J_- , computed from Eqs (2.24) and (2.25), versus x , the degree of supersaturation, are shown for Ge in Fig. 2.3. The most striking feature of these graphs is the exceptionally strong dependence of J_+ and J_- upon the degree of supersaturation. As x increases at 2K from 1.8 to 2.2, J_+ increases by 9 orders of magnitude from 10^{-3} to 10^6 drops $\text{cm}^{-3} \text{sec}^{-1}$. Similarly J_- increases at 2K by 14 orders of magnitude, from 10^{-4} to 10^{10} drops $\text{cm}^{-3} \text{sec}^{-1}$, for a decrease in x of only 0.007. At 1.5K and 1.25K the variation of these currents with x , shown in Fig. 2.3, is somewhat slower but still extremely steep. The variation of the currents J_+ and J_- with x is so rapid that we can speak of thresholds x_+ and x_- at which J_+ and J_- respectively "turn on". The same mathematical phenomenon occurs in classical nucleation theory. Workers in cloud physics have defined

the threshold x_+ as that value of x for which the minimum detectable concentration of drops $N_{\min}$ is formed in the observation time Δt ,

$$J_+ \Delta t = N_{\min} \quad (2.26)$$

Typically $J_+ \sim 10^2 \text{ drops cm}^{-3} \text{ sec}^{-1}$ at threshold for sensitive luminescence detection of EHD in Ge. The threshold x_- can be defined in the same way. In chapter 3 we give precise definitions of x_+ and x_- which do not depend upon experimental sensitivity. However, this improvement is primarily conceptual; the actual values of x_+ and x_- obtained by the two methods do not significantly differ.

A second major feature of the behavior of the FE-EHD system illustrated by Fig. 2.3 is that both the rates of formation and breakup are negligible at 1.5K and 2K for a range of values of x between the thresholds x_- and x_+ . If the FE density lies in this range, the concentration of drops N cannot change appreciably in a physically reasonable time and is determined only by the history of excitation. A rough estimate of the time required to reach dynamic equilibrium ($J_+ = J_-$) is given by the magnitude of J_+ and J_- where they intersect. At 1.5K the curves meet at $J_+ = J_- \approx 10^{-6} \text{ sec}^{-1} \text{ cm}^{-3}$, implying an equilibration time $\sim 10^6 \text{ sec}$; this time becomes astronomically long at 2K. Therefore any practical experiment performed on Ge at these temperatures can only observe metastable states of the system. These effects provide an explanation of the hysteresis observed^{2.8,2.9,2.10} in the luminescence of EHD in Ge. This hysteresis was found to

persist for times longer than 4000 sec,^{2,9} (see chapter 5) indicating that individual drops in the samples used survived for comparable times. In general a number of mechanisms may be present which destroy drops, for example inhomogeneous 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. In either case, equilibrium arguments are inapplicable to the FE-EHD system in Ge above $T \sim 1.3K$.

However, at temperatures $T \lesssim 1.3K$ the situation changes. As shown in Fig. 2.3, the separation $x_+ - x_-$ of the thresholds decreases as the temperature is reduced below 2K; at 1.25K the thresholds cross. At this temperature drops created at the formation threshold $x_+ = 5.6$ in Fig. 2.3, are immediately destroyed by the large breakup rate J_- . In order to stably create drops, the degree of supersaturation must be increased to the equilibrium threshold $x_e = 5.8$ where J_+ and J_- are equal and the system is in dynamic equilibrium. This threshold can be defined by the condition that the population $h_s \Delta v_s$ of the droplet well in ψ_v is equal to the minimum detectable drop concentration N_{min} . The physical reason metastability disappears in Ge below $T \sim 1.3K$, is that the FE density near the saturated value n_s is far too small to support the volume decay of EHD of finite size. Equivalently, the evaporation coefficient $\alpha_v \approx \beta n_s$ becomes very small; when $\alpha_v \tau_0 < 1$, the lifetime term in Eq. (2.17) becomes large at the critical size and dominates ψ_c , the potential barrier to nucleation. Once the degree of supersaturation x has been increased to a value sufficient to create

a drop well in ψ_v , the potential barrier ψ_c is too small to impede condensation, so that drops form as soon as x exceeds the minimum value x_m (see Figs. 2.1(a) and 2.2(a)). In chapter 3 we consider the detailed temperature dependence of the FE density thresholds.

25 Inhomogeneous Nucleation

The problem of calculating the rates of drop formation J_+ and breakup J_- , and the size distribution h_v in dynamic equilibrium for EHD nucleated on condensation centers is quite similar to that for homogeneous nucleation. In this section we describe only the differences in the two calculations and summarize the results.

The FE-EHD system we consider is identical to that of section 22 except that ME complexes and drops of all sizes $v > 1$ are bound to nucleation centers and are therefore no longer free to move. Consequently the total Helmholtz free energy f_v of a drop becomes

$$f_v = f_v^{\text{int}} - B_v, \quad (2.27)$$

where the internal free energy f_v^{int} is given by Eq. (2.6), and B_v is the binding energy of the drop on the center. Because the density N_i of nucleation centers is assumed to be fixed, the "classical" ($\tau_0 \rightarrow \infty$) probability that a drop of size v is present on a given center is proportional to $\exp[-(f_v - v\mu_x)/kT]$. This expression replaces d_v in the calculation of the evaporation coefficient α_v . Carrying out the calculation of the size distribution in dynamic equilibrium, we find:

$$h_v = (N_i/Z) \exp[-(\psi_v - B_v)/kT] ; \quad (2.28)$$

$$Z \equiv \sum_{v=0}^{\infty} \exp [-(\psi_v - B_v)/kT] .$$

Here ψ_v is given by Eq. (2.17) as before, and Z is the analog of the partition function. An equation similar to Eq. (2.28) has also been obtained by Silver.^{2.12} Comparing the homogeneous and inhomogeneous expressions for h_v , Eqs. (2.16) and (2.28), we find that the binding energy B_v increases Eq. (2.28) by the factor $\exp(B_v/kT)$, but that the lower density of states decreases Eq. (2.28) by the factor (N_i/ZH_v) . The function Z normalizes h_v so that the total density of drop "sites" is equal to N_i . If the potential $\psi_v - B_v$ possesses a negative minimum at a size v_M less than the critical value v_c the size distribution saturates ($h_M \approx N_i$) and Z is given approximately by $\ln Z \approx -(\psi_M - B_M)/kT$, where the subscript M refers to the size v_M .

The calculation for the rates of formation J_+ and breakup J_- of EHD bound to nucleation centers is formally identical to the homogeneous case. In order to obtain final results, we need only substitute h_v from Eq. (2.28) into Eq. (2.24) for J_+ and into Eq. (2.25) for J_- . The qualitative features of the behavior of J_+ and J_- , illustrated by Fig. 2.3, remain unchanged; the only major effect of nucleation centers is to shift the positions of the thresholds, x_+ and x_- , for the creation and destruction of drops. Contrary to what one might expect, these shifts are not necessarily large. We consider the detailed behavior of the thresholds x_+ and x_- in chapter 3.

Of the various types of crystal imperfections, neutral impurities are probably most important as nucleation centers; experimentally we find dislocations are not effective,^{2,9} (see chapter 5) and vacancy clusters and deep traps can be practically eliminated by crystal growing techniques. The binding energy B_v of an EHD on a neutral impurity varies in general with v , but should have the size independent value B whenever the drop radius exceeds the screening length of the plasma; a reasonable estimate of the smallest size at which this occurs is $v \sim 10$. Because the critical size for Ge at 2K is $v_c \gtrsim 50$ from Fig. 1(e), we can ignore the possible shift in v_c caused by the size dependence of B_v . As a result the breakup rate J_- is independent of the value of B and differs from the homogeneous expression only by the factor H_s/H_c . A convenient parameter which determines the effect of impurities upon the formation rate J_+ is the barrier lowering $\Delta\psi$, which we define by $\Delta\psi \equiv B - kT \ln Z$.

Possibly the most important role of nucleation centers is to stabilize small multiexciton complexes. To date there is no experimental proof that free ME complexes exist in Ge or Si. If in fact any complexes of size $v \lesssim 10$ are not bound, many body collisions are required to bridge the gap in stable sizes and the homogeneous formation rate J_+ is greatly reduced. In this case EHD nucleation would occur first on centers regardless of the value of B .

Finally, we consider the effect of a possible electrical charge on EHD upon the formation rate, either for homogeneous or inhomogeneous nucleation. For classical fluids such as water, the electrostatic

self energy $E_c = e^2/2R_c$ of a singly charged critical drop is comparable to the potential barrier Δf_c for vapor densities near the uncharged formation threshold. It is a straightforward algebraic exercise to show that if $E_c/\psi_c > 2(3/4)^4 \approx 0.63$, the total drop free energy $\Delta f_v + e^2/2R$ decreases monotonically with R , and the potential barrier to nucleation is destroyed. Consequently, the presence of ions in the vapor greatly reduces the degree of supersaturation at which condensation occurs.

However, for Ge at $T = 2K$ this self energy is $E_c = e^2/2\epsilon R_c \lesssim 1.1$ meV where $\epsilon = 16$ is the dielectric constant, and $R_c \gtrsim 0.04$ μm from Fig. 2.1. This value of E_c is much smaller than the potential barrier $\psi_c \gtrsim 10$ meV and does not greatly alter the total drop free energy for smaller sizes.

Thus we conclude that the presence of a single charge on an EHD at temperatures $T \gtrsim 2K$ has only a small effect upon the position of the formation threshold. At lower temperatures $T \sim 1.5K$, where the values of R_c and ψ_c at the formation threshold are reduced, the effect of a single drop charge is somewhat larger, but still small compared to that of an impurity atom. Why are not embryos doubly charged? The answer is that the self energy of a doubly charged drop smaller than the critical size is $\gtrsim 5$ meV, larger than the binding energy ≈ 3 meV of a carrier in an EHD. Accounting for the existence of image charges, we conclude that an embryo which becomes doubly charged will very rapidly rid itself of the excess charge by the emission of a free carrier in a time of the order $R/v_F < 10^{-11}$ sec, where v_F is the Fermi velocity. Such an embryo does not exist long enough to grow larger and influence the process of nucleation.

CHAPTER 3. APPLICATION OF NUCLEATION THEORY TO OBSERVABLE PHENOMENA

In chapter 2 we calculated the non-equilibrium rates of formation J_+ and breakup J_- of macroscopic electron-hole drops (EHD) in a super-saturated free-exciton (FE) gas. We also calculated the distribution h_v (drops cm^{-3}) of EHD versus drop "size" v (e-h pairs) in dynamic equilibrium. We found that the FE-EHD system is characterized by metastable states at temperatures above $T \sim 1.3\text{K}$ in Ge, and that the expressions for the currents J_+ and J_- , and for the size distribution h_v , yield sharp thresholds in FE density.

In this chapter we use these expressions to predict quantitatively a number of experimentally observable phenomena in Ge assuming both homogeneous and inhomogeneous nucleation: Section 32, metastable time behavior; section 33, equilibrium and non-equilibrium thresholds in FE density, and hysteresis in EHD luminescence intensity; section 34, procedure for accurately determining the EHD surface tension from threshold data; section 35, non-equilibrium FE-EHD coexistence curves which can be used to extract the EHD condensation energy ϕ ; section 36, drop radius near threshold versus temperature. Coexistence curves for Si are also presented in section 35. These calculations are made between 1K and 4K for Ge, and between 3K and 15K for Si, and they assume spatial uniformity in the FE gas. The contents of this chapter have been previously published,^{3.1} with the exception of the effect of temperature-independent evaporation on the EHD-FE phase diagram.

A list of the parameters used in this calculation is given in Table 3.1. The value for Ge of ϕ is that of Lo,^{3.4} corrected for the temperature dependence reported by Thomas, Rice, and Hensel.^{3.5} This value of ϕ at T=0 agrees very well with the recently measured spectroscopic value^{3.9} $\phi = (20.9 \pm 2.3)\text{K}$, and the threshold measurement $\phi = (22.0 \pm 2.3)\text{K}$ described in chapter 5 of this thesis. The value of n_o for Ge in Table 3.1 also agrees very well with the recent measurement^{3.9} $n_o(10^{17} \text{ cm}^{-3}) = (2.38 \pm 0.05) - (0.017 \pm 0.002)T^2$. For Si the parameters ϕ and n_o were less well known at the time of the calculation. However the values given in Table 3.1 agree reasonably well with the more reliable recent measurements^{3.10} $\phi(\text{K}) = (95 \pm 1) + (0.068 \pm 0.012)T^2$ and $n_o(10^{17} \text{ cm}^{-3}) = (33.3 \pm 0.5) - (0.015 \pm 0.010)T^2$. For Si we estimated σ from the rough expression $\sigma \sim \frac{1}{2} \phi n_o r_o$, where the surface thickness was assumed to be equal to the Wigner-Seitz radius $r_o \equiv (3/4\pi n_o)^{1/3}$; this estimate $\sigma \approx 8 \times 10^{-3} \text{ erg cm}^{-2}$ agrees very well with the recently calculated^{3.11} value $\sigma = 8.75 \times 10^{-3} \text{ erg cm}^{-2}$. The value given for σ in Ge agrees with the measurement $\sigma = (2.6 \pm 0.3) \times 10^{-4} \text{ erg cm}^{-2}$ at T=0 described in chapter 5. The FE effective mass m^* and degeneracy for both Ge and Si are those of the lower ground state.^{3.7} The values of N_i , G_M , and Δt (see below) are representative of actual experiments on ultrapure Ge and Si. Guided by experimental work on bound multiexciton (ME) complexes,^{3.12,3.13} we chose the temperature independent values listed for $\Delta\psi$, the barrier lowering due to impurities (see chapter 2). Assuming $\Delta\psi \approx B$, the binding energy of a macroscopic EHD to a neutral

shallow impurity, the value $B \approx 50\text{K}$ for Ge in Table 3.1 agrees reasonably well with the recent calculations for donors^{3.14,3.15} $B \approx 60$ to 120K . Except for the calculations shown in Fig. 3.4 below, the possible temperature-independent evaporation rate discussed in chapter 2 is assumed to be zero.

3.1 Conservation Equation

In order to relate the results of chapter 2 to observable phenomena, we must specify the conditions under which a hypothetical experiment is performed. In the following calculations we assume that the source of excitation is uninterrupted, and that the generation rate G ($\text{cm}^{-3} \text{ sec}^{-1}$) of e-h pairs is uniform within the effective volume occupied by FE. In the steady state the FE and drop concentrations, n and N , are related to G by the conservation equation. Ignoring the rate of decay of free carriers we have

$$G = n/\tau_x + N\nu/\tau_o, \quad (3.1)$$

where τ_x and τ_o are the total FE and EHD lifetimes. In this chapter ν refers to the stable drop size (ν_s in chapter 2) unless noted. Because the drop concentration N depends upon previous values of G , we must specify the history of excitation. We consider two cases easily achieved experimentally:^{3.2,3.3} "up-going" data points taken by increasing G from zero to a constant value G_U , and "down-going" points taken by first briefly increasing G from zero to a fixed large value G_M , then decreasing G to a constant intermediate level G_D . To

simplify the analysis we assume that all changes in G are made slowly compared to the lifetimes τ_o and τ_x , so that the conservation equation, Eq. (3.1), holds at all times.

A qualitative description of the metastable behavior of n , N , and v for up-going and down-going excitation is useful in understanding the calculations to follow. In the up-going case the FE density n increases with the generation rate until the up-going threshold $G_+ = n_+/\tau_x$ is reached (chapter 2). The FE density is held near the threshold value n_+ by the very rapid increase in the EHD formation rate J_+ . Because the stable drop size v depends only on n , the size v_+ of drops produced is nearly constant and independent of the generation rate if the rate of increase of G is sufficiently slow. The condition to be met is that the time $\sim \tau_o$ required for embryos to grow to the stable size is small compared to the average time between embryo formation $\sim (J_+ L^3)^{-1}$ where L is the FE diffusion length. Because the rate of change of the generation rate above threshold is roughly $dG/dt \sim J_+ v_+ / \tau_o$, this is true only if $dG/dt \lesssim (v_+ / L^3 \tau_o^2)$. The corresponding lower limit on the risetime of G to twice the threshold value in G_e (see sections 35 and 36) is quite long, ~ 0.04 sec at 2K and ~ 5 sec at 1.5K. Calculations of N , v , and n for fast pulsed excitation performed by Staehli^{3.16} indicate that these quantities depend in general upon the risetime as well as the amplitude of the pulse. Once G reaches the final constant value G_U , the EHD formation rate J_+ is turned off by the reduction in the FE density through the conservation equation. The final concentration of drops is given approximately by

$$Nv_+ = (G_U - G_+) \tau_o, \quad (3.2)$$

where v_+ depends only on the temperature.

In the down-going case the concentration N_M of drops of size v_+ is produced by the initially large generation rate G_M in the manner described above. As G decreases below G_M , the EHD concentration must remain constant, because both the rates of formation and breakup are negligible (chapter 2). Therefore the FE density and the EHD size v fall with G until the down-going FE density threshold n_- is reached. As above, the FE density and EHD size remain near their down-going values n_- and v_- as drops break up into free excitons. Once the final value G_D has been reached, the breakup of EHD is halted by the resultant increase in FE density. For values of G_D such that $n \approx n_-$, the final concentration of drops is approximately given by

$$Nv_- = (G_D - G_-) \tau_o, \quad (3.3)$$

where v_- is also a function only of the temperature, and $G_- = n_-/\tau_x$ is the down-going threshold.

Before proceeding we consider the fact that the FE density is not spatially uniform in most experiments. Our expressions for the rates of formation and breakup, J_+ and J_- , remain locally valid in cases where n changes slowly compared to the FE mean free path; condensation occurs first where n is largest. For volume excitation, the generation rate varies smoothly over distances ~ 1 mm (see chapter 4) and thus the model is directly applicable; volume excitation was used to obtain the

central results reported in chapter 5 of this thesis. For relatively low levels of surface excitation, the drop bearing volume is small compared to the extent of the FE gas, and the spatial form of $n(x)$ is fixed; the FE density is everywhere proportional to the largest value near the excited surface. Consequently, a spatially uniform model can be used to describe the properties of EHD near threshold for both volume and surface excitation. Using much higher levels of optical excitation focussed to a small spot, several authors^{3.17,3.18} have reported phenomena involving the transport and destruction of EHD. Near threshold for unfocussed optical excitation, drops probably remain near the source of excitons, pinned to impurities either during or after nucleation. The fact that the observed hysteresis in the luminescence of EHD in Ge persists for periods of time longer than 1 hour^{3.2} (see chapter 5) provides strong evidence that single drops can exist for comparable times.

32 Metastable Time Development

In this section we obtain approximate solutions for the very slow time dependence of the EHD density following up-going and down-going steps in the generation rate. By doing so, we can explain the observed^{3.2} (see chapter 5) very slow drift of the EHD luminescence intensity. In section 33 we use these solutions to define precisely the thresholds n_+ and n_- .

In the up-going case we start with the relation $dN/dt = J_+$. For the formation rate we use the approximate expression

$$J_+ \approx C_+ \exp(n\tau_o/M_+ \tau_x) , \quad (3.4)$$

suggested by Fig. 2.3 in chapter 2. The coefficients M_+ and C_+ are determined by expanding the exact expression for J_+ about the threshold value (see section 33). In this way we find $M_+ = n_+ \tau_o / v_c \tau_x$, where the critical drop size v_c is evaluated at threshold. Assuming that the rate of change of G is slow enough (risetime $\gtrsim 1$ sec) that the size of drops produced remains constant at the up-going value v_+ , we use Eq. (3.1) for n to obtain the differential equation

$$dN/dt = C_+ \exp[(G\tau_o - Nv_+)/M_+] . \quad (3.5)$$

This equation can be integrated directly to yield N . We break the time integral into two parts: $\int_0^{t_r} dt \exp(G\tau_o/M_+)$ for the time $t_r \sim 1$ sec required for G to reach the constant value G_U , and $\exp(G_U \tau_o/M_+) \Delta t$ for subsequent times. Because $G_U \tau_o/M_+ \gtrsim v_c$ above threshold ($v_c \approx 50$ for Ge at 2K), we can neglect the first integral if $\Delta t > t_r$. We obtain

$$Nv_+ = M_+ \ln[1 + (C_+ v_+ \Delta t/M_+) \exp(G_U \tau_o/M_+)] . \quad (3.6)$$

Above threshold the argument of the logarithm in Eq. (3.6) is large (see section 33), and Eq. (3.6) reduces asymptotically to

$$Nv_+ \approx G_U \tau_o - M_+ \ln(M_+/C_+ v_+ \Delta t) . \quad (3.7)$$

An interesting feature of Eqs. (3.6) and (3.7) is that the drop concentration N increases logarithmically with time Δt . For Ge at 2K, $M_+ \approx 10^{11}$ pairs cm^{-3} ; thus Nv_+ increases by $\sim 2 \times 10^{11}$ pairs cm^{-3} for each factor of ten increase in Δt , a change which is large enough to be readily observable. Of course N cannot increase indefinitely; our assumption that the size v_+ remains constant breaks down when $\Delta Nv_+/\tau_o \sim n/\tau_x$; i.e. when the additional amount of EHD phase ΔNv_+ condensed in the time Δt becomes comparable to the FE density. From Eq. (3.7) and the definition of M_+ we find for Ge at 2K that the time required is $\Delta t \sim \exp v_c \sim 10^{22}$ sec, very long indeed.

We can calculate the slow time dependence of the down-going EHD density in a similar manner. Here the rate of change of the drop concentration is given by

$$dN/dt = -J_- \approx -NC_- \exp(-n\tau_o/M_- \tau_x) . \quad (3.8)$$

The coefficients M_- and C_- are defined in the same way as M_+ and C_+ ; we find $M_- = n_- \tau_o / (v_- - v_c) \tau_x$, where the critical size v_c is evaluated at the down-going threshold n_- . The differential equation analogous to Eq. (3.5) is

$$dN/dt = -NC_- \exp[-(G\tau_o - Nv_-)/M_-] , \quad (3.9)$$

where we assume v_- is constant. As before we divide the time integral of Eq. (3.9) into two parts and assume the elapsed time Δt is much greater than the fall time (for example 1 sec) of G to the constant

value G_D . In this way we find

$$E_1(Nv_-/M_-) = E_1(N_M v_-/M_-) + C_- \Delta t \exp(-G_D \tau_o/M_-), \quad (3.10)$$

where N_M is the initial concentration, and $E_1(x) \equiv \int_x^\infty dy e^{-y}/y$ is the exponential integral. Because $M_- \sim 10^8$ pairs cm^{-3} for Ge at 2K, the argument of E_1 is large for experimentally detectable amounts Nv_- of EHD phase, and we can substitute the asymptotic expression $E_1(x) \approx e^{-x}/x$ into Eq. (3.10). This yields

$$(N_M - N)v_- \approx M_- \ln\{(N/N_M) + (NC_- v_- \Delta t/M_-) \exp[-(G_D \tau_o - N_M v_-)/M_-]\}. \quad (3.11)$$

Whenever N falls appreciably below the initial value N_M , the argument of the logarithm is large, and Eq. (3.11) becomes approximately

$$Nv_- \approx G_D \tau_o - M_- \ln(NC_- v_- \Delta t/M_-). \quad (3.12)$$

Note that N is independent of the initial drop concentration N_M whenever the breakup rate J_- is appreciable. As in the up-going case, Nv_- from Eq. (3.12) varies logarithmically with time Δt . However, because $M_- \ll M_+$, the magnitude of the decrease in Nv_- with time is expected to be much smaller.

These solutions demonstrate that the time required for the FE-EHD system to reach dynamic equilibrium can be extremely long. A lower limit to this time is that value of Δt for which the up-going and down-going EHD "signals" Nv from Eqs. (3.7) and (3.12) are equal.

For Ge assuming homogeneous nucleation, the equilibrium time is $\geq 10^{19}$ sec at 2.0K, and $\geq 10^7$ sec at 1.5K. Actual measurements,^{3.2} (see chapter 5) of the up-going and downgoing EHD luminescence signals in ultra-pure Ge vary logarithmically with Δt as predicted for times in excess of 4×10^3 sec, supporting our theoretical model.

33 Hysteresis and Thresholds

The up-going (UP) and down-going (DOWN) solutions, Eqs. (3.6) and (3.11) for the EHD signal N_V are plotted versus generation rate for Ge in Fig. 3.1. The upper portion of the down-going curve is obtained from the conservation equation, Eq. (3.1), with $N = N_M$. Here homogeneous nucleation is assumed. In this section and in those to follow we concern ourselves only with the EHD signal at the fixed time of observation $\Delta t = 50$ sec. The vertical scale of Fig. 1(a) is chosen so that this figure can be directly compared to data from sensitive EHD luminescence experiments on Ge,^{3.2,3.3} where the noise level is typically $\delta(N_V) \sim 3 \times 10^{10}$ pairs cm^{-3} . Hysteresis in the EHD signal N_V due to the history of excitation is clearly shown in Fig. 3.1(a). Additional drops created by the initially large excitation in the down-going case remain after the generation rate is reduced and cause the large separation between the two curves. Figure 3.1(a) is in good agreement with actual hysteresis data^{3.2} (see chapter 5) taken with the same history of excitation assumed here.

As shown in Fig. 3.1, both the up-going and down-going signals N_V display sharp thresholds, G_+ and G_- , in the generation rate. The

behavior of Nv near these thresholds is shown in detail by the inserts, Figs. 3.1(c) and 3.1(b), where the horizontal scale has been expanded 10 times and 1000 times respectively. From these graphs it is evident that we can define the thresholds G_+ and G_- by linearly extrapolating to zero the EHD signal above threshold, as shown by the dotted lines in Figs. 3.1(b) and 3.1(c). By comparing the asymptotic expressions, Eqs. (3.7) and (3.12), for N above threshold with the simple linear forms Eqs. (3.2) and (3.3) we find immediately:

$$G_+ = (M_+/\tau_o) \ln(M_+/C_+ v_+ \Delta t) , \quad (3.13)$$

$$G_- = (M_-/\tau_o) \ln(N_M C_- v_- \Delta t / M_-) . \quad (3.14)$$

In Eq. (3.14) we have substituted the initial value N_M for the down-going drop concentration N in order to make the definition of G_- unique. As shown in Fig. 3.1(b), where the dashed line assumes $N = N_M$, the variation of G_- with N is very small and can be neglected. As noted in chapter 2, the dependence of these thresholds on the time of observation Δt is quite small; for Ge at 2K, the thresholds G_+ and G_- from Eqs. (3.13) and (3.14) vary by only 10% and 0.1% respectively for a factor of 10^3 change in Δt .

By substituting the threshold FE densities $n_{\pm} = G_{\pm} \tau_x$ from Eqs. (3.13) and (3.14) into the original approximate expressions, Eqs. (3.4) and (3.8), for the rates of drop formation J_+ and breakup J_- , we can put the threshold condition into a more convenient equivalent form:

$$J_{\pm} v_{\pm} \Delta t = M_{\pm} \quad . \quad (3.15)$$

Using the exact expressions for J_{+} and J_{-} from chapter 2, Eq. (3.15) can be easily solved numerically for the thresholds n_{+} and n_{-} . Note that Eq. (3.15) is similar to the threshold condition $J_{\pm} \Delta t = N_{\min}$ used in chapter 2, except that the fundamental parameters M_{+} and M_{-} replace the experimental minimum detectable concentration of drops $N_{\min}$. Thus thresholds linearly extrapolated from experimental data can be directly compared to those calculated from Eq. (3.15) with no uncertainty introduced by the definition of threshold or by the sensitivity of the apparatus.

At low temperatures ($T \lesssim 1.3\text{K}$ for Ge, and $T \lesssim 4.0\text{K}$ for Si) the potential barrier to nucleation becomes ineffective, hysteresis in the EHD signal Nv disappears, and dynamic equilibrium is achieved rapidly. Under these circumstances, a sharp "equilibrium" threshold G_e in the generation rate will be observed when the equilibrium concentration of drops $N = h_s \Delta v$ becomes significant. In order to develop an expression for the threshold condition, we use the approximate form for the EHD signal in dynamic equilibrium,

$$h_s v \Delta v \approx C_e \exp(n \tau_o / M_e \tau_x) \quad , \quad (3.16)$$

where h_s and Δv are the value and width of the size distribution h_v at the stable size v (see chapter 2). As before, the coefficients C_e and M_e are determined by expanding the exact expression for $h_s v \Delta v$ about

the threshold to be defined; we find $M_e = n_e \tau_o / v_e \tau_x$, where n_e and v_e are the threshold values of the FE density and the stable drop size. Substituting n from Eq. (3.16) into the conservation equation, Eq. (3.1), we find

$$G\tau_o = M_e \ln(h_s v \Delta v / C_e) + h_s v \Delta v, \quad (3.17)$$

which can be solved for $h_s v \Delta v$ as a function of G . For values of the EHD signal $Nv < M_e$, the signal Nv from Eq. (3.17) is approximately given by $Nv \approx C_e \exp(G\tau_o / M_e)$. Because C_e is very small ($C_e \sim 5 \times 10^{-13}$ pairs cm^{-3} for Ge at 1.2K), the EHD signal bends upward very sharply at threshold and rapidly approaches a linear dependence on G . We define the equilibrium threshold $G_e = n_e / \tau_x$ as that value for which the derivative $d(h_s v \Delta v) / d(G\tau_o)$ is equal to 1/2. From Eq. (3.17) we thus obtain the threshold condition

$$h_s v_e \Delta v = M_e, \quad (3.18)$$

where h_s is given by either of the exact expressions, Eqs. (2.16) or (2.28), for the size distribution h_v in dynamic equilibrium. This threshold condition, Eq. (3.18), is easily solved numerically and does not involve experimental parameters.

34 Determination of the Surface Tension

At a given temperature, a measurement of the experimental threshold ratio G_+ / G_- can be used to make an accurate determination of the surface

tension of the e-h liquid. The procedure is to fit the ratio of numerical solutions of Eq. (3.15) for G_+ and G_- to the ratio of linearly extrapolated up-going and down-going thresholds from data analogous to Fig. 3.1 taken at a fixed time of observation Δt . To demonstrate that the threshold ratio accurately determines the surface tension, consider the simple case of homogeneous nucleation for $T \gtrsim 2.5K$ where the down-going threshold is not appreciably super-saturated, i.e. $n_-/n_s \approx 1$. Then we have approximately

$$\left(\frac{\sigma}{kT}\right)^3 \approx \frac{3}{16\pi} [n_o \ln(n_+/n_-)]^2 \ln(J_o v_+ \Delta t / M_+) , \quad (3.19)$$

where J_o is the coefficient of the exponential factor in J_+ from Eq. (2.24). The value of σ from Eq. (3.19) is sensitive only to the experimentally well known values of n_+/n_- , n_o , and T . Because the logarithm is ~ 50 , uncertainties of several orders of magnitude in the parameters contained in the argument lead to only small errors in σ . At temperatures $T \lesssim 2.5K$, the down-going threshold n is also supersaturated, and the value of σ depends upon the additional parameters τ_o and the evaporation coefficient α_v (see chapter 2).

Graphs for Ge of the value of the surface tension σ versus the threshold ratio G_+/G_- are shown in Fig. 3.2. These values were calculated from the threshold condition Eq. (3.15) and the exact expressions, Eqs. (2.24) and (2.25), for the rates of drop formation J_+ and breakup J_- ; the values of parameters other than σ are given in Table 3.1. As shown in Fig. 3.2, the value of σ deduced from a given

threshold measurement G_+/G_- depends surprisingly little upon whether nucleation is assumed to be homogeneous, Fig. 3.2(a), or inhomogeneous, Fig. 3.2(b). These figures also demonstrate the accuracy of this method for determining the surface tension. The curves intersect the vertical axis for $G_+/G_- = 1$ at nonzero values of σ , because dynamic equilibrium is rapidly established if σ is not sufficiently large. Thus, from the single fact that hysteresis is observed in Ge at 1.5K^{3.2,3.3,3.19,3.20} (see also chapter 5), we can conclude that $\sigma \gtrsim 2.1 \times 10^{-4}$ erg cm⁻² at this temperature. Using the procedure described in this section, the author, Staehli, and Haller^{3.2,3.3} have made what we believe is the first reliable measurement of the EHD surface tension in Ge, $\sigma = (2.4 \text{ to } 2.8) \times 10^{-4}$ erg cm⁻² at $T = 0$. This value agrees with the more reliable measurement $\sigma = (2.6 \pm 0.3) \times 10^{-4}$ erg cm⁻² at $T=0$ obtained by fitting the EHD-FE phase diagram as described in chapter 5.

35 Modified Phase Diagram

Previously,^{3.8,3.20,3.21} the low density boundary of the FE-EHD phase diagram was assumed to be given by the saturated FE density n_s (see chapter 2). From the foregoing discussion it is clear that metastability and the EHD lifetime have a major effect on the regions of stability of the FE-EHD system. We can construct a modified "phase diagram" which correctly accounts for these effects by plotting the thresholds $n_{\pm} = G_{\pm} \tau_x$ from section 3.3 versus reciprocal temperature. The results for Ge are shown in Fig. 3.3 for both the homogeneous and inhomogeneous cases. The values of n_+ and n_- were obtained by

numerically solving the threshold condition Eq. (3.15). Both the up-going and down-going thresholds, Figs. 3.3(a) and 3.3(b) respectively, occur at FE densities well above the saturated value n_s , Fig. 3.3(c). Drops are always present when the FE density n exceeds n_+ , and are never present when $n < n_-$. In the region between the up-going and down-going thresholds, the presence of drops depends upon the history of excitation. As explained in chapter 2 and section 3.2, the variation of the thresholds n_+ and n_- is relatively small for times of observation in the range $10 \mu\text{sec} < \Delta t < 100 \text{ sec}$. Significant changes in n_+ and n_- with Δt occur only near the point where the two curves join. Thus the up-going curve of Fig. 3.3 applies to experiments performed with pulsed excitation (pulse risetime $\gtrsim 10 \mu\text{sec}$), as well as those with continuous excitation.

At temperatures below 2K the separation of the up-going and down-going thresholds, Figs. 3.3(a) and 3.3(b), decreases, disappearing at 1.3K for the homogeneous case and at 1.4K for the inhomogeneous case. For lower temperatures the FE-EHD system is in dynamic equilibrium, and the threshold for drop formation in Fig. 3.3 is given by the equilibrium threshold n_e from solutions of Eq. (3.18). In addition, the curves increasingly deviate from the saturated FE density, Fig. 3.3(c), as the temperature is lowered; near $T \sim 1\text{K}$ the equilibrium threshold becomes nearly temperature-independent. Both these phenomena are caused by the presence of the lifetime term in ψ_v , the effective free energy difference between a drop of size v and v free excitons, as explained in chapter 2. Preliminary measurements^{3.2,3.3,3.19} for Ge of the up-going and down-going thresholds in

excitation level versus temperature display all of the qualitative features of Fig. 3.3, supporting this theoretical model. In chapter 5 we find excellent quantitative agreement between theory and threshold data.

Contrary to what one might expect, the phase diagrams obtained by assuming homogeneous and inhomogeneous nucleation are quite similar. The primary effect of the binding energy B_v of drops to impurities (see chapter 2) is to reduce the supersaturation ratio of the up-going threshold, Fig. 3.3(a), at low temperatures and thereby increase slightly the temperature at which hysteresis disappears. The value of the barrier lowering due to impurities $\Delta\psi = B_v - kT\ln Z$ (see chapter 2) was assumed to be temperature independent in calculating Fig. 3.3. It is possible that impurities saturate with small exciton complexes before macroscopic drops form. If this is so, then the temperature dependence of the term $kT\ln Z$ in $\Delta\psi$ could be important at low T . Finally note that the similarity of the two phase diagrams of Fig. 3.3 makes difficult the experimental determination of the type of nucleation from the temperature dependence of threshold data.

As discussed in chapter 1, previous threshold measurements^{3.8,3.20,3.21} of the EHD condensation energy ϕ were made by fitting data apparently taken on the up-going curve, Fig. 3.3(a), to the saturated FE density, Fig. 3.3(c). The values obtained, typically $\phi \approx 17K$, disagree with the spectroscopic measurements,^{3.4,3.8,3.9} typically $\phi \approx 23.5K$ at $T=2K$, which were used in calculating Fig. 3.3. The apparent value of ϕ deduced in this way from the slope of the up-going threshold, Fig. 3.3(a),

between 2K and 4K is $\phi \approx 15\text{K}$. As pointed out earlier,^{3.2,3.3} the failure to understand and use hysteresis effects seems to explain the apparent discrepancy between spectroscopic the older threshold measurements of the condensation energy.

When the temperature-independent evaporation rate^{3.22} $c v^{2/3}$ is included in the calculation as discussed in chapter 2, the thresholds are modified. Figure 3.4 illustrates the effect of this term on the phase diagram in Ge for various values of the coefficient c . For $c < 5 \times 10^4 \text{ sec}^{-1}$ the calculated thresholds between 1.25K and 2K are practically independent of c . However, as c increases from $5 \times 10^4 \text{ sec}^{-1}$ to $5 \times 10^6 \text{ sec}^{-1}$, the low-temperature plateau of the phase diagram moves to higher FE density, the threshold separation decreases, and the temperature at which hysteresis disappears increases. As discussed in chapter 5, actual low temperature threshold data show evidence for these effects, and a fit of theory to these data yields $c \sim 10^5 \text{ sec}^{-1}$.

Phase diagrams for the FE-EHD system in Si, calculated in the same way as for Ge, are shown in Fig. 3.5. These curves exhibit all of the qualitative features of the phase diagrams for Ge, Fig. 3.3. These features occur at higher temperatures simply because the condensation energy for Si^{3.8} $\phi \approx 79\text{K}$ is approximately 4 times greater than for Ge. Because the values of the parameters used to calculate Fig. 3.5 were not as well established as those for Ge, these phase diagrams are expected to be less accurate than Fig. 3.3. However, these values have been somewhat justified by recent measurements and calculations as discussed in the introduction to this chapter. The largest error

expected in Fig. 3.5 is that due to the value used for ϕ , which was $\sim 16\text{K}$ smaller than the recent measurement^{3.10} $\phi = 95\text{K}$ at $T=0$. Nevertheless, these phase diagrams display two qualitative features of major interest. First, metastability of the FE-EHD system in Si disappears for temperatures below $T \approx 5\text{K}$; thus no hysteresis effects are expected at liquid He temperatures. Second, and more importantly, the threshold for drop formation in Si below 5K occurs at a measurably high FE density, $n_e \sim 2 \times 10^{13} \text{ cm}^{-3}$, which is approximately temperature independent. If drop formation occurred at the saturated FE density, the threshold at 2K would be unphysically small, $n_s \approx 0.6 \text{ cm}^{-3}$. To our knowledge no measurements have been reported of the phase diagram in Si which could be directly compared to Fig. 3.5. However, EHD thresholds have apparently been observed^{3.8} at 2K for moderate levels of excitation. Also threshold measurements^{3.23} at temperatures above 15K agree reasonably well with the threshold FE densities shown in Fig. 3.5.

36 Drop Radius

A plot of the EHD stable radii at the up-going (UP) and down-going (DOWN) thresholds, R_+ and R_- respectively, is shown for Ge in Fig. 3.6. Below $T \sim 1.3\text{K}$ hysteresis vanishes and the drop radius shown is R_e , the value at the equilibrium threshold. The values of R_+ , R_- , and R_e were numerically computed from the expression Eq. (2.17) for the free energy difference ψ_v at the FE density thresholds shown in Fig. 3.3. The distribution of drop sizes is very sharply peaked about the stable

radius; at 2K the width is only $\delta R_+ \sim 1 \times 10^{-3} \mu\text{m}$. The radii predicted for homogeneous, Fig. 3.6(a), and inhomogeneous nucleation, Fig. 3.6(b), are quite similar, a consequence of the similarity of the phase diagrams, Fig. 3.3, for the two cases. As explained in chapter 2, the stable drop radius R is determined by the density of the surrounding FE gas. Above $T \sim 1.5\text{K}$ the following approximate expression^{3.8} is valid:

$$R \approx r_o \beta \tau_o (n - n_s) , \quad (3.20)$$

where $\beta \equiv \pi r_o^2 (8kT/\pi m^*)^{1/2}$ is the coefficient of the rate at which FE are absorbed by the drop. The strong temperature dependence of the radii shown in Fig. 3.6 is thus a direct consequence of the variation of the FE density thresholds with temperature, Fig. 3.3.

In an actual experiment one would expect to observe the radii shown in Fig. 3.6 only if the excitation level were very slowly and smoothly varied as described in section 31. If the excitation is increased more rapidly in the up-going case, a larger number of drops smaller than R_+ form, and the drop size depends upon the risetime and magnitude as well as the history of the excitation.^{3.16} Thus, under more general circumstances, the up-going and down-going radii of Fig. 3.6 are upper and lower limits to the steady state drop size. Drop radii observed in experiments using intense focussed excitation^{3.17} and short laser pulses^{3.6} are most likely determined by mechanisms other than nucleation.

At temperatures above $T \sim 2.5\text{K}$, the calculated up-going radius R_+ shown in Fig. 3.6 becomes quite large. Because the decay of e-h pairs

within a drop must be supplied by diffusion of excitons to its surface, the radius of a large drop is limited by the local depletion of FE. We can find the diffusion-limited up-going radius R_D by solving the steady-state diffusion equation. The appropriate boundary conditions on the FE density $n(r)$ are $n = n_+$ for $r \rightarrow \infty$, and $(4\pi R_D^2)dn/dr = v/\tau_0$ for $r = R$, where D is the diffusion constant. The latter condition states that the current of FE to the drop surface equals the decay rate v/τ_0 . Using Eq. (3.20) for the drop radius we find

$$R_D \approx \frac{1}{2} \frac{3D}{r_0 \beta n_0} \left\{ -1 + \left[1 + \frac{4r_0 \beta \tau_0 (n_+ - n_s)}{(3D/r_0 \beta n_0)} \right]^{1/2} \right\}. \quad (3.21)$$

This expression reduces to Eq. (3.20) at low temperatures. Below threshold at 3K the FE diffusion constant in Ge is^{3.8} $D \sim 1500 \text{ cm}^2 \text{ sec}^{-1}$ due to phonon scattering. At higher temperatures where the FE density above threshold is large, D must be determined by self diffusion. From the simple kinetic theory of gases the self-diffusion constant is

$$D = (4kT/\pi m^*)^{1/2} / 3cn_+, \quad (3.22)$$

where we use $c \sim 5 \times 10^{-11} \text{ cm}^2$ for the FE-FE collision cross section.

Because the drop radius varies from 0 to R_+ as n increases by only ~50% from n_s to n_+ , we have substituted the threshold value n_+ into Eq. (3.22). The resulting error in the computed radius is ~25%. The diffusion limited radius calculated from Eqs. (3.21) and (3.22) is

shown as the dashed curve in Fig. 3.6. While ineffective below $T \lesssim 2.5\text{K}$, FE diffusion limits the drop radius at higher temperatures to the nearly constant value $R_D \approx 15 \mu\text{m}$. The curve R_D in Fig. 3.6 is in reasonable agreement with the light-scattering measurements of Bagaev et al.^{3.24} Using volume excitation chopped at 1 kHz, they found that the drop radius increased from $R = 4 \mu\text{m}$ at 2.6K to $R = 10 \mu\text{m}$ at 3.5K. Because the risetime of their pulsed excitation is shorter than the minimum value for which Fig. 3.6 is directly applicable, it is reasonable that their measurements of R lie somewhat below R_D (see above).

As shown in Fig. 3.6, at low temperatures the drop radii R_+ , R_- , and R_e become quite small; R_e approaches $0.02 \mu\text{m}$ at $T = 1\text{K}$, which corresponds to the size $v \sim 10$ e-h pairs. As the drop radius becomes small, the fraction $\sim 3r_0/R$ of e-h pairs within the surface thickness $\sim r_0$ of the drop becomes significant, causing a change in spectroscopic lineshape and a shift to higher energy of the EHD luminescence. This effect has been observed experimentally by Etienne et al.^{3.25} who accounted for the existence of hysteresis. They deduced down-going drop radii increasing from $R_- \approx 0.025 \mu\text{m}$ at 1.43K to $R_- \approx 0.1 \mu\text{m}$ at 2.0K. These values of R_- are a factor of 2 to 3 smaller than those of Fig. 3.6, but show the correct temperature dependence. Although the analysis in Ref. 3.25 seems questionable, their data indicate that drop radii do indeed become quite small at low temperatures in agreement with our theoretical prediction.

CHAPTER 4. EXPERIMENTAL APPARATUS

All of the experimental results presented in this thesis were obtained by studying the near-infrared luminescence of electron-hole drops and free excitons in optically excited Ge. This method of excitation and detection of EHD and FE offers the advantages of flexibility, very high sensitivity, and unambiguous identification of the species of interest. A simplified schematic diagram of the apparatus is shown in Fig. 4.1. This diagram can be divided into three basic functional blocks: the source of excitation, consisting of the tungsten lamp, the Ge monitor detector, and associated optics and electronics; the samples, cooled to liquid He temperatures in an optical cryostat; and the detection apparatus, consisting of the spectrometer, the Ge luminescence detector, and the signal processing electronics. These three functional blocks will be described in detail in sections 41, 42, and 43, respectively.

The fact that this apparatus was used to study hysteretic phenomena in the EHD-FE system placed a number of highly unusual constraints on the design of its components. As we show later, the state of the FE-EHD system in Ge is sensitive to the entire history of excitation of the sample for times as long as $\sim 10^6$ sec preceeding a measurement, even though the response times of this system are of the order of 10^{-6} sec. Thus the excitation must be cycled in an accurately reproducible manner as illustrated in Fig. 4.1 and described in chapter 3, and the source of excitation must be nearly noise-free.

In order to study the metastable time development of the EHD luminescence intensity for periods of time of the order 10^3 sec, the excitation level and temperature must be carefully stabilized. Similarly the Ge samples must be free of any external mechanisms such as electrical contacts, which are known to destroy drops and thus erase the memory of the system. Considerable effort was also expended developing a very high sensitivity luminescence detection apparatus in order to study the FE-EHD system near threshold at temperatures below 2K, where the luminescence signals are exceedingly small.

41 Optical Excitation

When a crystal of ultrapure Ge at liquid He temperatures is illuminated by visible or near-infrared radiation, free carriers are excited; in this wavelength range one electron-hole pair is created for each photon absorbed. If the photon energy is greater than the direct energy gap. $E_{\text{gap}}^d \approx 890$ meV, this process can occur without phonon emission, and the absorption length of the radiation is correspondingly short, $\ell \lesssim 1$ μm ; we refer to this case as surface excitation. The electrons thus created rapidly relax to the indirect band edge and form free excitons within several μm of the illuminated surface. These excitons subsequently move ~ 1 mm into the crystal and recombine. Assuming this motion is diffusive, the spatial form $n(\vec{x})$ of the steady-state FE concentration below the threshold for drop formation is determined by the diffusion constant^{4.1} $D \approx 1500$ $\text{cm}^2 \text{sec}^{-1}$ at 3K and the FE lifetime $\tau_x \sim 5$ μsec , and $n(\vec{x})$ is everywhere proportional

to the e-h pair generation rate G at the surface. Thus we can establish a quantitative relationship between the exciton concentration $n(\vec{x})$ and the excitation level. A more direct method of excitation occurs if the incident photon energy is less than the direct gap E_{gap}^d , but substantially greater than the indirect gap $E_{\text{gap}}^i \approx 744$ meV. Then direct absorption is impossible, but electrons can be excited into the energy minimum at the zone edge. Because this process involves phonon emission, the absorption length is much longer, $\ell \gtrsim 0.1$ mm; we refer to this case as volume excitation. For the lowest excitation levels used in these experiments, the formation time of FE in this case is still very short ($\lesssim 1$ μ sec). However the FE diffusion length $L = \sqrt{D \tau_x} \sim 1$ mm can be made comparable to or smaller than ℓ by using the longest wavelength light which gives a reasonable level of excitation. If $\ell \gtrsim L$ the spatial form of $n(\vec{x})$ is determined primarily by the volume generation rate $G(\vec{x})$, and effects of FE transport are minimized.

For either type of excitation, the fundamental concept relating experiment to nucleation theory is that the incident radiation creates in the Ge crystal a FE gas of concentration $n(\vec{x})$ which, below threshold, is everywhere proportional to the excitation level.

Volume excitation is clearly preferable for studies of EHD nucleation phenomena, and was used whenever possible in taking the data presented in this thesis. This method of excitation minimizes the influence of possible undesirable surface effects such as the trapping of generated e-h pairs and the destruction of FE. Also, data taken in

this way can be directly compared with the nucleation theory of chapters 2 and 3, which assumes a spatially uniform FE gas, and the difficult problem of analyzing the coupled transport of FE and drops from the excited surface can be partially avoided. Finally, it was deemed necessary to use volume excitation in order to prove conclusively that the observed luminescence hysteresis was an intrinsic property of the FE-EHD system itself, not an artifact related to the sample surfaces.

As mentioned in the introduction to this chapter, the study of nucleation phenomena in the EHD-FE system imposes important restrictions on the manner in which the samples can be excited. The theoretical reasons for these restrictions are the excitation memory inherent in hysteretic effects and the metastable time variation of the EHD signal for a given fixed excitation level. The most obvious way to generate hysteresis curves for the EHD luminescence intensity I_d vs. excitation level P is to continuously record I_d as P is slowly swept from zero to a maximum value P_{max} , then back to zero; this method was used in previous work.^{4.2,4.3} However, because I_d varies with time, the results obtained depend upon the sweep rate in a complicated way, and cannot easily be compared with theory. Therefore, the data presented in this thesis were taken point-by-point as described in chapter 3 and illustrated in Fig. 4.1. Each "upgoing" (UP) point was taken by slowly and monotonically increasing the excitation from zero to a constant value P , recording the EHD signal I_d , then returning the excitation to zero to erase the memory of the system. This cycle is then repeated for different values

of P . Each downgoing (DOWN) point was taken by initially increasing the excitation from zero to a maximum value $P_{\max}$, then monotonically decreasing the excitation to a constant value P at which I_d is recorded, then returning to $P=0$; the cycle is repeated with the same value for $P_{\max}$, but different P . Because the EHD-FE system rapidly responds to and "remembers" changes in P ($\tau_x \sim 5 \mu\text{sec}$), the variation of P with time must be accurately monotonic, and the source of excitation must be free of noise spikes. Also, the final EHD signal recorded has been shown theoretically^{4.4} (see chapter 3) and experimentally^{4.5} to be sensitive to the rate of change of the excitation, if this rate is too rapid. In chapter 3 we found that I_d is expected to depend upon the leading edge of an exciting pulse at 2K for risetimes shorter than only 0.04 sec. Therefore changes in the up- and downgoing excitation cycles must be made very slowly and reproducibly, as shown in Fig. 4.1, in order to obtain reproducible results. Finally the excitation P must be held accurately constant for times $\sim 10^3$ sec in order to measure very small metastable changes in the EHD luminescence intensity with time.

These excitation requirements were met with a system, shown in Fig. 4.1, based upon a tungsten-halogen lamp. This light source has the advantages of intrinsic stability and low noise, and can be easily electronically regulated. The lamp radiates as a black body of temperature T roughly proportional to the input power; at the maximum operating temperature $T \approx 3200\text{K}$, the photon flux spectrum is peaked at the wavelength $\lambda \approx 2.8 \mu\text{m}$, and falls exponentially for shorter λ .

Because the useful wavelengths are shorter than $1.6 \mu\text{m}$, the usable lamp output is a highly non-linear function of the input voltage, and feedback regulation is desirable. The actual lamp used was a 12V, 100W, tungsten-iodide projection lamp with a fused Quartz envelope, manufactured by Eumig, model P8 Novo. Any tungsten-halogen lamp with a small, closely wound filament and similar characteristics would be suitable. This lamp was mounted in a fan-cooled chimney; the light was collected and refocused by two aspheric plano-convex Quartz lenses of focal length 3" and diameter 3", mounted with their convex sides facing. The light beam was approximately collimated by a double-concave glass lens of focal length 38 mm and diameter 33 mm, positioned near the focal point of the second Quartz lens; the final beam diameter thus obtained was $\approx 2 \text{ cm}$.

Volume excitation was achieved by passing the collimated light beam from the lamp through a four-cavity interference filter of bandpass (FWHM) 40 nm centered about the wavelength $\lambda = 1.52 \mu\text{m}$ as shown in Fig. 4.1. This value of λ was selected such that the photon energy $\approx 810 \text{ meV}$ was slightly smaller than the direct energy gap in Ge at 4.2K; thus absorption is an indirect process as described earlier. The bandwidth was chosen to insure that a negligible fraction of the radiation was surface absorbed, and also to limit the amount of light transmitted through the Ge samples, typically 3 mm thick. In addition, a 1 cm thick disc of antireflection coated high-purity Si was placed in the light beam to remove remnants of surface-absorbed radiation of wavelength $\lesssim 1.0 \mu\text{m}$. A measurement of the resulting

excitation spectrum is shown in Fig. 4.2. The measured value of the absorption length of this radiation in ultra-pure Ge at 4.2K increased from 0.85 mm to 1.30 mm over the bandpass (FWHM) of the interference filter. Thus the generation rate G ($\text{cm}^{-3} \text{sec}^{-1}$) of e-h pairs within uniformly illuminated Ge samples is well approximated by the expression

$$G(x) = G_0 \exp(-x/\ell) , \quad (4.1)$$

where $\ell \approx 1.1$ mm, x is the distance from the illuminated surface, and $G_0 = P/h\nu\ell$, with P (W cm^{-2}) the absorbed excitation power density and $h\nu$ the mean photon energy. The maximum total power attainable with this apparatus was ≈ 5 mW, measured after the interference filter.

The steady-state FE concentration $n(x)$ produced below EHD threshold by the generation rate $G(x)$ from Eq. (4.1) can be calculated by solving the one-dimensional FE diffusion equation. Assuming that the surface recombination rate of FE is negligible (see section 42), the appropriate boundary condition at $x=0$ is $dn/dx = 0$; i.e. the net current of FE is zero at the surface. Then

$$n(x) = G_0 \tau_x \frac{\ell/L}{1-(\ell/L)^2} [\exp(-x/L) - (\ell/L)\exp(-x/\ell)] \quad (4.2)$$

where $L = (D\tau_x)^{1/2}$ is the FE diffusion length. From this expression we find that $n(x)$ is practically constant near the illuminated surface; with $L = 0.7$ mm, the FE concentration at $x=0.5$ mm is only 10% smaller than that at $x=0$. Thus this method of volume excitation creates a nearly uniform concentration of FE in a relatively large volume of the

excited crystal.

When a total power larger than that possible with 1.52 μm radiation was required, surface excitation was employed. This was achieved by replacing the Si and interference filters shown in Fig. 4.1 by a 7 cm thick filter of distilled water; otherwise the apparatus was unchanged. The water filter attenuates radiation of wavelength greater than 1.4 μm by a factor in excess of 10^{15} ; thus the power transmitted through the Ge sample to the detector is negligible and cannot obliterate the desired luminescence signals. The result is a smooth broad excitation spectrum which varies somewhat with excitation power; the photon flux increases with λ through the visible range, peaks at $\lambda \approx 0.85 \mu\text{m}$, and is cut off for $\lambda \gtrsim 1.0 \mu\text{m}$. At the peak wavelength, the absorption length in Ge at 4.2K is $\ell \approx 0.5 \mu\text{m}$; the value of ℓ varies from $\ell \approx 0.1 \mu\text{m}$ at $\lambda = 500 \text{ nm}$ to $\ell \approx 1.0 \mu\text{m}$ at $\lambda = 1.0 \mu\text{m}$. No evidence of e-h trapping due to surface states was observed with this excitation spectrum, i.e. the FE luminescence intensity was accurately proportional to P below threshold at all temperatures below 4.2K. Neglecting surface recombination, the steady state FE density profile $n(x)$ is given by Eq. (4.2) in the limit $\ell \ll L$:

$$n(x) = (G_0 \ell \tau_x / L) \exp(-x/L), \quad (4.3)$$

where $G_0 \ell \approx P/h\nu$, with $P(\text{W cm}^{-2})$ the absorbed power density and $h\nu$ the photon energy corresponding to $\lambda = 0.85 \mu\text{m}$. Note that $n(x)$ from Eq. (4.3) decreases linearly with x near the sample surface; thus the region of uniform FE concentration is much smaller than for volume excitation.

The maximum total power attainable in this case was ≈ 200 mW, measured after the water filter.

For both volume and surface excitation, the light beam was focussed onto the Ge sample mounted in an optical cryostat by an aspheric plano-convex Pyrex condenser of focal length 65 mm and diameter 72 mm, as shown in Fig. 4.1. The size of the excitation beam on the Ge crystal was adjusted by varying the position of the Pyrex lens to be approximately $1 \text{ cm} \times 1 \text{ cm}$, several times the size of the sample; thus the entire front surface of the sample was uniformly illuminated in all cases. This excitation geometry is highly favorable for threshold measurements on the EHD-FE system. As the excitation is increased an entire plane inside the crystal passes through the threshold FE concentration at once, vs. a simple point for spot excitation; therefore the EHD luminescence, collected from the entire crystal, displays a sharper threshold. This geometry greatly increases the sensitivity of the apparatus, by increasing the sample volume occupied by FE and EHD.

An essential feature of this apparatus is the accurate measurement of the e-h pair generation rate within the Ge sample, and thus the FE concentration. This was achieved by using a Ge monitor detector as shown in Fig. 4.1. Approximately 10% of the exciting radiation was removed from the beam by a thin plate-glass beamsplitter and focussed onto the detector by an aspheric Pyrex condenser of focal length 65 mm and diameter 72 mm. The detector itself was a large ($10 \times 10 \times 3 \text{ mm}^3$) p-i-n photodiode fabricated from ultrapure Ge by E. E. Haller at Lawrence Berkeley Laboratory, mounted in vacuum, cooled to approximately 80K in a small liquid N_2 cold-finger dewar, and reverse biased

with 15V. The mounting geometry was such that the radiation entered a $3 \times 10 \text{ mm}^2$ face of the detector and passed between the junctions, which were applied to the $10 \times 10 \text{ mm}^2$ sides; thus the monitor is sensitive to volume absorbed light. Under these conditions the diode current I is proportional to the total rate of generation of carriers within the intrinsic region. Because the monitor was made of the same material as the Ge samples, the monitor current I_M is insured to be accurately proportional to the total carrier generation rate within the excited samples as desired. This characteristic is important for surface excitation, where the spectral character of the light varies with excitation level.

In order to relate the monitor current to the absolute FE concentration in the samples, the excitation apparatus was calibrated with a Scientech 1 inch optical calorimeter. This instrument measures optical power and has a flat wavelength response from the ultra-violet to the far infrared. The calorimeter was placed after the empty dewar in the position occupied by the chopper in Fig. 4.1, and recorded the total excitation power transmitted through a hole in the sample holder from which the Ge sample had been removed, otherwise the optics were identical to those used for taking data. The resulting reading was corrected for the transmission of the three exit windows of the dewar and the exit lens, assuming a 10% loss in each element. The absorbed power density $P(\text{mW cm}^{-2})$ was then calculated from the area of the hole, 0.25 cm^2 , and the ideal transmission of one Ge surface, 64%. For volume excitation, the result was

$$P(\text{mW cm}^{-2}) = 0.079 I_M(\mu\text{A}) . \quad (4.4)$$

For surface excitation with $I_M \sim 50 \mu\text{A}$,

$$P(\text{mW cm}^{-2}) = 0.144 I_M(\mu\text{A}) . \quad (4.5)$$

The difference between these results is entirely accounted for by the difference between the average photon energies, $h\nu = 0.816 \text{ eV}$ and $h\nu = 1.46 \text{ eV}$ respectively. Finally, the peak FE concentration within the samples was calculated from Eq. (4.4) or (4.5) by using Eq. (4.2) or (4.3) respectively, with the result for volume excitation:

$$n(0) = (P\tau_x/h\nu)/(\ell + L), \quad (4.6)$$

and for surface excitation:

$$n(0) = P\tau_x/h\nu L . \quad (4.7)$$

The value of τ_x was measured in each sample used, and the value^{4.1}
 $D = 1500 \text{ cm}^2 \text{ sec}^{-1}$ was used for the FE diffusion constant which was assumed to be temperature-independent; together these numbers determine $L = (D\tau_x)^{1/2}$. The overall absolute accuracy of this calibration procedure for volume excitation is probably limited to roughly a factor of two by uncertainties in the diffusion model for the transport of FE, the value of D , and the unknown mechanism which determines τ_x . For surface excitation only, the possible surface recombination of FE introduces an additional source of error which could be quite large.

Control of the excitation level during an experiment was automated by a specially-constructed electronic apparatus which accomplished two major goals in the design of this system: 1) feedback stabilization of the excitation, and 2) accurately reproducible cycling of the excitation level. As shown in Fig. 4.1, feedback stabilization was achieved by comparing the output of the monitor detector to the output of a reference function generator, and by using the amplified difference to control the voltage of a programmable DC power supply (Hewlett-Packard/Harrison model 6260A) which drove the tungsten lamp.

A block diagram of the electronic apparatus constructed showing the connections to other equipment is given in Fig. 4.3. Circuit diagrams for the four basic functional blocks shown in Fig. 4.3, the reference function generator, the current amplifier for the monitor detector, the variable-gain differential amplifier, and the timing logic, are given in Figs. 4.4a to 4.4c and Fig. 4.5 respectively.

Stabilization of the lamp output to the level determined by the function generator was accomplished by the current and the differential amplifiers. The current amplifier, Fig. 4.4b, is in a standard configuration, with selectable full scale currents of 0.1, 1, 10, and 100 μ a corresponding to 1V output. A separate current range switch is enabled while logic signal L1 is high, so that the initial excitation in the downgoing case can be set at a level much larger than that at which the signal is recorded. The differential amplifier, Fig. 4.4c, consists of two operational amplifiers, one wired for a fixed voltage gain of 10, and one with a gain adjustable from 1 to 100, so that the total gain

can be varied from 10 to 1000. The output V_{PS} is clipped at 12.5V and -0.6V by the Zener diode to protect the lamp and the power supply.

In order to achieve the best regulation the gain was set at the largest value at which the feedback system was stable, determined by monitoring the voltage V_I on an oscilloscope during an excitation cycle. The values of feedback gain thus determined were ≈ 200 for volume excitation and ≈ 125 for surface excitation. With these gain settings the performance of the system was excellent: the unregulated drift in the lamp output, $\approx 5\%$ in 10^3 sec at worst, was reduced by the feedback circuit to less than 0.05% in 10^3 sec. Thus very small changes in EHD luminescence over times $\sim 10^3$ sec could be measured with confidence, as required in the study of the metastable behavior of the EHD-FE system.

Manipulation of the lamp output to create accurately reproducible cycles of excitation such as those shown in Fig. 4.1 was controlled by the reference function generator, Fig. 4.4a, and the timing logic, Fig. 4.5. The output V_R of the function generator can be switched to any one of three DC levels, each independently adjustable from 0 to 1V, by logic signals L1 to L3; the time for which each level is enabled is controlled by switches SW1 to SW3 in Fig. 4.5 and can be independently varied from 1 sec to 2048 sec. Normally signal L0 is high and the reference voltage V_R is grounded; an excitation pulse is created by successively switching V_R to one or more levels. The order in which these levels are enabled is controlled by the mode switch, Fig. 4.5, and can be set in the sequences L0, L3, L0; or L0,L1,L3,L0; or L0,L1,L2,L3,L0. In all cases L1 corresponds to the large initial excitation

for taking a "downgoing" data point, and L3 corresponds to the final level at which the signal is recorded. Thus the sequence L0,L3,L0 yields an "upgoing" (UP) point, and the sequence L0,L1,L3,L0 yields a "downgoing" (DOWN) point as shown in Fig. 4.1. Steps in the output V_R , Fig. 4.4a, are smoothed by a buffered RC filter with selectable time constants of 1, 3, and 10 sec, so that the excitation pulse has a very long risetime as required, and V_R changes exponentially from one level to the next. In order to ensure that the excitation decreases monotonically from L1 to L2 or L3, when the two current range switches, Fig. 4.4b, have different settings, V_R can be preset to $\approx 150\%$ of full scale by the 1 msec pulse SR at the falling edge of L1.

The timing logic shown in Fig. 4.5 also controlled the operation of a Northern Scientific model NS-905 multi-channel analyzer (MCA), which was used to integrate the luminescence signals. A list of the connections between the timing logic and the MCA is given in Table 4.1. At the beginning of each cycle, initiated by closing the "start" switch, the pulse $\overline{EP}$ advances the MCA memory channel addressed. The excitation then cycles as described above; when level L3 is reached, either $\overline{EADD}$ or $\overline{ESUB}$ is enabled after a delay determined by the switch SW4, which allows the excitation to reach a constant level. These signals cause the MCA to respectively add or subtract data into the memory channel addressed, integrating the signal as indicated in Fig. 4.1. Thus the data-taking procedure was very simple: in order to automatically cycle the excitation and record the signal it was only necessary to set the final excitation desired and depress the start button.

42 Germanium Samples

An essential aspect of the experimental work reported in this thesis is the investigation of the influence of impurities and of various other crystal defects on nucleation phenomena by the study of number of well-characterized Ge crystals. Such defects could, in principle, dominate the character of the observed hysteresis data and make comparison with theory to obtain the EHD surface tension and other parameters difficult. In fact, we find experimentally that the various defects present in ultrapure Ge have surprisingly little effect on hysteretic phenomena, easing comparison with theory and proving that these hysteresis effects are intrinsic to the FE-EHD system.

All of the measurements reported here were made on crystals of ultrapure Ge grown by W. L. Hansen and E. E. Haller of Lawrence Berkeley Laboratory. The method of production is described in detail elsewhere.^{4.6} Briefly, polycrystalline starting material is first zone-refined, then melted in a Quartz crucible in H_2 gas from which single-crystal boules of Ge are pulled by the Czochralski method. Because most of the material is used for particle detectors, exceptional care is exercised in the growing process to eliminate deep traps for free carriers. The crystals have been carefully studied by Far-infrared Fourier-transform spectroscopy^{4.6} in order to identify the various impurities present. These crystals contain primarily shallow impurities; the dominant acceptor is Al with an ionization energy of 10.2 meV, and the dominant donor is P with the ionization energy 12.0 meV. The net impurity concentration $|N_A - N_D|$ typically lies in the range 10^9 cm^{-3} to 10^{12} cm^{-3} ,

and the total impurity concentration $N_A + N_D = N_i$ is found to be less than 10 times larger than $|N_A - N_D|$ from measurements of the impurity profiles along the length of a boule; thus the crystals are not highly compensated and the material is truly ultrapure. As discussed in chapter 2, neutral impurities can influence the nucleation of EHD by binding small multi-exciton complexes and droplets, lowering the potential barrier ψ_c to drop growth by the amount $\Delta\psi \approx B$, the binding energy of a macroscopic drop to one impurity atom. Recently the value of B has been calculated by several authors^{4.7,4.8} with the results $B \approx 5$ to 10 meV for shallow donors. These results justify the estimate $B \approx 4.3$ meV used in the calculations for inhomogeneous nucleation in chapter 3.

Dislocations also have an important role in determining the properties of the Ge crystals used; some boules contain concentrations $\sim 10^2 \text{ cm}^{-2}$ to $\sim 10^4 \text{ cm}^{-2}$ of these defects whereas others are essentially dislocation-free. In dislocation-free Ge, lattice vacancies formed during growth precipitate into vacancy clusters and the resulting material always has 80 meV deep p-type traps of concentration $(2 \text{ to } 4) \times 10^{11} \text{ cm}^{-3}$, believed to be associated with divacancy-hydrogen complexes.^{4.9} Dislocations, if present in concentration $\gtrsim 10^2 \text{ cm}^{-2}$, attract and annihilate essentially all vacancies during the cooling process so that the resulting material is free of these deep traps. Therefore the influence of dislocations, vacancy clusters, and 80 meV traps on EHD nucleation can be studied by examining both dislocated and dislocation-free Ge crystals.

Dislocations might be expected to most strongly influence droplet nucleation, because they produce relatively large regions of high strain in the crystal. Because the total energy of FE and EHD shifts downward under sufficiently large uniaxial stress,^{4.10,4.11} these strained regions should attract and nucleate drops. The magnitude ϵ of the strain field associated with a dislocation in Ge has the form

$$\epsilon = fa/2\pi r \quad (4.8)$$

where f is a complicated angular function of the order of magnitude 1, $a = 0.566$ nm is the lattice constant, and r is the radial distance from the dislocation. Because the minimum uniaxial stress necessary to lower the EHD energy^{4.10} is $\approx 3 \times 10^8$ dyne cm^{-2} , and the shear modulus of Ge is $\sim 10^{12}$ dyne cm^{-2} , the energy of the e-h liquid about a dislocation can be reduced at distances $r \lesssim 0.3$ μm . This value is much larger than the critical radius $R_c \sim 0.03$ μm of EHD embryos. Furthermore, the binding energy per e-h pair of a drop on a dislocation can be greater than ϕ , the condensation energy. Therefore, one expects dislocations to strongly shift the threshold for EHD formation and to dominate the process of nucleation. However, this effect is not observed, as discussed in chapter 5. This evidence seems to indicate that the recombination rate at the dislocation core is large enough to destroy nascent EHD before they can grow to macroscopic size. Because dislocations in Ge are known^{4.12} to produce deep acceptor levels ≈ 0.19 eV below the conduction band associated with dangling bonds in the core which act as recombination centers, this assumption seems reasonable.

Vacancy clusters and the associated 80 meV acceptor levels are expected to have less influence on EHD nucleation than dislocations. Because the strain field surrounding a vacancy cluster falls off as $(a/r)^3$ rather than (a/r) , the region in which the e-h liquid energy is lowered ($r \lesssim 0.01 \mu\text{m}$) is too small to contain more than one e-h pair in the liquid. Thus the binding energy of an EHD on a vacancy cluster due to strain is expected to be of the order of a few meV, less than or comparable to that for an impurity atom. The EHD binding due to the associated 80 meV acceptors is expected to be much smaller than for shallow (≈ 10 meV) impurities, because the spatial extent of the deeper level is smaller, and the acceptor cannot be as effectively screened by the e-h liquid.

The ultrapure Ge used is known to contain a number of other impurities O, Si, H, and Cu, none of which is measurably electrically active in the concentrations present (with the exception of the divacancy-hydrogen level already discussed). All of these impurities can conceavably interact with drops via the strain fields surrounding each impurity atom, but none would be expected to have as large an effect as a vacancy cluster for example. The upper limits to the concentrations of O, Si, H, and Cu present are respectively $5 \times 10^{13} \text{ cm}^{-3}$, 10^{16} cm^{-3} , 10^{14} cm^{-3} , and 10^{12} cm^{-3} . Hydrogen and Copper atoms are both relatively mobile in Ge and form complexes with acceptors and donors respectively or precipitate out of solution. Thus the 40 meV acceptor level of Cu, for example, is not observed in good crystals.^{4.13}

A list of all the Ge samples used in this work is given in Table 4.2, together with their characteristics. These samples were specially selected to test the effects of impurity type and concentration over the range $3 \times 10^9 \text{ cm}^{-3}$ to $4 \times 10^{12} \text{ cm}^{-3}$ and the effect of dislocation density over the range 0 to 10^4 cm^{-2} . In all cases the sample number corresponds to the boule; the properties of the Ge (with the exception of τ_x) were obtained from the records of W. L. Hansen at the Lawrence Berkeley Laboratory, and are identified by the LBL boule number and the position of the cut along the length of the boule. Most of Table 4.2 is self-explanatory, however a few comments are required. The Miller indices listed are those of the excited face of the sample. We have no systematic evidence that the orientation of the crystal affects the experimental results for nucleation phenomena. The dislocation density was measured by visually inspecting a specially-etched face of the crystal and characterizing the density as low ($\sim 10^2 \text{ cm}^{-2}$), medium ($\sim 10^3 \text{ cm}^{-2}$) or high ($\sim 10^4 \text{ cm}^{-2}$); thus these values are only accurate to the order of magnitude. One pair of samples, 150D and 150V, were cut $\sim 1 \text{ cm}$ apart from a specially selected slice of Ge, half of which was dislocated and half was dislocation-free, in order to rigorously test the effect of dislocations on EHD nucleation. Finally, the values of τ_x listed were measured on the actual samples used by recording the decay of the FE luminescence at 4.2K. Those values marked a were obtained using chopped excitation,^{4.4} whereas those marked b were obtained above EHD threshold using GaAs laser excitation, by measuring the FE decay after the EHD luminescence had disappeared.^{4.14}

Because of the slow falling edge of the chopped excitation, the latter values are probably more accurate.

The samples were prepared in the following manner. First the sample was cut to the size $4 \times 9 \text{ mm}^2$ from a slice of Ge $\approx 3 \text{ mm}$ thick with a diamond saw. Then the piece of Ge was polished by hand on a glass plate to an optical finish, starting with 1200 mesh abrasive to remove saw damage and finishing with $3 \text{ }\mu\text{m}$ diamond paste. The polished sample was then etched for $\geq 60 \text{ sec}$ in CP-4 (see Ref. 4.12, for example) quenched immediately in analytic-reagent grade methanol, and washed in distilled water. Finally the samples were carefully inspected to ensure that the surface was smooth, well-etched, and free of cracks or chips. This etching procedure produces a surface which is electrically very good; the value of the surface recombination velocity is nominally $^{4.15} S \sim 10^2 \text{ cm sec}^{-1}$ for free carriers. Assuming the same value of S for FE, the fractional decrease in the steady-state FE concentration at the surface $^{4.16} S_{\tau_x}/L \sim 10^{-2}$ is negligible, and we thus expect to be able to neglect the effects of surface recombination of FE. The actual situation may be less ideal. Because each FE is a bound e-h pair, an exciton need only find a center to absorb its crystal momentum in order to rapidly recombine. Comparison of EHD thresholds measured on the same sample with surface and volume excitation (see Chapter 5) indicates that the quantum efficiency for surface excitation is $\geq 15\%$.

Mounting of the prepared samples was carefully done in a way, shown in Fig. 5.6, which avoided placing external stress or electrical contacts on the Ge crystals. Both of these mechanisms are known to destroy drops, and therefore interfere with the observation of

metastable states of the EHD-FE system. The sample holder was a 0.060 inch thick Cu plate in which holes were cut 3.0 mm wide by 9.0 mm high as indicated in Fig. 5.6 to pass the exciting light. The samples, typically $4 \times 3 \times 9 \text{ mm}^3$, were mounted on the plate with gentle wire springs, and the Ge was mechanically and electrically insulated from both the plate and the springs by 0.010 inch thick mylar pads as shown in Fig. 4.6. This sample size and orientation (9 mm side vertical) was chosen so that 1) the minimum dimension was several FE diffusion lengths to avoid effects of the surfaces not excited, and 2) the vertical dimension was as large as the image of the spectrometer slit on the sample to maximize the amount of luminescence collected.

The mounted samples were immersed in liquid helium in an optical cryostat constructed at the University of California, Department of Physics. As shown in Figs. 4.1 and 4.6, exciting radiation passed through the front window of the cryostat and the hole in the sample holder, whereas the FE and EHD luminescence was collected from the opposite (back) face of the sample. The temperature of the liquid He bath was varied by pumping with a mechanical vacuum pump which could cool the bath to $\approx 1.5\text{K}$, and when necessary with an additional large 33 l sec^{-1} mechanical pump yielding a minimum bath temperature $\approx 1.2\text{K}$. The bath temperature was controlled by a large-throughput pressure regulator connected between the bath and the smaller pump, which reduced the temperature drift with time to less than $\sim 0.03\text{K}$ per hour above 1.5K . The temperature was determined by measuring the He vapor pressure with either a Hg manometer or a Zimmerli gauge.

Below the λ point of liquid He, where most of the data were taken, sample heating due to the excitation is calculated to be $\lesssim 0.01\text{K}$ for the excitation levels used ($P < 10 \text{ mW cm}^{-2}$) and can be neglected. Thus the temperature of the Ge samples could be accurately measured and controlled, as required for measurements of the metastable time development and the phase diagram of the EHD-FE system.

43 Signal Detection Apparatus

A special effort was made in the design of the detection apparatus to optimize sensitivity to the 709 meV and 714 meV luminescence of electron-hole drops and free excitons, in order to study the EHD-FE system near threshold at low temperatures, where the luminescence signals are very weak. The components which contribute most to the extremely high sensitivity of this apparatus are the ultra-sensitive Ge detector and the signal integrating electronics to be described below.

As shown in Fig. 4.1, FE and EHD luminescence was collected from the back face of the Ge samples by an aspheric plano-convex Pyrex lens of focal length 65 mm and diameter 72 mm, and focussed onto the entrance slit of the spectrometer. A rotary mechanical chopper was used to modulate the signal at 380 Hz for phase sensitive detection, and two type 7-56 Corning glass filters (not shown) removed second and higher order spectra. The spectrometer was a 1/4 m Jarrell-Ash f/3.5 instrument equipped with a 890 groove mm^{-1} grating blazed at the wavelength 1 μm , and with 1 mm wide entrance and exit slits,

yielding a spectral resolution (FWHM) of 5.9 nm. In order to record the intensities of the LA phonon replicas of the EHD and FE luminescence lines, the spectrometer was set at the wavelengths 1748.0 nm and 1734.0 nm respectively. With these settings and spectral resolution, the relative fractions of the EHD and FE luminescence lines transmitted by the spectrometer were 56.6% and 62.3% respectively, determined by convoluting the lineshapes^{4.17} with a triangular slit function of the correct width. Thus the recorded signals were proportional to the total integrated intensities of the EHD and FE lines.

An intrinsic Ge particle detector was used as an exceptionally sensitive photodetector to record the EHD and FE luminescence. The detector, fabricated by E. E. Haller at Lawrence Berkeley Laboratory, consisted of a $5 \times 10 \times 10 \text{ mm}^3$ block of ultrapure Ge with diffused Li and evaporated Cr blocking contacts on the opposite $10 \times 10 \text{ mm}^2$ faces. This detector was mounted in a variable-temperature, ultra-high vacuum, cold-finger dewar similar to those used for particle detectors with the exception of a Quartz window to pass the luminescence, which was focussed on a $5 \times 10 \text{ mm}^2$ face. Between experiments the detector was stored at $\approx 100\text{K}$, continuously cooled by liquid nitrogen.

The success of this device as a photodetector at $\lambda \sim 1.75 \mu\text{m}$ lies in the fact that the band gap of Ge decreases with temperature, so that the EHD luminescence, which lies well below the gap at 4.2K, is indirectly absorbed at higher T. Because the detector was made 10 mm thick, the absorption length of the luminescence need be only less than $\sim 1 \text{ cm}$ in order to have acceptable quantum efficiency. Fortunately,

this condition is satisfied for detector temperatures sufficiently low that the thermal generation rate of free carriers is not the primary source of noise. The detector temperature actually used during an experiment was $T = 168 \pm 5\text{K}$. Curves of the relative response of the detector over this temperature range are shown in Fig. 4.7; these data were obtained by illuminating the front slit of the spectrometer with a tungsten lamp. Assuming 100% efficiency for wavelengths shorter than $1.66\text{ }\mu\text{m}$, the quantum efficiency of the device at 166K is 59% for FE and 48% for EHD luminescence as indicated in Fig. 4.7.

Therefore the absorption length of this light in the Ge is $\sim 1\text{ cm}$, and the EHD and FE luminescence produces free carriers throughout much of the intrinsic region of the detector depleted by the applied reverse bias of 90V. These carriers are in turn swept to the contacts by the internal electrical field. Thus the current through the device is proportional to the incident photon flux. The response time of this detector is limited by the collection time of the free carriers and can be quite fast. Assuming an internal field of 50V cm^{-1} , the transit time across the 5 mm width of the device given by the carrier mobility $\mu \sim 10^4\text{ cm}^2\text{V}^{-1}\text{sec}^{-1}$ at 170K is $\sim 1\text{ }\mu\text{sec}$. This value can be reduced to $\sim 200\text{ nsec}$ by increasing the applied bias to 300V. However, for shorter wavelengths which are surface-absorbed the response time is much longer, $\sim 1\text{ msec}$, probably because the denser e-h plasma screens the collecting internal electrical field.

The signal from the detector was DC coupled to the sensitive current amplifier shown in Fig. 4.8, designed by Jan DeVries of the

Space Sciences Laboratory. The input FET of this circuit was specially selected for low noise, and the entire amplifier was encased in a mu-metal shield to reduce magnetic pick-up. The gain and speed of this amplifier are controlled by the feedback resistance and capacitance; thus the 100 Megohm resistor used with its residual capacity of ~ 0.5 pf gave a gain of 10^8 VA^{-1} and an RC response time $\sim 50 \text{ } \mu\text{sec}$.

The total noise of the detector-preamplifier combination was measured under the conditions used during an experiment (90V bias, 380 Hz) with a PAR-186A lock-in amplifier used as a noise meter connected to the output of the preamplifier. At the detector temperature 100K, the leakage current measured by a Kiethley model 160B multimeter was $\approx 30 \text{ pA}$. By dividing the noise voltage indicated on the PAR 186A by 10^8 VA^{-1} , the preamplifier gain, we obtained the rms noise referred to the input $i_n \approx 40 \text{ fA Hz}^{-1/2}$, due to the amplifier alone ($1 \text{ fA} = 10^{-15} \text{ A}$). At the operating temperature 168K, the leakage current increased to 4.6 nA and the rms noise to $i_n \approx 50 \text{ fA Hz}^{-1/2}$. This increase in total noise is consistent with the shot noise $39 \text{ fA Hz}^{-1/2}$ expected from 4.6 nA. Thus we conclude that the system is primarily amplifier noise limited for detector temperatures $\lesssim 170\text{K}$, but is dominated by leakage current noise at higher T.

Values for the noise-equivalent power (NEP) and the detectivity D^* , which characterize this device, can be calculated from the measured value of i_n above. The noise power is given by $\text{NEP} = i_n h\nu / 2\eta = 4 \times 10^{-14} \text{ WHz}^{-1/2}$ where $h\nu = 0.71 \text{ eV}$ is the incident photon energy in electron-volts and $\eta \approx 0.5$ is the quantum efficiency.

The detectivity is given by

$$D^* = A^{1/2}/NEP \approx 2 \times 10^{13} \text{ cm W}^{-1} \text{ Hz}^{1/2} \quad (4.8)$$

where $A \cong 0.5 \text{ cm}^2$ is the active area of the device. This value of D^* is more than two orders of magnitude greater than that for commercial cooled PbS detectors commonly used to study EHD luminescence. Thus this detector allows the measurement of luminescence signals which cannot be observed with more conventional devices, and is an essential part of the apparatus.

The signal from the preamplifier was further conditioned by the selective clipper shown in Fig. 4.9 to remove noise spikes due to cosmic rays absorbed by the detector. This circuit normally has an inverting voltage gain of 44 provided by the 733 video amplifier. When a fast risetime ($< 10 \text{ } \mu\text{sec}$) pulse of voltage greater than the threshold value (typically 15 mV) occurs, the 711 comparator fires, turning on the FET, and shorting the output for $\approx 200 \text{ } \mu\text{sec}$. Thus fast spikes are removed without affecting the chopped luminescence signal. Although the improvement in signal to noise ratio was only marginal, this device was included in the apparatus.

The remaining electronics shown in Fig. 4.1 form a signal averaging system capable of directly integrating the luminescence signal for very long times to achieve high sensitivity. This system is based on a Northern Scientific NS-905 multi-channel analyzer (MCA) operated in the multi-channel scaler (MCS) mode, with a memory capacity of 512 channels. The signal from the selective clipper is first

synchronously detected by a PAR corp. HR-8 lock-in amplifier set for a time constant of 0.1 sec. The output of the lock-in amplifier is connected to a Vidar voltage-to-frequency converter with a full-scale output of 100 kHz. The frequency of the resulting pulse train is then divided by 100 by two 7490 TTL integrated circuits and connected to the MCS input of the MCA. In order to integrate and store the signal for a given data point, the MCA is gated for a fixed time (24 sec) by the signal EADD from the timing logic as shown in Figs. 4.1 and 4.5 and described in section 41. During this time pulses at the MCS input are added into the memory channel addressed, so that the final count in that channel is proportional to the integral of the signal. The timing logic also advances the channel addressed so successive data points are stored in successive channels. When all 512 channels have been used, the contents of the memory can be read out on a teletype machine. Thus this system can automatically digitize, integrate, and store the data from an entire experiment. Because the integration times used were so long, the amount of data which can be taken during one day is severely limited, and automation and direct integration of the signal are very important. If the lock-in amplifier were used alone, set for the time constant 24 sec, the setting time to 1% accuracy, 120 sec, would reduce the total number of data points which could be recorded by roughly a factor of four.

CHAPTER 5. EXPERIMENTAL RESULTS AND ANALYSIS

In this chapter we present the results of a thorough experimental investigation of EHD nucleation phenomena in ultrapure Ge. The luminescence emitted by electron-hole drops and free excitons in optically excited Ge was used as a sensitive measure of the relative concentrations of these species. The study of the variation of the EHD and FE luminescence intensities vs. excitation, history of excitation, time, and temperature yields a great deal of information about the FE-EHD system: Section 51, basic hysteresis curves for FE and EHD at various temperatures which exhibit well-defined thresholds for EHD formation and breakup, and measurement of the EHD radiative enhancement factor ρ ; section 52, the metastable time development of the EHD signal; section 53, variation of excitation thresholds vs. impurity type and concentration, and dislocation density, and measurement of the EHD surface tension σ from hysteresis curves; and section 54, detailed analysis of the FE-EHD phase diagram between 1.2K and 2.0K yield accurate measurements of σ and the condensation energy ϕ , and an estimate of the temperature-independent evaporation rate of EHD.

As described in chapter 4, the FE and EHD luminescence was spectrally selected by a spectrometer equipped with broad slits for high sensitivity. For the excitation and collection geometry used, (see chapter 4) the luminescence intensities I_d and I_x of EHD and FE respectively are given by

$$I_d = C(f_d/\tau_o^r) \int_0^d NV \, dx \quad (5.1)$$

$$I_x = C(f_x/\tau_x^r) \int_0^d n \, dx \quad (5.2)$$

where the constant of proportionality C is the same for both cases. Here N is the drop concentration, v is the number of e-h pairs contained in one drop, n is the FE density, x is the distance into the Ge sample from the excited surface, τ_o^r and τ_x^r are the radiative lifetimes for EHD and FE, and f_d and f_x are the relative detection efficiencies for EHD and FE including the slit function of the spectrometer and the detector response (see chapter 4). In short, the signals I_d and I_x are proportional to the integrals with respect to depth into the sample of the total concentrations Nv and n of e-h pairs condensed into EHD and FE. The variation of Nv and n in space is expected to be one-dimensional, because the entire front surface of the samples is uniformly excited. In all cases, the signals I_d and I_x refer to the LA-phonon replica of the EHD and FE luminescence. This replica was used because it is the strongest and is allowed by selection rules for phonon emission, with no expected temperature dependence.

51 Hysteresis Curves for Electron-Hole Drops and Free Excitons

When the EHD luminescence signal I_d is recorded while the excitation P is continuously swept from zero to a maximum value $P_{\max}$, then back to zero, a hysteresis curve is generated: the signal I_d on the downgoing branch is larger than that on the upgoing branch, and the

thresholds for the creation and breakup of EHD differ substantially. This effect was discovered by Lo et al.^{5.1} using this method of excitation. These authors noted irreproducibility in the results obtained for I_d . In order to avoid apparently irreproducible effects of the metastable time development of the EHD signal, and to ease comparison with nucleation theory, all of the data presented in this thesis was taken point-by-point as described in chapter 4. Upgoing data points were each taken by increasing the excitation from zero to a constant value P at which the upgoing EHD and FE signals I_d^+ and I_x^+ were recorded; downgoing points were each taken by initially increasing the excitation from zero to a large value P_{max} , then decreasing the excitation to a constant value P at which the downgoing EHD and FE signals I_d^- and I_x^- were recorded.

Hysteresis curves for EHD and FE in Ge at 2.1K recorded in this manner are shown in Fig. 5.1. These data were taken using surface excitation (see chapter 4) in order to obtain a wide range of excitation power. A large hysteresis is evident in both the EHD and FE signals I_d and I_x shown in Fig. 5.1. Drops created by the large initial excitation $P_{max} = 0.9 \text{ W cm}^{-2}$ in the downgoing case, remain as the excitation is reduced and cause the separation between the curves for I_d^- and I_d^+ . These signals display sharp, separate excitation thresholds for the creation and destruction of EHD at $P_+ \approx 20 \text{ mW cm}^{-2}$ and at $P_- \approx 5 \text{ mW cm}^{-2}$ respectively, which differ by a factor of four. Far above threshold the EHD signals I_d^+ and I_d^- join and vary linearly with excitation P as expected, because the majority of carriers created

enter the EHD phase. Below threshold, the FE signals I_x^+ and I_x^- do not display hysteresis and increase linearly with excitation as one expects for a simple system composed only of free excitons. At the respective thresholds P_- and P_+ the FE signals I_x^- and I_x^+ break downward from their linear dependence on P as an increasing fraction of excited e-h pairs enter the EHD phase. As a result, the FE signals display an inverted hysteresis which is consistent with the conservation of excited carriers as described in chapter 3 by Eq. (3.1). Thus the hysteresis curves of Fig. 5.1 exhibit large supersaturation effects analogous to those found for ordinary liquids such as water. All of the basic hysteresis phenomena for EHD and FE described above for Fig. 5.1 were observed for every sample studied at this temperature for both surface and volume excitation and are truly characteristic of the EHD-FE system in ultrapure Ge. These phenomena are in good qualitative agreement with the predictions of nucleation theory (see chapters 2 and 3); we present a detailed analysis in the following paragraphs.

An interesting feature of Fig. 5.1 not discussed further below, is the disappearance of hysteresis in I_x and I_d for excitation powers larger than $P \approx 0.1 \text{ W cm}^{-2}$; this phenomenon occurred at large P for all samples studied with surface excitation. Conceivably this effect could be caused by sample heating. However the estimated temperature rise for $P = 0.1 \text{ W cm}^{-2}$ is only $\sim 0.1\text{K}$, too small a change to be effective. A more likely explanation is that phonons created by the surface excitation exert a sufficiently large force on EHD (the so-called phonon wind^{5.2}) to move them away from the excited surface into the

interior of the crystal where they disappear, thus destroying the memory of the EHD-FE system. Using the experimental estimate of Bagaev et al.,^{5.2} we find that the force exerted on a drop of 3 μm radius (see chapter 3) for $P = 0.1 \text{ W cm}^{-2}$ by the phonon wind is $F \sim 20 \text{ meV } \mu\text{m}^{-1}$, possibly large enough to dislodge the drop from an impurity to which it is bound by the energy $\sim 10 \text{ meV}$.^{5.3}

A linear plot of the hysteresis curves for EHD and FE near threshold at 1.82K is shown Fig. 5.2. This data and that shown in the following figures of this section were taken using volume excitation (see chapter 4). Compared to the original hysteresis data of Lo et al.,^{5.1} these results are greatly improved in that they exhibit much higher sensitivity and are strictly reproducible. The curves in Fig. 5.2 clearly show all of the basic hysteretic phenomena described for Fig. 5.1 above. The EHD signal I_d exhibits a large hysteresis, and sharp thresholds at $P_+ \approx 0.52 \text{ mW cm}^{-2}$ and $P_- \approx 0.37 \text{ mW cm}^{-2}$ as indicated in Fig. 5.2 for the creation and destruction of EHD. The FE signals I_x^+ and I_x^- vary linearly with P for low excitation and break downward at the respective thresholds P_+ and P_- , yielding an inverted hysteresis. These features are consistent with the condensation of FE into e-h drops as described in chapters 2 and 3. In fact, these data obey the conservation equation $P \propto I_x + aI_d$ for excited electrons and holes obtained from Eq. (3.1) in chapter 3, indicating that FE and EHD are the only important species present in the system. A least squares fit of this expression to the data of Fig. 5.2 yields $a \approx 4.6 \times 10^{-2}$, a value which is smaller than unity

partially because the FE lifetime τ_x is much smaller than that for EHD (see Eq. 3.1).

Before proceeding further, we can use hysteresis data such as that shown in Figs. 5.1 and 5.2 to determine the radiative enhancement factor ρ of the electron-hole liquid. This quantity is defined as the ratio of the electron density at the position of a hole to the average liquid density n_0 and is a sensitive measure of the degree of electron-hole correlation in the liquid. Therefore, an experimental determination of ρ is of considerable importance in assessing the validity of many-body theory used to calculate the properties of the EHL. We measure ρ by extracting the ratio τ_x^r/τ_0^r of the radiative lifetimes for FE and EHD from hysteresis data as described below.

The only assumption necessary to find the ratio τ_x^r/τ_0^r is that the conservation equation, Eq. (3.1), holds for both branches of the hysteresis curves for FE and EHD at a given excitation level P ; no nucleation theory is involved in the calculation. Using Eqs. (5.1) and (5.2) for the EHD and FE signals at the same excitation power P , we find immediately

$$\tau_x^r/\tau_0^r = (\tau_x/\tau_0)(f_x/f_d)(I_d^- - I_d^+)/(I_x^+ - I_x^-) . \quad (5.3)$$

The measured total lifetimes τ_x and τ_0 , and the instrumental functions f_x and f_d for FE and EHD are given in chapter 4. From data taken on samples 145, 150D, and 150V (see Table 4.1) using surface excitation we find $\tau_x^r/\tau_0^r = 4.7 \pm 1.7$. The values of τ_x^r/τ_0^r obtained were roughly independent of excitation P near threshold and of temperature in the

range 1.8 to 2.2K, where the data were taken. The error given above for τ_x^r/τ_o^r is due to variation between Ge samples, and is much larger than the noise in the signals I_d and I_x . This value for the ratio τ_x^r/τ_o^r is to be compared with the earlier estimates $\tau_x^r/\tau_o^r = 4.4 \pm 1.1$ from decay data^{5.4} and $\tau_x^r/\tau_o^r = 16$ from luminescence efficiency.^{5.5} The value of τ_x^r/τ_o^r above, measured at separate given levels of excitation, is comparable to the value obtained by fitting the conservation equation to an entire set of hysteresis curves at once. For example, the coefficient $a \approx 4.6 \times 10^{-2}$ from the volume excitation data of Fig. 5.2 above yields $\tau_x^r/\tau_o^r \approx 7.9$.

Given τ_x^r/τ_o^r , one can find the enhancement factor ρ by assuming that the matrix elements for the radiative decay of FE and EHD are identical. Thus

$$\rho = (|\psi(o)|^2/n_o)(\tau_x^r/\tau_o^r) \quad (5.4)$$

where $|\psi(o)|^2 = 1/\pi a_x^3$ is the magnitude of the exciton wavefunction at the origin in relative coordinates, with a_x the Bohr radius. Using the most recent value^{5.6} $a_x = 11.4$ nm, we find for the enhancement factor

$$\rho = 4.4 \pm 1.6. \quad (5.5)$$

This measurement compares reasonably well with the theoretical value^{5.7} $\rho = 2.3$ for Ge. However, the large variation of the measured value of ρ with sample casts doubt on the overall accuracy of this and other^{5.4,5.5} measurements of the enhancement factor to date. It seems likely that this variation is associated with effects of the unknown

mechanism which determines the FE total lifetime τ_x , and that more accurate, reliable measurements of ρ will be possible when this mechanism is understood.

We return now to the discussion of hysteresis curves. Nucleation theory predicts that the downgoing threshold P_- is a unique function of the temperature and time of observation for a given sample, and is independent of the initial large excitation $P_{\max}$ used to record the data. Hysteresis curves for EHD taken at 1.80K are shown in Fig. 5.3 for several different values of the initial excitation $P_{\max}$ in the downgoing case. As shown in Fig. 5.3, the threshold $P_- = 0.63 \text{ mW cm}^{-2}$ for EHD breakup accurately reproduces as the initial level is increased from $P_{\max} = 2.52 \text{ mW cm}^{-2}$, just above the upgoing threshold, to $P_{\max} = 4.72 \text{ mW cm}^{-2}$, in agreement with theory.

The curves shown in Fig. 5.3 also provide a good opportunity to discuss the semi-quantitative theoretical description of EHD nucleation given in Section 31. The upgoing branch I_d^+ , Fig. 5.3a is expected to be characterized by an increasing concentration N of drops of nearly constant size v , where v is the number of e-h pairs in a given drop, and the FE density above threshold should be locally fixed at the threshold value n_+ . Unfortunately, the EHD signal I_d^+ is proportional to the product Nv , so the separate variation of these quantities cannot be tested. In the downgoing case as the final excitation P is reduced below $P_{\max}$, the drop concentration is expected to remain constant while the size v and the FE density n decrease. When n locally reaches the threshold value n_- , EHD begin to break up, and the concentration N is

expected to decrease with P while the size v remains nearly constant. Note that the excitation level at which EHD locally begin to breakup is larger than the threshold value P_- and is proportional to $n_-/\tau_x + N_M v_-/\tau_o$, where N_M is the drop concentration created by $P_{\max}$. The signals I_d^- in Figs. 5.3b to 5.3d all display a break in slope at a critical value P_c of the excitation near the downgoing threshold, indicated for Fig. 5.3b. Moreover, the difference $(P_c - P_-)$ is proportional to the initial excitation $P_{\max}$, as expected from the relation given above. No break in slope is observed for Fig. 5.2 simply because $P_{\max}$ is relatively much larger than for Fig. 5.3. These features suggest that EHD begin to breakup at the excitation P_c in Fig. 5.3; we will test this assumption shortly.

Unfortunately, the detailed shape of the curves shown in Figs. 5.2 and 5.3 cannot be directly compared with the theoretical hysteresis curves of Chapter 3 (Fig. 3.1), because the latter assume spatially uniform excitation. The analysis for non-uniform excitation is quite complicated, and should include FE diffusion. However, because the absorption length $\ell \approx 1$ mm for volume excitation is larger than the FE diffusion length $L \approx 0.7$ mm, we can construct a simple model neglecting FE diffusion in which the results of Chapter 3 hold locally. Using the nearly exact expressions Eqs. (3.6) and (3.11) for the drop concentration, the integral of Eq. (5.1) for the EHD signal is computed numerically for the generation rate $G(x) = G_o \exp(-x/\ell)$. The downgoing expression, Eq. (3.11), is inapplicable when $n > n_-$; in this case we obtain Nv by solving the conservation equation Eq. (3.1)

with v determined by the approximate expression Eq. (2.20) for the stable radius. The parameters used in the calculation are those of Table 3.1 corrected for the improved values obtained by fitting the phase diagram as described in Section 54.

Results of this procedure are shown in Fig. 5.4; the horizontal and vertical scales have been adjusted so that this figure can be directly compared with Fig. 5.3. Here the integral $n_d = \int Nv \, dx$ from Eq.(5.1) is plotted vs. G_0 for values of the initial generation rate G_M in the downgoing case chosen to correspond to the values of $P_{\max}$ in Figs. 5.3b to 5.3d. The overall agreement between the calculation Fig. 5.4 and the data Fig. 5.3 is very good, providing a confirmation of nucleation theory. In particular, the shape of the upgoing branch of the theoretical hysteresis curves is in excellent agreement with that of the EHD signal I_d^+ in Fig. 5.3a, and the ratios of the calculated and experimental thresholds $G_+/G_- = 2.9$ and $P_+/P_- = 2.6$ are nearly the same. The primary differences between theory and experiment are found in the downgoing curves: the calculated curves n_d in Figs. 5.4b to 5.4d are relatively smaller than the EHD signals I_d^- in Figs. 5.3b to 5.3d, and they do not exhibit breaks in slope near threshold. These differences are consistent with the existence of a region of quasi-uniform excitation within the Ge crystal created by FE diffusion, as discussed in Chapter 4.

The theoretical prediction that the drop concentration N remains locally constant along the downgoing branch of hysteresis curves for excitation levels $P > P_c$ can be experimentally tested by using a

specially constructed cycle of excitation. From the data of Fig. 5.3, we expect N to vary slowly with P for $P > P_c$, but to decrease rapidly as the excitation falls below P_c , reaching zero at P_- . Data taken under the same experimental conditions as Fig. 5.3d, but with an additional step in the downgoing excitation cycle, are shown in Fig. 5.5. In recording this data, the initial level $P_{\max}$ was the same as for Fig. 5.3d, and the final level P at which the EHD signal was recorded was fixed at the constant value $P = 1.42 \text{ mW cm}^{-2}$, just below the formation threshold P_+ (see Fig. 5.3a). As shown in the insert to Fig. 5.5, only the additional excitation level P_2 was varied, from zero to the value of P . Thus, if the drop concentration remains constant during the dip in excitation to the level P_2 , the final signal I_d shown in Fig. 5.5 will be independent of P_2 ; if N decreases I_d will also decrease. As indicated in Fig. 5.5, the recorded luminescence signal I_d is nearly constant for $P_2 > P_c$, indicating that N changes very little as expected. For $P_2 < P_c$ the EHD signal decreases sharply with P_2 , and reaches zero at the destruction threshold P_- , indicating that the number of EHD also decreases with P_2 to zero at P_- . The values of P_c and P_- shown in Fig. 5.5 accurately agree with those of Fig. 5.3d. Thus "motion" along a given downgoing hysteresis curve such as Figs. 5.3b to 5.3d is reversible for excitation levels between P_c and $P_{\max}$, but becomes irreversible for levels lower than P_c , because the number of EHD decreases. The division of each downgoing curve into a range of excitation where N remains constant and a range in which N decreases for volume excitation strongly suggests that a region of

quasi-uniform excitation is created within the crystal by FE diffusion as mentioned above; thus the detailed shape of Figs. 5.3 and 5.5 and the values of P_c are determined by geometrical effects and cannot be directly compared with theory.

The hysteresis curves shown in Figs. 5.1 to 5.3 were all taken at temperatures $T \approx 2K$. For ordinary liquids such as water metastable supersaturation effects become larger as the temperature is reduced. However, for EHD in Ge at temperatures below 2K the opposite is the case. A series of hysteresis curves for EHD taken on the same sample (315) at various temperatures between 1.9K and 1.2K is shown in Figs. 5.6 through 5.9. As T decreases from 1.86K in Fig. 5.6 to 1.25K in Fig. 5.9, the thresholds P_+ and P_- for the creation and destruction of EHD approach each other; at 1.25K hysteresis in the EHD signal is entirely absent. As discussed in Chapters 2 and 3 this effect is expected from EHD nucleation theory and is a direct consequence of the finite lifetime of the e-h liquid. The temperature at which hysteresis disappears, $T \approx 1.3$ to 1.4K from Figs. 5.8 and 5.9, is in excellent agreement with the theoretical value $T = 1.3$ to 1.4K from Fig. 3.3.

Another novel effect predicted by EHD nucleation theory and caused by the EHD lifetime can be seen by examining the thresholds P_- for the breakup of EHD in Figs. 5.6 through 5.9. As T decreases from 1.86K to 1.25K, P_- decreases from 0.70 mW cm^{-2} to 0.22 mW cm^{-2} , only a factor of 3.2. If P_- were proportional to the saturated vapor density, as is the case for ordinary liquids, one would expect P_- to

decrease by a factor ≈ 800 for the same change in T . Thus the measured thresholds for EHD breakup differ greatly from those predicted by the saturated FE density below 2K, and the threshold P_- appears to approach a temperature-independent value at the lowest T (see Figs. 5.8 and 5.9). These effects are in good agreement with EHD nucleation theory as shown in Fig. 3.3. The threshold ratios P_+/P_- obtained from Figs. 5.6 through 5.9 also agree well with the theoretical values from Fig. 3.3. A quantitative fit of nucleation theory to EHD threshold data is given and discussed in detail in Section 54.

As shown in Figs. 5.6 to 5.9, the sensitivity of the apparatus is large enough that excitation thresholds P_+ and P_- are clearly visible even at the lowest temperature measured, 1.25K, where P_+ is comparable to the illumination provided by room light. In order to extract well-defined values for P_+ and P_- from such data we develop approximate analytic expressions for integrated theoretical hysteresis curves such as Fig. 5.4, valid near threshold. Again we neglect FE diffusion and assume that the spatially uniform model of Chapters 2 and 3 is locally valid for volume excitation. For the spatially uniform generation of e-h pairs, we expect the EHD signals I_d^+ and I_d^- to approach threshold linearly (see Eqs. 3.2 and 3.3), and the FE signals I_x^+ and I_x^- just above threshold to be approximately constant, because the FE density is fixed at the threshold values. Using the simple linear expressions Eqs. (3.2) and (3.3) in the integral Eq. (5.1) for the EHD signal instead of the more accurate expressions used to calculate Fig. 5.4 we find

$$I_d^{\pm} \approx C(f_d/\tau_o^r) G_{\pm} \tau_o \ell [(G_o/G_{\pm}) - 1 - \ln(G_o/G_{\pm})] . \quad (5.6)$$

where $G(x) = G_o \exp(-x/\ell)$ is the volume generation rate. Note that all of the variation of I_d with G_o in Eq. (5.6) is contained in the expression within the square brackets. Near threshold the logarithm can be expanded yielding

$$I_d^{\pm} \approx C(f_d/\tau_o^r) G_{\pm} \tau_o \ell [(G_o - G_{\pm})^2 / 2G_{\pm}^2] . \quad (5.7)$$

Thus the EHD signal I_d is expected to increase quadratically with P near threshold as a consequence of the excitation geometry. The variation of the FE signal I_x just above threshold can be worked out within this model in a similar manner; we find from Eq. (5.2),

$$I_x^{\pm} \approx C(f_x/\tau_x^r) G_{\pm} \tau_x \ell [\ln(G_o/G_{\pm}) + 1] . \quad (5.8)$$

Again the variation of I_x with G_o is given by the expression in square brackets. From Eq.(5.8) we find that I_x is expected to increase logarithmically with P above threshold with no break in slope at threshold. Inspection of Fig. 5.2 indicates that both the EHD and FE signals I_d and I_x vary with excitation P qualitatively as predicted by Eqs. (5.7) and (5.8).

As illustrated in Fig. 5.10, the procedure used to extract excitation thresholds from hysteresis data was to plot the square root of the EHD signals I_d^+ and I_d^- near threshold vs. P and linearly extrapolate $I_d^{1/2}$ to zero. The statistical error for the values P_+ and P_- obtained by this method was typically $< 10\%$. As shown in Fig. 5.10

the signals I_d^+ and I_d^- obey the quadratic expression Eq. (5.7) quite well, as do the data for other hysteresis curves taken with volume excitation. It seems likely that the cubic variation of I_d with P near threshold originally observed by Pokravskii^{5.8} and used as evidence for a fixed drop concentration is an effect of the excitation geometry he used. The thresholds P_+ and P_- obtained as described above are indicated for comparison in Figs. 5.6 to 5.9. This method of threshold extraction is used in section 54 to determine the EHD-FE phase diagram.

52 Metastable Time Development

The existence of hysteresis in the luminescence data of the preceeding section immediately indicates that the EHD-FE system can be in a metastable state for times as long as the 18 sec delay used in recording the data. In this section we study the metastable time development of the EHD signals I_d^+ and I_d^- for much longer delays as the system approaches equilibrium. Lo, Feldman and Jeffries^{5.1} originally found that the signals I_d^+ and I_d^- approached each other slowly and that hysteresis could be maintained for times as long as 300 sec. However, they also noted the presence of jumps and irreproducibility in I_d , which we have found were caused by noise in the Hg arc lamp excitation used. We present data below which show that the EHD signals I_d^+ and I_d^- vary logarithmically with time as predicted by EHD nucleation theory in Chapter 3, and prove that metastable states of the EHD-FE system can actually exist for times as long as 6×10^4 sec. These conclusions were first presented in a preliminary account of this work.^{5.9}

The method used to study the metastable time development of the EHD-FE system is described below. For either the upgoing or downgoing EHD signal I_d^+ or I_d^- , the excitation was cycled as described above in section 51. However, once the final level P was reached, the excitation was held accurately constant by the feedback stabilization system (see Chapter 4) and the signal I_d was integrated over successive 8 sec intervals. In this way a plot of the signal I_d^+ or I_d^- was obtained vs. the delay Δt following the last change in excitation.

A plot of data obtained in this manner using volume excitation for sample 315 at 1.80K is shown in Fig. 5.11. The excitation power $P \approx 2.3 \text{ mW cm}^{-2}$ is the same for both curves in Fig. 5.11, and was chosen just above the threshold P_+ for the creation of EHD (c.f. Fig. 5.3). The most striking feature of this data is that the system is still far from equilibrium after the delay $\Delta t = 4 \times 10^3 \text{ sec}$. Over this period of time the upgoing signal I_d^+ increases logarithmically with Δt as shown in the lower portion of Fig. 5.11. This type of time variation is quite unusual in solid state physics, but is predicted by EHD nucleation theory as described in Chapter 3. Thus the logarithmic variation of I_d^+ with Δt in itself is evidence for nucleation phenomena. It is interesting to note that the apparent risetime (10% to 90%) of the EHD signal I_d^+ in Fig. 5.11 is extremely long, $\approx 1 \times 10^3 \text{ sec}$. This value is 10^7 times longer than that expected from the EHD lifetime $\tau_0 \approx 40 \text{ } \mu\text{sec}$ alone and is dramatic evidence for EHD nucleation. The kinetics of EHD formation manifested in the luminescence signal on a much shorter time scale have been studied

first in Ge by Staehl:^{5.10} and later in Si by Shah et al.^{5.11}

The downgoing EHD signal I_d^- in Fig. 5.8 initially decreases logarithmically with Δt but approaches the simple exponential dependence $I_d \propto \exp(-\Delta t/\tau)$ for $\Delta t > 10^3$ sec with $\tau \approx 6 \times 10^4$ sec as indicated by the solid curve. The initial logarithmic variation of I_d^- with Δt is evidence for nucleation as for the upgoing case, but the subsequent exponential decay is most likely due to an external mechanism which destroys EHD. Once individual drops are destroyed in the downgoing case, they are not replaced, and the drop concentration decreases exponentially for a constant rate of destruction. The surprising feature of this data is that the destruction time $\tau \approx 6 \times 10^4$ sec for this sample is extremely long. Because EHD cannot be supplied with carriers if they move ~ 1 mm into the crystal, this evidence indicates that individual drops are practically immobile under the conditions of this experiment. Recent measurements^{5.12} of the time development of the spatial distribution of EHD near threshold prove that drops must be pinned to crystal imperfections for low levels of excitation and place the upper limit $D_d \lesssim 10^{-7} \text{ cm}^2 \text{ sec}^{-1}$ on the EHD diffusion constant. These new results are not in conflict with those of a number of experiments^{5.13} performed with relatively high levels of excitation in which EHD are shown to move rapidly through the crystal.

Now we consider the magnitude of the logarithmic slope $dI_d/d(\log \Delta t)$ of curves for I_d^+ and I_d^- such as those shown in Fig. 5.11. The comparison of this slope with the theory presented in Chapter 3 is greatly complicated by the spatial variation of the generation rate

$G(x)$ for volume excitation and by the difficulty of relating the signal I_d in mV to the integral $n_d = \int_0^d dx Nv$ from Eq. (5.1) of the amount of e-h liquid present in the sample. We roughly estimate the latter by comparing the hysteresis curves and theory shown above in Figs. 5.3 and 5.4; thus we find n_d (pairs cm^{-3}) $\sim 10^{10} I_d(\text{mV})$. In order to treat the spatial variation of $G(x)$, we use the simple model neglecting FE diffusion described for the calculation of Fig. 5.4, in which the theory of Chapter 3 applies locally. The integral n_d is then computed numerically for various times Δt from the nearly exact expressions Eqs. (3.6) and (3.11) for the drop concentration, as described above.

The results for the upgoing integral n_d^+ calculated in this way at 1.80K for the value G_0 corresponding to P in Fig. 5.8 vary nearly logarithmically with Δt as expected, with the slope $dn_d^+/d(\log \Delta t) = 1.2 \times 10^{10} \text{ cm}^{-2}$ per decade. Thus the calculated slope of the EHD signal is $dI_d^+/d(\log \Delta t) \sim 1 \text{ mV per decade}$, which agrees very well with the value 2 mV per decade measured from Fig. 5.11, providing further evidence for the validity of nucleation theory. However, the downgoing slope $dI_d^-/d(\log \Delta t) \approx 0.5 \text{ mV per decade}$ measured from Fig. 5.11 for $\Delta t < 10^3 \text{ sec}$ is orders of magnitude larger than the calculated value. The reason for this discrepancy is unclear at present. It seems likely that the slope of the calculated drop breakup rate J_- vs. n from Chapter 2 is unphysically steep; thus the value used for the coefficient M_- of the logarithmic time variation of Nv_- in Eq. (3.11) could be much too small. Another possible source of error is the neglect of FE diffusion in the above calculation.

For different levels of excitation, the logarithmic slope of the EHD signals I_d^+ and I_d^- vs. Δt changes. At 1.80K the upgoing slope increased to $dI_d^+/d(\log \Delta t) \approx 5$ mV per decade from 2 mV per decade as the excitation increased from $P = 2.13 \text{ mW cm}^{-2}$ to $P = 2.90 \text{ mW cm}^{-2}$. This increase is consistent with theory; the calculated slope in this case is proportional to the volume of the sample occupied by EHD (see Chapter 3), which increases with excitation power. The downgoing slope measured at 1.80K increased to $dI_d^-/d(\log \Delta t) \approx 1.1$ mV per decade as the excitation decreased to $P = 0.76 \text{ mW cm}^{-2}$, very near the downgoing threshold. At this excitation the signal I_d^- was observed to decrease logarithmically all the way to zero in $\Delta t \approx 1000$ sec. Expressed as a fraction of the initial signal I_d^- , the downgoing slope in this case increased by a factor of 20 as threshold was approached. This increase is qualitatively in accord with nucleation theory as discussed in Chapter 3.

Plots of the signals I_d^+ and I_d^- vs $\log \Delta t$ for the same sample (315) at 1.50K are shown in Fig. 5.12. As for Fig. 5.11, the excitation $P = 0.55 \text{ mW cm}^{-2}$ was chosen just above the upgoing threshold, and is the same for both curves. Like the data at 1.80K, both the EHD signals I_d^+ and I_d^- shown in Fig. 5.12 initially vary logarithmically with Δt as predicted by nucleation theory. The slope $dI_d^+/d(\log \Delta t) \approx 0.8$ mV per decade for the upgoing curve in Fig. 5.12 agrees reasonably well with the value $dI_d^+/d(\log \Delta t) \sim 0.4$ mV per decade estimated from the integral $dn_d^+/d(\log \Delta t) = 0.37 \times 10^{10} \text{ cm}^{-2}$ per decade calculated as described above. As for the data at 1.80K, the downgoing slope

$dI_d^-/d(\log \Delta t) \approx 5$ mV per decade from Fig. 5.12 is several orders of magnitude larger than the calculated value. Thus the metastable time development of the EHD-FE system at 1.50K is similar in some respects to that at 1.80K, and comparable agreement with theory is found.

A striking feature of Fig. 5.12 not present in the data at 1.80K is that the EHD-FE system actually reaches equilibrium at $\Delta t \approx 100$ sec. As shown in Fig. 5.12, the signals I_d^+ and I_d^- join at $\Delta t \approx 100$ sec, and the noise in both signals increases substantially, presumably because the system slowly fluctuates about equilibrium. The small downward slope of I_d^+ and I_d^- for $\Delta t > 100$ sec is compatible with that expected from the very small upward drift $\Delta T \sim 0.01K$ in the measured temperature of the liquid He bath while the data were taken. The fact that the equilibration time $\approx 10^2$ sec from Fig. 5.12 is very much smaller than the time $\sim 10^7$ sec at 1.50K predicted by nucleation theory in Chapter 3, is a result of the relatively large slope of I_d^- , not predicted by theory. It is interesting to note that the shorter equilibration times predicted by theory at lower temperatures are caused by a decrease in magnitude of the predicted hysteresis rather than an increase in the rate of change of the drop concentration. The calculated coefficients M_+ and M_- (see Chapter 3) which determine these rates only change from $1.6 \times 10^{11} \text{ cm}^{-3}$ to $3.7 \times 10^{10} \text{ cm}^{-3}$ and from $1.2 \times 10^9 \text{ cm}^{-3}$ to $2.2 \times 10^9 \text{ cm}^{-3}$ respectively as the temperature is decreased from 1.80K to 1.50K.

The fact that hysteresis is present in the signals I_d^+ and I_d^- of Fig. 5.12 for times $\Delta t < 100$ sec, but not for times $\Delta t > 100$ sec

underscores the importance of recording both signals at a fixed time Δt of observation if these data are to be compared with nucleation theory. The data of Fig. 5.12 also indicate indirectly that the measured values of the excitation thresholds P_+ and P_- depend upon the time Δt . Direct evidence for this effect is given in Fig. 5.13, where I_d^- vs. Δt is plotted for the same sample (315) at 1.50K but a lower level of excitation $P = 0.44 \text{ mW cm}^{-2}$ very near the downgoing threshold P_- . As shown in Fig. 5.13, the downgoing signal I_d^- decreases logarithmically, reaching zero at $\Delta t \approx 200 \text{ sec}$. Thus the excitation level used for Fig. 5.13 lies above the downgoing threshold for $\Delta t < 200 \text{ sec}$, but below this threshold for $\Delta t > 200 \text{ sec}$. Variation of the thresholds for the formation and breakup of EHD with the time of observation is predicted by nucleation theory and discussed in Chapter 3.

At temperatures below $\approx 1.3\text{K}$, EHD nucleation theory predicts that hysteresis is entirely absent and that the EHD-FE system is in dynamic equilibrium. A plot of the signals I_d^+ and I_d^- vs. Δt at 1.25K recorded on the same sample (315) as the data above is shown in Fig. 5.14. Again, the excitation power $P = 0.37 \text{ mW cm}^{-2}$ was chosen just above the threshold for the formation of drops. As shown in Fig. 5.14 the signals I_d^+ and I_d^- at this temperature are equal as expected from the lack of hysteresis in the curves shown in Fig. 5.9 for 1.25K. More importantly, the signals I_d^+ and I_d^- in Fig. 5.14 are accurately constant for $\Delta t > 10 \text{ sec}$, indicating that the equilibration time at 1.25K is less than 10 sec, and proving that metastability is entirely absent for longer times.

53 Effect of Impurities and Dislocations on Nucleation; Surface Tension Measurement

For ordinary liquids such as water, the process of droplet nucleation is dominated by contaminants and surfaces unless the vapor is carefully purified and held in a clean container. Various impurities can act as nucleation centers by binding nascent drops, lowering or destroying altogether the potential barrier to nucleation. Thus the observed supersaturation ratio n_+/n_s of the threshold vapor density n_+ for drop formation in a dirty system can be much less than the homogeneous value. Also, the final concentration of nucleated drops of ordinary liquids is typically constant, equal to the density of nucleation centers.

In this section we present an experimental study of the influence of shallow impurities, dislocations, and vacancy clusters on the process of EHD nucleation in ultrapure Ge crystals. As discussed in detail in Section 42, these defects are those expected to be most active as nucleation centers in the crystals studied. Briefly, we find that dislocations are ineffective as nucleation centers, and that EHD most probably form on neutral shallow impurities. The theory for this type of inhomogeneous nucleation is presented in Chapters 2 and 3. In contrast to the case for ordinary liquids, these impurities are expected to have only a small effect on the observed supersaturation ratio n_+/n_s for EHD formation. Also, the EHD concentration N is only a small fraction of the impurity concentration, and N is expected to increase with excitation in a manner qualitatively

identical to that for homogeneous nucleation. In the latter part of this section we use the measured excitation threshold ratios P_+/P_- for different samples to determine the EHD surface tension σ using nucleation theory as described in Section 34. The variation of the value of σ with temperature is also presented for various types of EHD nucleation.

Unless stated otherwise the data presented in this section was recorded using an unstabilized tungsten lamp as a source of surface excitation; otherwise the apparatus and procedure used was that described in Chapter 4. As discussed in Section 41, volume excitation is preferred for quantitative hysteresis measurements. However, no major differences were found between the results of surface and volume excitation, and we believe that the conclusions of this section are accurate. Excitation thresholds P_+ and P_- were extrapolated from linear plots of the EHD signals I_d^+ and I_d^- vs. P . The measured parameter used in this section to study the effect of crystal defects and to determine the EHD surface tension is the ratio P_+/P_- of the excitation thresholds for the creation and destruction of EHD at a given temperature. A careful analysis of the temperature variation of the calibrated FE density thresholds n_+ and n_- for volume excitation is presented in Section 54 together with a more reliable measurement of σ obtained by fitting the entire FE-EHD phase diagram at once.

As discussed in Section 42, dislocations might be expected to be very effective nucleation centers for EHD in Ge. The large strain field surrounding a dislocation attracts free excitons and considerably

lowers the energy per e-h pair of the e-h liquid. A detailed analysis of EHD nucleation on dislocations is quite difficult; qualitatively one expects a pronounced shift (by a factor $\sim 10^2$) of the threshold P_+ to lower excitation, because FE are attracted to regions of maximum strain, and a substantial change in the threshold ratio P_+/P_- .

The effect of dislocations on EHD nucleation was studied by measuring the thresholds P_+ and P_- for eight crystals of ultrapure Ge. These samples were cut to the same size, and identically etched and mounted. Two samples were essentially undislocated with vacancy clusters and associated 80 meV acceptor levels present (see Section 42); the other six were free of vacancy clusters but were dislocated in the range 10^2 cm^{-2} to 10^4 cm^{-2} . One pair of samples (150D and 150V) was cut $\sim 1 \text{ cm}$ apart from the same slice of Ge, in order to ensure common characteristics other than dislocations and vacancy clusters. The hysteresis curves for the EHD signals I_d^+ and I_d^- vs. P measured on all eight samples at $T \approx 2.1\text{K}$ were qualitatively identical. No major shift in the excitation threshold P_+ with dislocation density was observed, either for surface or for volume excitation. For example, the thresholds for EHD formation measured with volume excitation on samples 150D and 150V at $T = 2.0\text{K}$ were respectively $P_+ = 1.8 \text{ mW cm}^{-2}$ and $P_+ = 0.61 \text{ mW cm}^{-2}$; this difference is roughly comparable to that expected from the FE lifetime alone (see Table 4.1).

A plot of the measured threshold ratios P_+/P_- vs. dislocation density for all eight samples at 2.1K is shown in Fig. 5.15. The sample numbers and the dominant impurity types are indicated in the

figure. As shown in Fig. 5.15, the measured ratios P_+/P_- exhibit no significant correlation with either dislocation density or type of electrical impurity. The apparent scatter of the measured values for P_+/P_- is primarily caused by the variation of P_+/P_- with impurity concentration (see below). Using volume excitation the measured ratios for samples 150D and 150V were respectively $\ln(P_+/P_-) = 0.99$ and $\ln(P_+/P_-) = 0.83$ at $T = 2.0K$ confirming this conclusion. Thus neither the EHD hysteresis curves nor the excitation thresholds P_+ and P_- exhibited any significant variation with dislocation density in the range 0 to 10^4 cm^{-2} . Because dislocations are expected to be very effective nucleation centers, we conclude that the e-h recombination rate at the dislocation core must be sufficient to destroy nascent EHD nucleated on dislocations before they can grow to macroscopic size. That is, dislocations may nucleate EHD embryos, but these are so quickly destroyed that they do not contribute significantly to the luminescence signals I_d observed. This conclusion also suggests that dislocations can be a significant center for the non-radiative recombination of FE.

Barring dislocations, shallow electrical impurities are expected to be most effective as nucleation centers in the crystals studied (see Section 42). Because the excited samples are continually flushed with free carriers, and the impurity ionization time at 2K is extremely long, the vast majority of these impurities are expected to be electrically neutral. A replot of the data of Fig. 5.15 for the threshold ratio P_+/P_- vs. net impurity concentration $|N_A - N_D|$ is shown in Fig. 5.16; the data for the undislocated samples has been omitted

because $|N_A - N_D|$ is controlled by 80 meV deep levels in this case. As shown in Fig. 5.16, the measured threshold ratios P_+/P_- are significantly correlated with impurity concentration; P_+/P_- decreases by roughly a factor of 1.5 as $|N_A - N_D|$ increases from $3 \times 10^9 \text{ cm}^{-3}$ to $4 \times 10^{12} \text{ cm}^{-3}$. A similar but smaller decrease in the threshold ratio with total impurity concentration $N_i = N_A + N_D$ is predicted by inhomogeneous nucleation theory for neutral impurities as described in Chapter 2; the calculated values P_+/P_- decrease by approximately 15% as N_i increases from 10^{10} cm^{-3} to 10^{13} cm^{-3} . The correlation of the measured values P_+/P_- with impurity concentration is strong evidence that the nucleation of EHD actually observed takes place on shallow electrical impurities, at least for the more impure crystals studied.

The conclusion that EHD form on shallow impurity atoms is important to the analysis of threshold data in terms of nucleation theory, and thus the measurement of the EHD surface tension σ and condensation energy ϕ . Because the concentration of EHD is typically very small ($\sim 10^7 \text{ cm}^{-3}$), an undetectable density of unusual defects could in principle dominate the process of nucleation. The identification of impurities as active nucleation centers in the samples studied rules out this possibility. Also, the calculated thresholds for homogeneous nucleation and inhomogeneous nucleation on impurity atoms (see Chapter 3) are quantitatively too similar to identify the type of nucleation by analysis of the data for only one sample. The similarity of these two cases is in marked contrast to the behavior of ordinary liquids as discussed above. Possibly the most important effect of impurity atoms

is to stabilize small multi-exciton complexes which grow into macroscopic EHD.

As described in Chapter 3, we can use measurements of the excitation threshold ratio P_+/P_- such as those above to determine the EHD surface tension σ . The procedure, described in detail in Section 34, is to calculate σ using EHD nucleation theory from the value of P_+/P_- measured at a given temperature. The values used for the EHD parameters other than σ are those given in Table 3.1, and the temperature-independent evaporation rate c is not included in the calculation. Because P_+/P_- is a rapidly varying function of σ (see Fig. 3.2), this method yields accurate results for the surface tension. Also, the temperature variation of the measured values of σ can be studied, assuming different types of nucleation. However, this method has the disadvantage that the individual variation of P_+ and P_- with T is not included in the analysis. An improved measurement of σ obtained by fitting the entire measured FE-EHD phase diagram at once is presented in Section 54.

Table 5.1 lists the threshold ratios P_+/P_- measured at 2.1K for seven different samples of ultrapure Ge and the values of the surface tension σ calculated from P_+/P_- for four different assumptions regarding the type of nucleation. Repeated measurements for samples 315, 393, and 391 demonstrate the reproducibility of the method. As shown in Table 5.1, the measured values of σ repeat very well from sample to sample and depend surprisingly little upon the type of nucleation assumed in the analysis. As the net impurity concentration increases

from $3 \times 10^9 \text{ cm}^{-3}$ for sample 315 to $4 \times 10^{12} \text{ cm}^{-3}$ for sample 400, the value for σ deduced decreases slightly, by $\approx 20\%$; no correlation is found with dislocation density. The values of σ calculated assuming homogeneous nucleation and inhomogeneous nucleation on neutral impurities with the barrier lowering $\Delta\psi = 50\text{K}$ (see Chapter 2) are practically identical, as we expect from the similarity of the calculated thresholds in these two cases (see Fig. 3.3). As the value assumed for $\Delta\psi$ increases from 50K to 200K, the surface tension calculated for inhomogeneous nucleation increases by $\approx 40\%$. Using our result that EHD form an impurity atoms and the value $\Delta\psi = 100\text{K}$, which agrees with the recently calculated value^{5.3} $B \approx 10 \text{ meV}$ for the binding energy of an EHD on a neutral donor, we average the results shown in Table 5.1 for this case to obtain

$$\sigma = (2.6 \pm 0.2) \times 10^{-4} \text{ erg cm}^{-2} \quad (5.9)$$

at 2.1K, where the error shown is purely statistical. By simply averaging all of the results for σ shown in Table 5.1, we find a similar value $\sigma = (2.6 \pm 0.4) \times 10^{-4} \text{ erg cm}^{-2}$ at 2.1K. The systematic error for σ introduced by uncertainties in the parameters used in the analysis is comparable to that shown in Eq. (5.9). Replacing the value $\phi = 2.0 \text{ meV}$ at $T = 0\text{K}$ used for the EHD condensation energy in the analysis for Eq. (5.9) by the recent spectroscopic measurement^{5.6} $\phi = 1.8 \text{ meV}$ at $T = 0\text{K}$ we find the mean value $\sigma = 2.4 \times 10^{-4} \text{ erg cm}^{-2}$ at 2.1K.

In general the surface tension (actually the surface free energy) of a liquid varies with temperature. Because the e-h liquid is a

degenerate Fermi liquid we expect the form of this temperature dependence to be $\sigma = w(1 - \delta_\sigma T^2)$ well below the critical temperature^{5.14} $T_c = 6.5\text{K}$, where w is the surface energy at $T = 0$. Reinecke and Ying^{5.15} have suggested that $\delta_\sigma = T_c^{-2} = 2.4 \times 10^{-2} \text{ K}^{-2}$; actually this value should be an upper limit to δ_σ , because one expects significant higher order corrections to σ near the critical point. The quantity calculated by theorists is the surface energy w rather than σ . Although the expected difference between σ and w at 2.1K is quite small $((T/T_c)^2 = 0.10)$, it is interesting to study the temperature dependence of the measured value of σ in order to make a comparison with theory. More importantly, such a study is a test of the validity of EHD nucleation theory used to determine σ .

A graph of the surface tension σ calculated from the threshold ratios P_+/P_- measured for sample 315 between 1.4K and 2.1K is shown in Fig. 5.17, for three different assumptions regarding the type of nucleation. As shown in Fig. 5.17 the curves for all three assumptions are consistent with the expected temperature dependence; the slopes yield $\delta_\sigma \approx 0$ for homogeneous nucleation and $\delta_\sigma \approx 0.1\text{K}^{-2}$ and $\delta_\sigma \approx 0.2 \text{ K}^{-2}$ for $\Delta\psi = 50\text{K}$ and 100K , respectively, assuming inhomogeneous nucleation. Thus EHD nucleation theory provides an accurate description of the thresholds for drop formation and breakup below 2.1K. However, the systematic errors present in the theoretical analysis are too large to allow confidence in the measurement of δ_σ , which depends upon small changes in σ . In the following section we use the value^{5.15} $\delta_\sigma = T_c^{-2}$ in a careful analysis of the measured EHD-FE phase diagram to determine the surface energy w , which can be directly compared with theory.

54 Free-Exciton-Electron-Hole Drop Phase Diagram

In this section we present a detailed measurement and analysis of the threshold phase diagram for FE and EHD in ultrapure Ge at temperatures between 1.2K and 2.0K, which we believe is the most careful frequent of this problem to date. A brief account of this work has appeared previously.^{5.16} We observe very large deviations from the simple phase diagram expected for ordinary liquids. These departures from simple behavior are caused by the impossibility of attaining thermodynamic equilibrium in the FE-EHD system, due to metastable effects of the EHD surface tension and the finite lifetimes of EHD and FE. We find excellent quantitative agreement between the measured threshold phase diagram and that calculated using EHD nucleation theory as described in Chapters 2 and 3. Because the calculated thresholds are sensitive functions of the EHD condensation energy ϕ and the surface tension σ , a fit of theory to experiment yields accurate values for these parameters; $\phi = 1.9 \pm 0.2$ meV and $\sigma = (2.6 \pm 0.3) \times 10^{-4}$ erg cm⁻² at $T = 0$.

In ordinary usage, the term "phase diagram" assumes thermodynamic equilibrium between species and is thus not strictly applicable to the EHD-FE system. Because this system is characterized by metastability and other non-equilibrium processes at low temperatures ($T \lesssim 3K$), the phase diagram for EHD and FE in the conventional sense cannot be directly measured and has little physical meaning. Hereafter we use the term EHD-FE phase diagram to denote a plot vs. temperature of the threshold FE densities n_+ and n_- for the creation and destruction of

EHD, which define the regions of stability for EHD in the n, T plane. Although these thresholds are determined by non-equilibrium processes, the physical meaning of such a plot corresponds to that for ordinary liquids.

In the original experimental work^{5.1,5.8,5.17,5.18} on the EHD-FE phase diagram, thermodynamic equilibrium was assumed in order to extract a value for the condensation energy ϕ from threshold data. These values, typically $\phi \approx 1.5$ meV, differ substantially from more reliable spectroscopic measurements,^{5.19,5.20} typically $\phi \approx 1.9$ meV. Recent threshold measurements,^{5.21,5.22} analyzed with the same assumption, yield similar values $\phi \approx 1.6$ meV. Westervelt, Staehli, and Haller^{5.23} first correctly explained that the origins of this discrepancy were non-equilibrium effects in the FE-EHD system as described in Chapters 2 and 3. The same theoretical conclusion was reached independently by Silver.^{5.24} Westervelt et al.^{5.9,5.23} also reported the first measurements of the complete FE-EHD phase diagram for Ge including the thresholds for the destruction of EHD, and found good qualitative agreement between experiment and EHD nucleation theory, including the disappearance of hysteresis below $T \approx 1.4$ K. The ratio P_+/P_- of the excitation thresholds was used in this work^{5.9,5.23} to determine the EHD surface energy $w = (2.4 \text{ to } 2.8) \times 10^{-4} \text{ erg cm}^{-2}$ as described in Section 53. Subsequently, Etienne et al.^{5.25} have also measured the FE-EHD phase diagram including hysteresis with similar experimental results. However, they do not find good agreement between threshold data and their treatment of EHD nucleation, and conclude only that w lies in the range

$(1.8 \text{ to } 2.6) \times 10^{-4} \text{ erg cm}^{-2}$; we discuss their work further below. Recently, Thomas et al.^{5.20,5.13} claimed to have accurately measured the FE-EHD phase diagram spectroscopically, simply by determining the condensation energy ϕ and the density of states for FE which are then substituted into the theoretical expression for the saturated FE density n_s (see Eq. 2.8). From the discussion above it is clear that hysteresis and lifetime effects dominate the phase diagram below 3K, and that the saturated density n_s is therefore inapplicable. Furthermore, the absolute accuracy of their calculated phase diagram is only a factor ≈ 3 at 2K, no better than that obtained by calibrated threshold measurements.

Two central difficulties must be overcome in order to produce a careful measurement of the FE-EHD phase diagram which can be quantitatively compared with nucleation theory. First, it is imperative that the existence of hysteresis effects be correctly accounted for. Thus both branches of the phase diagram, n_+ and n_- , must be measured using a stable, noise-free source of excitation cycled in a well-defined and reproducible manner, as described in Chapter 4. Because the observed thresholds vary with the time of observation Δt at low temperatures, (see Fig. 5.13), the data should also be recorded at a fixed value of this time Δt which can later be used in the analysis. Second, a technique must be developed to quantitatively relate the observed thresholds in excitation power to the peak value of the FE density n within the Ge crystal. In the discussion below, we give a detailed analysis of this problem and describe the procedure used in this experiment.

The largest value of the FE density within a sample of Ge uniformly excited across one entire surface (the geometry used in this work) is given by

$$n = P\tau_x\eta/h\nu L_{\text{eff}}, \quad (5.10)$$

where $P(\text{mW cm}^{-2})$ is the absorbed excitation power for photons of energy $h\nu$, τ_x is the FE lifetime, η is the quantum efficiency for the production of excitons, and L_{eff} is the effective depth of penetration of FE into the sample. For surface excitation L_{eff} is simply equal to the FE diffusion length $L = (D\tau_x)^{1/2}$ with D the diffusion constant; for volume excitation assuming negligible surface recombination.

$L_{\text{eff}} = L + \ell$ where $\ell \approx 1 \text{ mm}$ is the absorption length of $1.52 \mu\text{m}$ radiation. Another measure of the peak FE density n is the intensity I_x of the FE luminescence below the threshold for drop formation; for the experimental geometry used here we have

$$I_x = CnL_{\text{eff}} = CP\tau_x\eta \quad (5.11)$$

where C is a constant of proportionality. Note that I_x from Eq. (5.11) for a given value of the excitation P , is independent of the depth of penetration L_{eff} of FE into the sample. For the apparatus described in Chapter 4, the excitation power P is accurately monitored and calibrated, and the photon energy $h\nu$ is well known. Thus the primary uncertainties in Eqs. (5.10) and (5.11) are due to the quantum efficiency, the FE lifetime and the spatial distribution of FE within the sample. For quantitative comparison of the measured phase diagram with theory it is essential that these parameters do not vary with temperature;

their absolute values are somewhat less important.

We can test the effects of the quantum efficiency η , the FE lifetime τ_x , and the spatial distribution of FE by comparing the hysteresis curves obtained for EHD and FE using volume and surface excitation on the same sample at the same temperature. We also test the long-term reproducibility of the data for these two cases by repeating the measurements. Hysteresis curves for EHD in sample 315 at $T = 1.82\text{K}$ are shown in Fig. 5.18 for surface excitation and in Fig. 5.19 for volume excitation. In both figures the data were recorded in order of decreasing excitation, first for the upgoing curve, then for the downgoing curve. After the data for Run 1 were recorded, (elapsed time $\sim 4 \times 10^3$ sec), the process was repeated to obtain Run 2 as indicated in Figs. 5.18 and 5.19. As shown in Fig. 5.18, the data obtained using surface excitation do not reproduce well for Runs 1 and 2, despite the fact that the short-term reproducibility from point to point is very good. Both the EHD signals I_d^+ and I_d^- , and the excitation thresholds P_+ and P_- differ substantially for the two runs shown in Fig. 5.18. On the other hand, the data obtained using volume excitation, shown in Fig. 5.19, are strictly reproducible. This evidence indicates that the sample surface can have a considerable effect on the density of FE produced by optical excitation. Direct evidence that the sample surface can rapidly destroy FE in Ge was recently presented by Elliot et al.^{5,26} It is not clear whether the difference between Runs 1 and 2 in Fig. 5.18 is caused by the relatively large initial excitation $P_{\max} = 14.0 \text{ mW cm}^{-2}$ used to record

the downgoing points, or by other effects. However, volume excitation is obviously preferable for quantitative measurements of the EHD-FE phase diagram. Previously reported measurements of the EHD-FE phase diagram^{5.9,5.25} were taken using surface excitation and are thus subject to irreproducible effects. Because the threshold ratios $P_+/P_- \approx 4.8$ and $P_+/P_- \approx 5.4$ for Runs 1 and 2 in Fig. 5.18 reproduce reasonably well, the effect of surface excitation upon the measurements given in Section 53 is expected to be less serious.

By comparing the FE signals I_x^+ for surface and volume excitation recorded below the threshold P_+ , where $I_x^+ \propto P$ approximately, we obtain a measure of the quantum efficiency η . For sample 315 at $T = 1.80K$, we find that I_x , and therefore the product $\eta\tau_x$ from Eq. 5.11, are ≈ 3.6 times smaller for surface excitation, using the same values of the absorbed photon flux $P/h\nu$ in both cases. Even if the surface recombination rate for volume excitation is very large, the overall quantum efficiency η is no smaller than $\eta = [1+(L/\ell)]^{-1} \approx 60\%$ for $L \approx 0.7$ mm and $\ell \approx 1.0$ mm, the values appropriate for this sample. Assuming that the lifetime τ_x is the same for both cases, we can thus conclude that $\eta \approx 16\%$ for surface excitation on this sample. This value of η corresponds to the surface recombination velocity $S = (L/\tau_x)(\eta^{-1}-1) \approx 1 \times 10^5$ cm sec⁻¹, considerably larger than the estimate $S \approx 10^2$ cm sec⁻¹ for free carriers at room temperature (see Section 42). Thus the surface recombination of FE can be an important factor in the FE density calibration of threshold measurements. Note that the threshold P_+ in Fig. 5.18 for surface excitation (corrected

for the difference in mean photon energy $h\nu$) is ≈ 1.5 times greater than that for volume excitation. Using the appropriate values for L_{eff} in Eq. (5.11), we find the ratio 3.6 for the product $\eta\tau_x$ for surface and volume excitation, in excellent agreement with the result from I_x above.

Because the mechanism which determines the short FE lifetime τ_x in the samples studied has not yet been positively identified, it is important to establish that this parameter is in fact a true exponential lifetime, and to study the variation of τ_x with temperature and excitation level. As described in Chapter 4, we measured the lifetime τ_x for several samples by recording the decay of the FE luminescence at 4.2K following short, pulsed GaAs laser excitation, after the EHD luminescence had disappeared. In all cases (see Table 4.2) this decay was exponential as expected, indicating that τ_x does not vary with FE density n . Hensel et al.^{5.13} have suggested that τ_x is determined by recombination at impurity atoms and therefore that $\tau_x \propto N_i^{-1}$, where N_i is the total impurity concentration. Inspection of Table 4.2 shows no correlation between τ_x and N_i , ruling out this mechanism. However, the shorter values of τ_x in Table 4.2 are associated with the more highly dislocated samples, suggesting dislocations as an active recombination site.

Unfortunately, the lifetime τ_x could not be directly measured at temperatures much less than 4K, because the EHD luminescence cut-off time becomes very long.^{5.4} In order to study the variation of τ_x with temperature and excitation power, the steady-state FE luminescence

signal I_x^+ was recorded vs. P using volume excitation at levels below the threshold P_+ for drop formation at various temperatures between 1.5K and 4.2K. The results are shown vs. temperature as a series of constant-excitation contours in Fig. 5.20; the excitation power P for each curve is indicated. As shown in Fig. 5.20, the FE signal I_x for a given excitation is accurately independent of temperature, except for the signals recorded at 4.2K, which are slightly smaller. From Eq. (5.11) for I_x , we conclude that the product $\eta\tau_x$ is practically temperature independent between 1.5K and 4.2K. Assuming that the overall quantum efficiency η for volume excitation does not vary with T (which is true both in the limits of negligible and strong surface recombination), the data of Fig. 5.20 indicate that the FE lifetime is constant in this temperature range.

This study of the FE signal I_x vs. excitation is important, because the threshold FE densities n_+ and n_- at low temperatures are comparable to the concentration of impurities and other defects in the samples studied (see Section 42), and FE trapping by these defects could be significant in principle. A plot of I_x^+ vs. P for volume excitation of sample 315 below the threshold P_+ for EHD formation at $T = 2.00K$ is given in Fig. 5.21. As shown in this figure, the FE signal I_x varies linearly with excitation for $P \gtrsim 0.5 \text{ mW cm}^{-2}$ as indicated by the solid line. However, for smaller values of excitation $P \lesssim 0.5 \text{ mW cm}^{-2}$, the slope of I_x vs. P decreases, suggesting the existence of a small concentration of active traps for FE. At 4.20K similar behavior is observed, except the break in slope of I_x vs. P

occurs at a slightly larger value of the excitation, $P \approx 0.8 \text{ mW cm}^{-2}$. Thus the FE density produced by volume excitation is somewhat smaller than that predicted assuming $n \propto P$. Because the excitation thresholds P_+ and P_- at $T \sim 1.5\text{K}$ are of the order $\sim 0.3 \text{ mW cm}^{-2}$ in this sample (see Fig. 5.8), non-linearity in I_x vs. P such as that shown in Fig. 5.21 can be significant, and should be included in the FE density calibration.

Finally, we consider the possibility that the FE diffusion length $L = (D\tau_x)^{1/2}$ changes with temperature. This parameter enters the FE density calibration through the effective depth L_{eff} of FE in the sample, as indicated for Eqs. (5.10) and (5.11) above. To our knowledge, the only measurement of the FE diffusion constant D at low temperatures ($T < 4\text{K}$) in Ge is that of Pokrovskii and Svistunova^{5.27} who find $D \approx 1500 \text{ cm}^2 \text{ sec}^{-1}$ at 3K below the threshold FE density for drop formation. This value of D is consistent with that estimated^{5.13} from the carrier-phonon scattering time $\tau_p \approx 10^{-9} \text{ sec}$ in Ge at 3K^{5.28}, $D = \tau_p kT/m^* = 1400 \text{ cm}^2 \text{ sec}^{-1}$. Therefore we assume that FE diffusion at low temperatures and FE density is limited by phonon-scattering. Because the value of the scattering time τ_p is proportional to $T^{-3/2}$ for free carriers,^{5.28} we expect that the FE diffusion constant varies as $D \propto T^{-1/2}$ with temperature. Thus the FE diffusion length $L = (D\tau_x)^{1/2} \propto T^{-1/4}$ is expected to be only slowly temperature-dependent; as T increases from 1.3K to 2.0K, the range of our threshold measurements, L decreases by only $\approx 20\%$. For surface excitation a corresponding change in expected in $L_{\text{eff}} = L$ in Eqs. (5.10) and (5.11). For volume excitation, the temperature variation of $L_{\text{eff}} = L + \ell$ is

even smaller, because the absorption length $\ell \approx 1$ mm is larger than $L \approx 0.7$ mm, and this variation can be safely neglected.

In the following paragraph we describe the method actually used to measure the FE-EHD phase diagram for Ge. Volume excitation was used in recording all of the data in order to avoid irreproducible effects of the sample surface such as those described above (see Figs. 5.18 and 5.19) and to simplify the analysis of the spatial distribution of free excitons. Hysteresis curves for both the EHD and FE signals I_d^+ and I_x^+ such as those shown in Fig. 5.2 were recorded during one experimental run at a number of temperatures between 1.2K and 2.0K. At higher temperatures the maximum excitation available with this apparatus was insufficient to reach the threshold P_+ for drop formation. Excitation thresholds P_+ and P_- were extrapolated from plots of $I_d^{1/2}$ vs. P for the data at each temperature as described in Section 5.1. In order to correct for the non-linearity of I_x vs. P (see Fig. 5.21), we assumed that the thresholds n_+ and n_- in FE density were proportional to the FE signals I_x^+ and I_x^- measured for each temperature at the corresponding excitation thresholds P_+ and P_- , as shown in Eq. (5.11). Because the length L_{eff} in Eq. (5.11) is expected to be essentially temperature-independent for volume excitation, this method yields accurate relative values for n_+ and n_- . To determine the constant of proportionality C in Eq. (5.11) and thus the absolute FE density, we used Eq. (5.10) with $\eta = 1$ for the FE density vs. P and used Eq. (5.11) to compare this value with the FE signal I_x recorded at 2.0K for the relatively large excitation $P \approx 4 \text{ mW cm}^{-2}$. The values of the parameters

τ_x , $h\nu$, and ℓ in Eq.(5.11) were measured for the sample used as described in Chapter 4, and the FE diffusion constant was assumed to have the temperature-independent value^{5.27} $D = 1500 \text{ cm}^2 \text{ sec}^{-1}$. Compared to the values obtained by simply assuming $n \propto P$, the FE thresholds determined in this manner exhibited a steeper temperature dependence, and were smaller by a factor ≈ 1.5 at $T \sim 1.3\text{K}$. Thus, the relative values of the threshold FE densities n_+ and n_- obtained by this method are substantially more accurate than those obtained from excitation thresholds alone as in earlier work;^{5.9,5.25} no absolutely calibrated measurements of both n_+ and n_- have been previously reported.

The measured FE-EHD phase diagram for sample 315 obtained in this manner is shown in Fig. 5.22 as the data points together with a theoretical fit described below. The qualitative features of Fig. 5.22 are in excellent agreement with EHD nucleation theory as described in Chapters 2 and 3 and with the hysteresis data presented in Section 51. The measured FE density thresholds n_+ and n_- shown in Fig. 5.22 display a pronounced hysteresis which decreases with temperature and disappears below $T \approx 1.4\text{K}$. Both thresholds vary only slowly with temperature and lie well above the saturated FE density n_s predicted by equilibrium thermodynamics, indicated by the dashed curve. Furthermore, the slope of the upgoing branch n_+ of the phase diagram is substantially smaller than that of n_s , explaining the small values obtained for previous "threshold" measurements^{5.1,5.8,5.17,5.18,5.21,5.22} of the condensation energy ϕ . From the data of Fig. 5.22 it is clear that the FE-EHD phase

diagram below 2K is dominated by the effects of metastability and the EHD lifetime, and that equilibrium thermodynamics provides a very poor description of the system. Any threshold experiment which neglects these non-equilibrium effects in either the data taking procedure or the analysis can be expected to yield inaccurate results.

In order to make a quantitative comparison of the measured FE-EHD phase diagram with nucleation theory and accurately measure the EHD surface energy w and the condensation energy ϕ , a least-squares fit of the thresholds n_+ and n_- predicted by the theory described in Chapters 2 and 3 to the data of Fig. 5.22 was made using w and ϕ at $T = 0$ as adjustable parameters. Because the calculated phase diagram is very sensitive to the values of w and ϕ , they must be adjusted to make a valid comparison. For the same reason, this procedure is an accurate and reliable method to determine the values of these parameters. In order to obtain the best fit at the lowest temperatures, the coefficient c of the temperature-independent evaporation rate^{5.29} of EHD was also included in the theory, as a third adjustable parameter.

To ensure accurate results the temperature dependence of the parameters σ , ϕ , and n_0 and the actual non-parabolic density of states for FE were included in the theory. As discussed in Section 5.3, the surface energy σ is expected to vary with temperature as $\sigma = w(1 - \delta_\sigma T^2)$; we used the value $\delta_\sigma = T_c^{-2}$ with the critical temperature^{5.14} $T_c = 6.5\text{K}$. For the condensation energy we used $\phi = \phi_0(1 + \delta_\phi T^2)$, where the coefficient $\delta_\phi = 0.18\text{ K}^{-2}$ has been measured spectroscopically.^{5.20} Recently, the actual non-parabolic density of states for FE in Ge has

been measured by Thomas et al.,^{5.20} and accurately calculated by Altarelli and Lipari^{5.30} with excellent agreement between theory and experiment. Because the experimental results are significantly broadened at the low energy edge by the spectral resolution of their apparatus, we could not use them to calculate the actual effective density of states D_x for FE which enters Eq. (2.8) for the saturated FE density n_s . Instead, we calculated D_x by numerically integrating the dispersion relation given for FE by Altarelli and Lipari.^{5.30} The results for $1K < T < 5K$ accurately fit the polynomial expansion (error $\lesssim 0.5\%$):

$$D_x = \gamma_x (m^* kT / 2\pi\hbar^2)^{3/2} (0.98 + 0.045T + 0.0106T^2) \quad (5.12)$$

where $m^* = 0.436 m_0$ is the density-of-states effective mass and T is expressed in K. An attempt to include the effect of non-parabolicity on the FE mean speed $\bar{v}$ was also made by assuming spherical symmetry and numerically evaluating the integral for $\bar{v}$ with the result

$$\bar{v} = (8kT/\pi m^*)^{1/2} (1.14 - 0.050T + 0.0020T^2) \quad (5.13)$$

where $m^* = 0.436 m_0$ and T is expressed in K as above. From Eqs. (5.12) and (5.13) we find that the temperature corrections to D_x and $\bar{v}$ due to non-parabolicity are negligible below 2K; even at 4K these corrections are relatively small, $\lesssim 35\%$. The most significant result of this calculation is the "improved" value $m^* = 0.436 m_0$ for the FE density-of-states effective mass, which is $\approx 30\%$ larger than the value $m^* = 0.335 m_0$ from Table 3.1, which was also used by Thomas et al.^{5.20} to estimate the size of the effect of non-parabolicity on D_x . Thus we conclude

that the effect of recent measurements^{5.20} and calculations^{5.30} of the FE density of states on D_x below 4K is primarily accounted for by a simple change in the value of m^* . Nevertheless, the full expressions Eqs. (5.12) and (5.13) were used in the analysis below. The values of the other parameters used to calculate the phase diagram are those given in Table 3.1, with the exception of the maximum generation rate G_M , the observation time Δt , the lifetimes τ_o and τ_x , and the impurity concentration N_i ; for these quantities the actual experimental values were used (see Chapter 4).

The fitting procedure was carried out for two separate assumptions: homogeneous nucleation of EHD and inhomogeneous nucleation on neutral impurity atoms with the value $\Delta\psi = 50K$ for the barrier lowering (see Chapter 2). The FE density thresholds n_+ and n_- were numerically calculated from the threshold condition Eq. (3.15); the threshold density n_e for a significant population of EHD in dynamic equilibrium with the FE gas was also found from Eq. (3.18). Whenever the threshold n_e was respectively greater or smaller than the calculated values of n_+ or n_- , this threshold was used to compare with the data; this algorithm corresponds to the physical situation as discussed in Chapters 2 and 3. Because the relative accuracy of the FE density calibration for n_+ and n_- described above is expected to be much better (by a factor > 10) than the absolute accuracy, the absolute calibration was not used in the fitting procedure. Thus the shape of the measured phase diagram was accurately fitted; the measured absolute values for n_+ and n_- were used as a check on the results. The actual calculations

were done numerically on the CDC 7600 computer at Lawrence Berkeley Laboratory. A rough estimate of the error in the resulting values of the fitted parameters was made by visually comparing the thresholds calculated for slightly different values of w , ϕ_0 and c with the experimental data.

The theoretical FE-EHD phase diagram obtained by this procedure is shown as the solid curves in Fig. 5.22. The results obtained assuming homogeneous and inhomogeneous nucleation differed very little; the fit obtained assuming EHD formation on impurity atoms is slightly better, as we expect from the discussion in Section 5.3, and is given in Fig. 5.22. As shown in Fig. 5.22, we find excellent agreement between the experimental data and the calculated curves over the entire temperature range of the measurement. This agreement is a strong confirmation of the validity of EHD nucleation theory, and provides confidence in the results obtained for the fitted parameters w and ϕ_0 . Recently, the threshold FE density n_+ at low temperatures ($T \gtrsim 2K$) has also been measured for Si by Dite et al.^{5.31} These measurements agree reasonably well with nucleation theory as shown in Fig. 3.5, providing additional evidence for the validity of this approach. The lack of agreement between theory and experiment found by Etienne et al.^{5.25} is due to their use of surface excitation, which can yield irreproducible results (see Figs. 5.18 and 5.19) their unjustified assumption that $n \propto P$ for all temperatures (see Fig. 5.21), and the failure to include the term c in the analysis.

The FE density scale shown in Fig. 5.22 is that from the theoretical calculation. The absolute calibration for the data points in Fig. 5.22 yields values of the FE density approximately four times smaller than the theory. To check on this discrepancy, the fitting procedure was repeated using absolute rather than the relative values for the data. The fit thus obtained was considerably poorer than that shown in Fig. 5.22, both qualitatively and quantitatively. Because the absolute accuracy of the FE density calibration is not expected to be better than roughly a factor of two, we feel that this discrepancy is not serious and therefore that the results shown in Fig. 5.22 are more accurate and reliable. However, it is surprising that the measured values of $n_{\pm}$ are smaller than the theory. Such an effect could be due to an increased FE lifetime in the interior of the sample, or possibly to a localized increase in the FE density in the strain well about dislocations, present in this sample.

Now we present the results for the EHD surface energy w , the condensation energy ϕ_0 at $T = 0$, and the coefficient c , obtained by fitting the entire FE-EHD phase diagram as described above. Because the calculated phase diagram is quite sensitive to the values of w and ϕ_0 , the fit accurately determines these important parameters. This measurement is also the first in which ϕ_0 and w are both independently determined by threshold data. As mentioned previously, the results obtained assuming homogeneous and inhomogeneous nucleation differed only slightly. Overall we find

$$\phi_o = 1.9 \pm 0.2 \text{ meV} , \quad (5.14)$$

$$w = (2.6 \pm 0.3) \times 10^{-4} \text{ erg cm}^{-2} . \quad (5.15)$$

The fit was sensitive only to the order of magnitude of c ; for this parameter we find $c \sim 10^5 \text{ sec}^{-1}$. Hensel et al^{5.13,5.17} have suggested that the temperature-independent evaporation rate of EHD arises from excitations in the e-h liquid near the surface caused by the radiative recombination of e-h pairs. The value $c \sim 10^5 \text{ sec}^{-1}$ above corresponds to the emission of one FE for each recombination within $\approx 15 \text{ nm}$ of the EHD surface; this length is comparable to the surface thickness $\approx 20 \text{ nm}$ for EHD lending credability to this model.

The value of the condensation energy $\phi_o = 1.9 \pm 0.2 \text{ meV}$ from Eq. (5.14) obtained by fitting the phase diagram is in excellent agreement with the most careful spectroscopic measurement^{5.6} $\phi = 1.8 \pm 0.2 \text{ meV}$, and with the theoretical value $\phi_o = 1.8 \text{ meV}$ obtained from the most detailed calculations of the e-h liquid pair binding energy^{5.32} $E_g = 5.9 \text{ meV}$ and the FE binding energy^{5.30} $E_x = 4.15 \text{ meV}$. Thus we have conclusively shown that the long-standing discrepancy between so-called "threshold" and spectroscopic measurements of ϕ_o is completely explained by the proper application of EHD nucleation theory. Although the fact that this discrepancy can be resolved by nucleation theory has been discussed previously,^{5.9,5.23-5.25} this is the first actual measurement of the condensation energy from threshold data which includes metastability and lifetime effects in the analysis. In fact, the accuracy of this method is comparable to

that obtained spectroscopically. The sensitivity of the measured thresholds to the value of ϕ is due to the fact that the saturated FE density $n_s \propto \exp(-\phi/kT)$ is a very sensitive function of ϕ at temperatures $\sim 2K$. For $T \gtrsim 2K$ we can measure ϕ from the absolute value of the calibrated threshold FE density n_+ by simply scaling the results of nucleation theory to fit the data, assuming $n_+ \propto n_s$, which is true for classical nucleation. In this way we find $\phi \approx 2.1$ meV from the data at 2.0K in Fig. 5.22, which agrees reasonably well with the more accurate value given above.

A list of experimentally measured values of the EHD surface tension σ and the theoretically calculated surface energy $w(\sigma$ at $T=0)$ reported to date is given in Table 5.2. As shown in Table 5.2, the original calculations^{5.33-5.36} for the surface energy yielded values typically $w \approx 1 \times 10^{-4}$ erg cm⁻². Recently, by including exchange and correlation effects in the gradient expansion used in more complete calculations, Vashishta et al.^{5.37} and Rose et al.^{5.38} have obtained considerably larger results $w = (3.5 \text{ to } 4) \times 10^{-4}$ erg cm⁻² and $w = (2.4 \pm 0.5) \times 10^{-4}$ erg cm⁻², which are more reliable. The first measurements of the EHD surface tension σ were those of Bagaev et al.^{5.39} and Westervelt et al.^{5.23,5.9} Bagaev et al. estimated σ from the temperature dependence of the drop concentration N measured by light scattering and absorption. Making the ad hoc assumption that $N \propto J_+$, the initial EHD formation rate for chopped excitation, they found $\sigma \approx 1.8 \times 10^{-4}$ erg cm⁻². Because the rate J_+ is expected to rapidly decrease in time following the leading edge of an exciting pulse (see Sections 31 and 32, and Ref. 5.10), the

accuracy of this assumption must be questioned. As shown in Table 5.2, Westervelt et al.^{5.9,5.23} found $w \approx 2.6 \times 10^{-4} \text{ erg cm}^{-2}$ from threshold data, in agreement with the value given above in Eq. (5.13) using the method described in Section 53. This method has the disadvantage that the temperature-dependence of the individual thresholds P_+ and P_- is not included in the analysis. Two measurements of σ by Etienne et al. using different methods are also shown in Table 5.2. A third experiment by this group^{5.41} measured the shift in the EHD luminescence line due to the effect of the surface tension on small drops, but did not independently determine σ . The first value^{5.25} $\sigma = (1.8 \text{ to } 2.6) \times 10^{-4} \text{ erg cm}^{-2}$ was obtained from their measurement of the FE-EHD phase diagram. Because these authors were unable to find good agreement with nucleation theory as discussed above, they measured σ by adjusting this parameter so that the slope vs. $1/T$ of the calculated thresholds n_+ between 2K and 4.2K yielded an apparent value of the condensation energy $\phi = 1.47 \text{ to } 1.55 \text{ meV}$, assuming the true value is given by 2.0 meV. The second technique used by this group was the observation of capillary-wave resonances of EHD in the attenuation of ultrasonic waves at 1.8K. In principle this method provides a direct measurement of the surface tension. However, the value deduced for σ from the observed resonant frequency is proportional to the cube of the drop radius R . Because the value $R = 2 \text{ } \mu\text{m}$ for the initial drop radius used in the analysis was not measured in this experiment, and is not an intrinsic property of the system ($R \approx 8 \text{ } \mu\text{m}$ at 2K from Ref. 5.8) it could easily be in error by at least 50%. Thus their result $\sigma = 3 \times 10^{-4} \text{ erg cm}^{-2}$ is

uncertain by a factor $\gtrsim 3$. Until R is accurately measured with the ultrasonic attenuation on the same apparatus, this method cannot be relied upon to yield accurate results.

Thus we believe that the measurement of the EHD surface energy $w = (2.6 \pm 0.3) \times 10^{-4} \text{ erg cm}^{-2}$ from Eq. (5.15) obtained by fitting the entire FE-EHD phase diagram is substantially more accurate and reliable than those previously reported. As shown in Table 5.2, this value is in reasonable agreement with the recent calculations of Vashishta et al.^{5.37} and of Rose et al.^{5.38} This result also justifies a posteriori the measurement of σ from threshold ratios P_+/P_- described in Section 53 and previously reported.^{5.9,5.23}

CHAPTER 6. CONCLUSIONS

Because a detailed discussion of the application of nucleation theory to hysteresis and threshold data is given in Chapter 5, we briefly summarize here only the most important results. Using a modified form of the Becker and Döring rate equations, we calculated in Chapter 2 the non-equilibrium rates J_+ and J_- of formation and breakup of electron-hole drops in a supersaturated gas of free excitons. These rates, largely determined by the value of the EHD surface energy w , yield sharp FE density thresholds n_+ and n_- for EHD formation and breakup, and predict large metastable effects in the FE-EHD system above $T \approx 1.4\text{K}$. At temperatures $\lesssim 1.4\text{K}$, the effect of the EHD lifetime becomes dominant, metastability is destroyed, and the thresholds are determined by the calculated population of EHD in dynamic equilibrium with the FE gas. In both cases, the calculated thresholds lie well above the saturated FE density n_s , which determines the phase boundary for ordinary liquids.

In Chapter 3 we used these results to give a detailed quantitative theoretical description of the process of EHD nucleation from a FE gas in Ge. We calculated both the excitation hysteresis curves and the metastable time development expected for the EHD luminescence intensity. The calculated thresholds n_+ and n_- yield the full FE-EHD phase diagram for Ge and Si including the effects of metastability and the EHD lifetime, and provide a correct procedure to accurately determine the EHD condensation energy ϕ and the surface energy w from threshold data. We also presented calculated limits for the EHD drop radius R vs.

temperature. These results were obtained for two separate assumptions: homogeneous nucleation, and nucleation of EHD on neutral impurity atoms.

Our experimental results were obtained using an extremely sensitive apparatus described in Chapter 4, specially developed for the study of hysteresis and threshold phenomena in the luminescence of EHD and FE from optically excited Ge. Volume excitation of the Ge samples was used whenever possible to minimize effects of the sample surfaces and to simplify the comparison with nucleation theory. We also made a study of the effect of dislocations and impurity atoms on EHD nucleation by examining a large number (eight) of specially selected ultrapure Ge samples.

High-sensitivity measurements of the hysteresis curves and the metastable time development of the EHD and FE luminescence intensity from Ge between 1.2K and 2.1K were obtained by cycling a highly stable source of optical excitation in an accurately reproducible manner. The experimental data, presented in Chapter 5, are in good qualitative and quantitative agreement with EHD nucleation theory. In section 51 we use hysteresis data for EHD and FE to obtain an estimate $p \sim 4.4$ for the EHD radiative enhancement factor; this experimental result is in good agreement with Fermi liquid theory. In section 52 we show that hysteresis can exist in the FE-EHD system for times as long as 6×10^4 sec; this fact implies that EHD are practically immobile under suitable circumstances, and has possible technological applications. We also show that the "upgoing" and "downgoing" EHD luminescence

intensities I_d^+ and I_d^- approach equilibrium logarithmically. The apparent risetime (10% to 90% of final value) of the EHD signal I_d^+ is measured to be as long as $\sim 10^3$ sec, a factor $\sim 10^7$ longer than that expected from the EHD lifetime $\tau_0 \approx 40$ μ sec alone. These effects are predicted by nucleation theory and give a striking demonstration of the importance of metastable effects in the EHD-FE system. In Section 53, we show that dislocations are ineffective as nucleation centers for observable EHD, and that EHD observed most probably form on neutral impurity atoms in ultrapure Ge. We also study the temperature dependence of the EHD surface tension σ measured from threshold data between 1.5K and 2.1K and conclude that this dependence is consistent with that expected for a degenerate Fermi liquid.

A careful study of the excitation thresholds P_+ and P_- for the creation and destruction of EHD presented in Chapter 5 establishes that these are unique and well-defined quantities for volume excitation. Using an experimental analysis of the FE luminescence intensity to calibrate the corresponding FE density thresholds n_+ and n_- , we accurately measure the FE-EHD phase diagram for ultrapure Ge between 1.2K and 2.0K, including the effects of hysteresis and metastability. The experimental data are in excellent quantitative agreement with the phase diagram calculated with EHD nucleation theory. A fit of theory to experiment yields an accurate measurement of the EHD surface energy $w = (2.6 \pm 0.3) \times 10^{-4}$ erg cm⁻², and the first correct measurement of the condensation energy from threshold data, $\phi_0 = 1.9 \pm 0.2$ meV at $T = 0$.

The experimental results described above establish that the EHD-FE system in Ge at low temperatures and levels of excitation is accurately described by EHD nucleation theory. Although hysteresis effects in the luminescence of EHD and FE in Ge seemed highly unusual and even somewhat implausible when they were discovered, particularly because of the very long time scales involved, we have shown that they are a natural consequence of the process of nucleation of electron-hole drops.

ACKNOWLEDGEMENTS

I am very grateful to Professor Carson D. Jeffries for the continued advice, support, and encouragement he has given me during the course of this work. I have never worked with a person who was more truly helpful than he has been. I am also grateful to Professor Charles Kittel for many useful comments and suggestions regarding nucleation theory. Dr. Jean Louis Staehli shared the work of constructing the experimental apparatus and recording the early data on hysteresis effects, including the results presented in Section 53. I also owe him thanks for the many hours we spent discussing this work. Dr. William L. Hansen and Dr. Eugene E. Haller generously provided the crystals of ultrapure Ge used in these experiments and shared their extensive knowledge of crystal defects and impurities. Dr. Haller also constructed the ultra-sensitive Ge photodetector which was essential to the success of this work. I also thank Dr. Robert Marciewicz, Dr. James Wolfe, John Furneaux, Anthony Hansen, Susan Kelso, and Bernard S. Black for discussions of the theory, apparatus, and results.

This work was done under the auspices of the U.S. Energy Research and Development Administration.

CHAPTER 1 REFERENCES

- 1.1 L. V. Keldysh, in Proc. IX Int. Conf. on Physics of Semiconductors, Moscow, ("Nauka", Leningrad, 1968), p. 1303.
- 1.2 Ya. E. Pokrovskii, Phys. Stat. Sol. (a) 11, 385 (1972).
- 1.3 C. Benoit à la Guillaume, M. Voos and F. Salvan, Phys. Rev. B5, 3079 (1972); B7, 1723 (1973).
- 1.4 V. S. Bagaev, Springer Tracts in Modern Physics 73, 72 (1975).
- 1.5 C. D. Jeffries, Science 189, 955 (1975).
- 1.6 J. C. Hensel, T. G. Phillips and G. A. Thomas, in Solid State Physics, to be published.
- 1.7 T. M. Rice, in Solid State Physics, to be published.
- 1.8 M. Lax and J. J. Hopfield, Phys. Rev. 124, 115 (1961).
- 1.9 G. A. Thomas, M. Capizzi, W. Weber, E. I. Blount and M. Lax, Phys. Rev. Lett. 37, 1000 (1976).
- 1.10 T. K. Lo, B. J. Feldman and C. D. Jefferies, Phys. Rev. Lett. 31, 224 (1973).
- 1.11 T. K. Lo, Ph.D. Thesis, University of California, Berkeley, 1973 (unpublished).
- 1.12 M. Altarelli and N. O. Lipari, Phys. Rev. Lett. 36, 619 (1976); Phys. Rev. B15, 4883 (1977); Phys. Rev. B15, 4898 (1977).
- 1.13 V. I. Sidorov and Ya. E. Pokrovskii, Fiz. Tech. Poluprov 6, 2405 (1972) [Sov. Phys. Semiconductors 6, 2015 (1973)].
- 1.14 A. Frova, G. A. Thomas, R. E. Miller and E. O. Kane, Phys. Rev. Lett. 34, 1572 (1975).
- 1.15 E. O. Kane, Phys. Rev. B11, 3850 (1975).

- 1.16 A. S. Kaminskii and Ya. E. Pokrovskii, Zh. Eksp. Teo. Fiz. Pisma Red. 11, 381 (1970) [JETP Lett. 11, 255 (1970)].
- 1.17 R. Sauer, Phys. Rev. Lett. 31, 376 (1973).
- 1.18 K. Kosai and M. Gershenzon, Phys. Rev. B9, 723 (1974).
- 1.19 R. W. Martin, Solid State Comm. 14, 369 (1974).
- 1.20 R. Sauer and J. Weber, Phys. Rev. Lett. 36, 48 (1976).
- 1.21 T. N. Morgan in Proc. XIII Int. Conf. on the Physics of Semiconductors, Rome, ed. by F. G. Fumi (Tipografia Marves, Rome, 1976), p. 825.
- 1.22 G. Kirczenow and M. L. W. Thewalt, Bull. Am. Phys. Soc. 22, 350 (1977).
- 1.23 G. A. Thomas, and T. Rice, Sol. St. Comm. 23, 359 (1977).
- 1.24 G. A. Thomas, T. G. Phillips, T. M. Rice and J. C. Hensel, Phys. Rev. Lett. 31, 386 (1973); G. A. Thomas, A. Frova, J. C. Hensel, R. E. Miller and P. A. Lee, Phys. Rev. 13, 1692 (1976).
- 1.25 T. K. Lo, Solid State Comm. 15, 1231 (1974).
- 1.26 P. Vashishta, S. G. Das and K. S. Singwi, Phys. Rev. Lett. 33, 911 (1974).
- 1.27 G. A. Thomas, T. M. Rice and J. C. Hensel, Phys. Rev. Lett. 33, 219 (1974).
- 1.28 R. M. Westervelt, T. K. Lo, J. L. Staehli and C. D. Jeffries, Phys. Rev. Lett. 32, 105 (1974); 32, 1331 (E) (1974).
- 1.29 R. M. Westervelt, J. L. Staehli, E. E. Haller and C. D. Jeffries, in Lecture Notes in Physics vol. 57, ed. by M. Ueta and Y. Nishina (Springer-Verlag, Berlin, 1976) p. 270.

- 1.30 R. M. Westervelt, in Proc. XIII Int. Conf. on the Physics of Semiconductors, Rome, ed. by F.G. Fumi (Tipografia Marves, Rome, 1976), p.902.
- 1.31 J. H. Rose and H. B. Shore, Bull. Am. Phys. Soc. 21, 223 (1976); and to be published.
- 1.32 P. Vashishta, R. K. Kalia and K. S. Singwi, in Lecture Notes in Physics, vol. 57, ed. by M. Ueta and Y. Nishina (Springer-Verlag, Berlin, 1976), p. 187.
- 1.33 C. Kittel, Thermal Physics (John Wiley and Sons Inc., New York, 1969), p.326.
- 1.34 J. C. Hensel, T. G. Phillips and T. M. Rice, Phys. Lett. 30, 227 (1973).
- 1.35 J. C. McGroddy, M. Voos and O. Christensen, Solid State Comm. 13, 1801 (1973).
- 1.36 R. M. Westervelt, J. L. Staehli and E. E. Haller, Bull. Am. Phys. Soc. 20, 471 (1975); J. L. Staehli, R. M. Westervelt and E. E. Haller, ibid, p. 471.
- 1.37 O. Volmer, Z. Phys. Chem. (Leipzig) 119, 277 (1926)
- 1.38 R. Becker and W. Döring, Ann. Phys. 24, 719 (1935); R. Becker, Theory of Heat, 2nd ed. (Springer-Verlag, New York, 1967) p. 239.
- 1.39 See J. Frenkel, Kinetic Theory of Liquids (Oxford Univ. Press, Oxford, 1946) p. 390.
- 1.40 J. E. McDonald, Amer. J. Phys. 30, 870 (1962); 31, 31 (1963).
- 1.41 F. F. Abraham, Homogeneous Nucleation Theory (Academic Press, New York, 1974).

- 1.42 J. Lothe and G. M. Pound, J. Chem. Phys. 36, 2080 (1962).
1.43 R. N. Silver, Phys. Rev. B11, 1569 (1975).

CHAPTER 2 REFERENCES

- 2.1 R. M. Westervelt, Phys. Stat. Sol. (b) 74, 727 (1976).
- 2.2 R. Becker and W. Döring, Ann. Physik 24, 719 (1935); R. Becker, Theory of Heat, 2nd Ed. (Springer-Verlag, New York, 1967), p. 239.
- 2.3 J. C. Hensel and T. G. Phillips, in Proc. XII Int. Conf. on the Physics of Semiconductors, Stuttgart, M. H. Pilkuhn, Ed. (B. G. Teubner, Stuttgart, 1974), p.51.
- 2.4 R. S. Markiewicz, Thesis, University of California, Berkeley (unpublished, 1975).
- 2.5 C. Benoit à la Guillaume, M. Voos, and F. Salvan, Phys. Rev. B5, 3079 (1972), and B7, 1723 (1973).
- 2.6 Ya. Pokrovskii, Phys. Stat. Sol. (a) 11, 385 (1972).
- 2.7 T. L. Reinecke and S. C. Ying, Phys. Rev. Lett. 35, 311 (1975).
- 2.8 T. K. Lo, B. J. Feldman, and C. D. Jeffries, Phys. Rev. Lett. 31, 224 (1973).
- 2.9 R. M. Westervelt, J. L. Staehli, E. E. Haller, and C. D. Jeffries, in Lecture Notes in Physics, Vol. 57, ed. by M. Ueta and Y. Nishina (Springer-Verlag, Berlin, 1976), p. 270.
- 2.10 C. D. Jeffries, Science 189, 955 (1975).
- 2.11 J. Frenkel, Kinetic Theory of Liquids (Oxford Press, Oxford, 1946), p. 390.
- 2.12 R. N. Silver, Phys. Rev. B11, 1569 (1975).
- 2.13 T. K. Lo, Solid State Comm. 15, 1231 (1974).

- 2.14 G. A. Thomas, T. M. Rice and J. C. Hensel in Proceedings of the Twelfth International Conference on the Physics of Semiconductors, Stuttgart, 1974, edited by M. H. Pilkuhn (B. G. Teubner, Stuttgart, 1974), p. 105.
- 2.15 R. M. Westervelt, T. K. Lo, J. L. Staehli, and C. D. Jeffries, Phys. Rev. Lett. 32, 1051 (1974); (E) 32, 1331 (1974).

CHAPTER 3 REFERENCES

- 3.1 R. M. Westervelt, Phys. Stat. Sol. (b) 76, 31 (1976).
- 3.2 R. M. Westervelt, J. L. Staehli, E. E. Haller and C. D. Jeffries, in Lecture Notes in Physics, vol. 57 ed. by M. Ueta and Y. Nishina (Springer-Verlag, Berlin, 1976), p. 270.
- 3.3 R. M. Westervelt, J. L. Staehli and E. E. Haller, Bull. Am. Phys. Soc. 20, 471 (1975); J. L. Staehli, R. M. Westervelt and E. E. Haller, ibid., p. 471.
- 3.4 T. K. Lo, Solid State Comm. 15, 1231 (1974).
- 3.5 G. A. Thomas, T. M. Rice, and J. C. Hensel, in Proceedings of the Twelfth International Conference on the Physics of Semiconductors, Stuttgart, 1974, edited by M. H. Pilkuhn (B. G. Teubner, Stuttgart, 1974), p. 105.
- 3.6 R. M. Westervelt, T. K. Lo, J. L. Staehli and C. D. Jeffries, Phys. Rev. Lett. 32, 1051 (1974); (E) 32, 1331 (1974).
- 3.7 S. Zwerdling, B. Lax, L. M. Roth and K. J. Button, Phys. Rev. 114, 80 (1959).
- 3.8 Ya. Pokrovskii, Phys. Stat. Sol. (a) 11, 385 (1972).
- 3.9 G. A. Thomas, T. G. Phillips and J. C. Hensel, Phys. Rev. Lett. 31, 386 (1973); G. A. Thomas, A. Frova, J. C. Hensel, R. E. Miller and P. A. Lee, Phys. Rev. B13, 1692 (1976).
- 3.10 R. B. Hammond, T. C. McGill and J. W. Mayer, Phys. Rev. B13, 3566 (1976).

- 3.11 R. K. Kalia and P. Vashishta, Bull. Am. Phys. Soc. 22, 269 (1977).
- 3.12 R. W. Martin, Solid State Comm. 14, 369 (1974).
- 3.13 R. Sauer in Proceedings of the Twelfth International Conference on the Physics of Semiconductors, Stuttgart, 1974, edited by M. H. Pilkuhn (B. G. Teubner, Stuttgart, 1974), p. 42.
- 3.14 D. L. Smith, Sol. State Comm. 18, 637 (1976).
- 3.15 L. M. Sander, H. B. Shore and J. Rose, Bull. Am. Phys. Soc. 22, 269 (1977).
- 3.16 J. L. Staehli, Phys. Stat. Sol. (b) 75, 451 (1976).
- 3.17 M. Voos, K. L. Shaklee and J. M. Worlock, Phys. Rev. Lett. 33, 1161 (1974).
- 3.18 B. J. Feldman, Phys. Rev. Lett. 33, 359 (1974).
- 3.19 C. D. Jeffries, Science 189, 955 (1975).
- 3.20 T. K. Lo, B. J. Feldman and C. D. Jeffries, Phys. Rev. Lett. 31, 224 (1973).
- 3.21 J. C. McGroddy, M. Voos and O. Christensen, Solid State Comm. 13, 1801 (1973).
- 3.22 J. C. Hensel and T. G. Phillips, in Proc. XII Int. Conf. on the Physics of Semiconductors, Stuttgart, M. H. Pilkuhn, Ed. (B.G. Teubner, Stuttgart, 1974) p. 51.
- 3.23 J. Shah, M. Combescot and A. H. Dayem, to be published.
- 3.24 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)].
- 3.25 B. Etienne, C. Benoit à la Guillaume and M. Voos, Phys. Rev. Lett. 35, 536 (1975).

CHAPTER 4 REFERENCES

- 4.1 Ya. E. Pokrovskii, *Physica Stat. Sol.(a)* 11, 385 (1972).
- 4.2 T. K. Lo, B. J. Feldman and C. D. Jeffries, *Phys. Rev. Lett.* 31, 224 (1973).
- 4.3 B. Etienne, C. Benoit à la Guillaume and M. Voos, *Phys. Rev.* B14, 712 (1976).
- 4.4 J. L. Staehli, *Physica Stat. Sol. (b)* 75, 451 (1976).
- 4.5 V. S. Bagaev, N. V. Zamkovets, L. V. Keldysh, N. N. Sibeldin and V. A. Tsuetkov, *Zh. Eksp. Teor. Fiz.* 70, 1501 (1976).
- 4.6 W. L. Hansen and E. E. Haller, *IEEE Trans. Nucl. Sci.* 21, 251 (1974); E. E. Haller and W. L. Hansen, *ibid.*, p. 279.
- 4.7 D. L. Smith, *Sol. State Comm.* 18, 637 (1976).
- 4.8 L. M. Sander, H. B. Shore and J. Rose, *Bull. Am. Phys. Soc.* 22, 269 (1977).
- 4.9 E. E. Haller, G. S. Hubbard and W. L. Hansen, *IEEE Trans. Nucl. Sci.* NS24, 48 (1977).
- 4.10 C. Benoit à la Guillaume, M. Voos and F. Salvan, *Phys. Rev.* B5, 3079 (1972).
- 4.11 V. S. Bagaev, T. I. Galkina and O. V. Gogolin, Proc. X Int. Conf. on Physics of Semiconductors, Cambridge, 1970, S. P. Keller, J. C. Hensel and F. Stern eds., CONF-700801 (U.S.A.E.C. Div. of Tech. Info., Springfield, Va., 1970), p.500.
- 4.12 R. G. Rhodes, Imperfections and Active Centers in Semiconductors (MacMillan, New York, 1964), p. 259.

- 4.13 W. L. Hansen, private communication.
- 4.14 R. M. Westervelt, T. K. Lo, J. L. Staehli and C. D. Jeffries,
Phys. Rev. Lett. 32, 1051 (1974); 32, 1331 (E) (1974).
- 4.15 J. C. Hensel, private communication.
- 4.16 S. M. Sze, Physics of Semiconductor Devices (Wiley-Interscience,
New York, 1969), p. 72.
- 4.17 T. K. Lo, Solid State Comm. 15, 1231 (1974).

CHAPTER 5 REFERENCES

- 5.1 T. K. Lo, B. J. Feldman and C. D. Jeffries, Phys. Rev. Lett. 31, 224 (1973).
- 5.2 V. S. Bagaev, L. V. Keldysh, N. N. Sibeldin and V. A. Tsvetkov, Zh. Eksp. Teor. Fiz. 70, 702 (1976).
- 5.3 L. M. Sander, H. B. Shore and J. Rose, Bull. Am. Phys. Soc. 22, 269 (1977).
- 5.4 R. M. Westervelt, T. K. Lo, J. L. Staehli and C. D. Jeffries, Phys. Rev. Lett. 32, 1051 (1974); 32, 1331(E) (1974).
- 5.5 C. Benoit à la Guillaume, F. Salvan and M. Voos, in Proc. X Int. Conf. on the Physics of Semiconductors, Cambridge, S. P. Keller, J. C. Hensel and F. Stern, Eds. (U.S.A.E.C., 1970), p.516.
- 5.6 G. A. Thomas, A. Frova, J. C. Hensel, R. E. Miller and P. A. Lee, Phys. Rev. 13, 1692 (1976).
- 5.7 P. Vashishta, S. G. Das and K. S. Singwi, Phys. Rev. Lett. 33, 911 (1974).
- 5.8 Ya. E. Pokrovskii, Phys. Stat. Sol. (a) 11, 385 (1972).
- 5.9 R. M. Westervelt, J. L. Staehli, E. E. Haller and C. D. Jeffries, in Lecture Notes in Physics, Vol. 57, ed. by M. Ueta and Y. Nishina (Springer-Verlag, Berlin, 1976), p. 270.
- 5.10 J. L. Staehli, Phys. Stat. Sol. (b) 75, 451 (1976).
- 5.11 J. Shah, A. H. Dayem and M. Combescot, to be published.
- 5.12 R. M. Westervelt and B. S. Black, Bull. Am. Phys. Soc. 22, 269 (1977); and to be published.

- 5.13 J. C. Hensel, T. G. Phillips and G. A. Thomas, Solid State Physics, to be published.
- 5.14 G. A. Thomas, T. M. Rice and J. C. Hensel, Phys. Rev. Lett. 33, 219 (1974).
- 5.15 T. L. Reinecke and S. C. Ying, Phys. Rev. Lett. 35, 311 (1975); 35, 547(E) (1975).
- 5.16 R. M. Westervelt, in Proc. XIII Int. Conf. on the Physics of Semiconductors, Rome, 1976, F. G. Fumi, ed. (Tipografia Marves, Rome, 1976), p. 902.
- 5.17 J. C. Hensel, T. G. Phillips and T. M. Rice, Phys. Rev. Lett. 30, 227 (1973).
- 5.18 J. C. McGroddy, M. Voos and O. Christensen, Solid State Comm. 13, 1801 (1973).
- 5.19 T. K. Lo, Solid State Comm. 15, 1231 (1974).
- 5.20 G. A. Thomas, A. Frova, J. C. Hensel, R. E. Miller and P. A. Lee, Phys. Rev. 13, 1692 (1976).
- 5.21 E. M. Gershenzon, G. N. Goltsman and N. G. Ptitsina, Zh. Eksp. Teor. Fiz. 70, 224 (1976).
- 5.22 T. Timusk, Phys. Rev. B13, 3511 (1976).
- 5.23 R. M. Westervelt, J. L. Staehli and E. E. Haller, Bull. Am. Phys. Soc. 20, 471 (1975); J. L. Staehli, R. M. Westervelt and E. E. Haller, ibid.
- 5.24 R. N. Silver, Phys. Rev. B11, 1569 (1975); and B12, 5689 (1975).
- 5.25 B. Etienne, C. Benoit à la Guillaume and M. Voos, Phys. Rev. B14, 712 (1976).

- 5.26 K. R. Elliot, D. L. Smith and T. C. McGill, Bull. Am. Phys. Soc. 22, 350 (1977).
- 5.27 Ya. E. Pokrovskii and K. I. Svistunova, Fiz. Tverd. Tela. 13, 1485 (1971) [Sov. Phys. - Solid State 13, 1241 (1971)].
- 5.28 R. Ito, H. Kawamura and M. Fukai, Physics Letters 13, 26 (1964); J. C. Hensel and K. Suzuki, Phys. Rev. B9, 4219 (1974).
- 5.29 J. C. Hensel and T. G. Phillips, in Proc. XII Int. Conf. on the Physics of Semiconductors, Stuttgart, M. H. Pilkuhn, ed. (B. G. Teubner, Stuttgart, 1974), p.51.
- 5.30 M. Altarelli and N. O. Lipari, Phys. Rev. Lett. 36, 619 (1976).
- 5.31 A. F. Dite, V. D. Kulakovskiy and V. B. Timofeev, Zh. Eksp. Teor. Fiz 72, 1156 (1977).
- 5.32 P. Vashishta, S. G. Das and K. S. Singwi, Phys. Rev. Lett. 31, 911 (1974).
- 5.33 T. M. Rice, Phys. Rev. B9, 1540 (1974).
- 5.34 L. M. Sander, H. B. Shore and L. J. Sham, Phys. Rev. Lett. 31, 533 (1973); 31, 1230(E)(1973).
- 5.35 H. Büttner and E. Gerlach, J. Phys. C 6, L433 (1973).
- 5.36 T. L. Reinecke and S. C. Ying, Phys. Rev. Lett. 35, 311 (1975); 35, 547(E) (1975).
- 5.37 P. Vashishta, R. K. Kalia and K. S. Singwi, in Lecture Notes in Physics, vol. 57 (Springer-Verlag, Berlin, 1976), p.187.
- 5.38 J. H. Rose and H. B. Shore, to be published.
- 5.39 V. S. Bagaev, N. N. Sibeldin and V. A. Tsvetkov, ZhETF Pis. Red. 21, 180 (1975) [JETP Lett. 21, 80 (1975)].

- 5.40 B. Etienne, L. M. Sander, C. Benoit à la Guillaume, M. Voos and J. Y. Prieur, Phys. Rev. Lett. 37, 1299 (1977).
- 5.41 B. Etienne, C. Benoit à la Guillaume and M. Voos, Phys. Rev. Lett. 35, 536 (1975).

Table 3.1: Values of the electron-hole drop (EHD) and free exciton (FE) parameters used in the calculation (see text).

Parameter	Symbol	Ge	Ref.	Si	Ref.
surface tension	$\sigma(10^{-4} \text{ erg cm}^{-2})$	$2.7 - 0.064 T^2$	3.2,3.3	80	-
condensation energy	$\phi(\text{K})$	$22.8 + 0.19 T^2$	3.4,3.5	79	3.8
EHD pair density	$n_o(10^{17} \text{ cm}^{-3})$	$2.38 - 0.025 T^2$	3.4	37	3.8
EHD lifetime	$\tau_o(\mu\text{sec})$	41	3.6	0.2	3.8
FE lifetime	$\tau_x(\mu\text{sec})$	7.7	3.6	2	3.8
FE effective mass	$m^*(m_o)$	0.335	3.7	0.60	3.7
FE degeneracy	γ_x	16	3.7	24	3.7
impurity concentration	$N_i(\text{cm}^{-3})$	1×10^{11}	-	1×10^{12}	-
maximum generation rate	$G_M(\text{cm}^{-3} \text{ sec}^{-1})$	1×10^{19}	-	1×10^{21}	-
observation time	$\Delta t(\text{sec})$	50	-	50	-
barrier lowering	$\Delta\psi(\text{K})$	50	-	100	-

Table 4.1. Connections between the timing logic and the Northern Scientific model NS-905 multi-channel analyzer (MCA); the signal names are those of the MCA.

Signal	Timing Logic Pin	MCA Pin
$\overline{\text{EP}}$	D	Y
$\overline{\text{EADD}}$	A	S
$\overline{\text{ESUB}}$	B	U
GND	H	NN

Table 4.2 List of Ge samples and characteristics

Sample number	size (mm ³)	boule	cut(cm.)	face	type	density(cm ⁻³)	density(cm ⁻²)	τ_x (μ sec)	
315	4 × 4 × 9	315	- 0.4	< 100 >	n	3 × 10 ⁹	~ 10 ⁴	3.5 ^a	3.8 ^b
150D	4 × 3 × 9	150	10.3	< 100 >	p	5 × 10 ¹⁰	10 ²	6.9 ^a	10.4 ^b
150V	4 × 3 × 9	150	10.3	< 100 >	p	3 × 10 ¹¹	0	11.4 ^a	
145	4 × 3 × 9	145	?	< 100 >	p	2 × 10 ¹¹	0		7.7 ^b
391	4 × 3 × 9	391	2.0	< 111 >	p	1.8 × 10 ¹¹	10 ⁴		
393	4 × 3 × 9	393	3.0	< 111 >	n	1.2 × 10 ¹¹	10 ⁴		
400	4 × 3 × 9	400	3.0	< 111 >	n	3.7 × 10 ¹²	10 ²		14.3 ^b
394	4 × 3 × 9	394	2.1	< 111 >	n	6 × 10 ¹⁰	10 ⁴	9.4 ^a	
356	3 × 18 × 20	356	1.6	< 100 >	p	1.7 × 10 ¹⁰	10 ³		

Table 5.1. Measured threshold ratios P_+/P_- and calculated EHD surface tension σ for homogeneous nucleation (Homo.) and nucleation on impurities for three values of the barrier lowering $\Delta\psi$ (see Chapter 2). For more sample characteristics see Table 4.2. Impurity type d denotes 80 meV acceptor levels associated with vacancy clusters.

Sample	Impurity		Dislocation Density (cm^{-2})	T(K)	P_+/P_-	Surface Tension $\sigma(10^{-4} \text{ erg cm}^{-2})$			
	Type	Density (cm^{-3})				Homo.	$\Delta\psi = 50\text{K}$	100K	200K
315	n	3×10^9	$\sim 10^4$	2.10	3.8	2.5	2.5	2.9	3.4
				2.10	4.3	2.7	2.6	3.0	3.5
150D	p	5×10^{10}	$\sim 10^2$	2.07	3.3	2.4	2.4	2.5	3.0
150V	d	3×10^{11}	~ 0	2.06	2.7	2.2	2.2	2.5	3.0
145	d	2×10^{11}	~ 0	2.04	3.4	2.4	2.5	2.8	3.3
393	n	1×10^{11}	$\sim 10^3$	2.09	2.8	2.2	2.2	2.5	3.0
				2.09	2.8	2.2	2.2	2.5	3.0
391	p	2×10^{11}	$\sim 10^4$	2.10	3.2	2.4	2.4	2.7	3.2
				2.09	3.0	2.3	2.3	2.6	3.1
400	n	4×10^{12}	$\sim 10^2$	2.09	2.5	2.1	2.1	2.4	2.8

Table 5.2 Theoretical and experimental values for the EHD surface tension σ and the surface energy $w = \sigma$ at $T = 0$.

<u>Theory</u>			
<u>$w(10^{-4} \text{ erg cm}^{-2})$</u>		<u>Authors</u>	<u>Ref.</u>
0.8		Rice	5.33
1		Sander et al.	5.34
0.8 to 2.2		Büttner and Gerlach	5.35
1.3		Reinecke and Ying	5.36
3.5 to 4		Vashishta et al.	5.37
2.4 ± 0.5		Rose et al.	5.38
<u>Experiment</u>			
<u>$\sigma(10^{-4} \text{ erg cm}^{-2})$</u>	<u>T(K)</u>	<u>Authors</u>	<u>Ref.</u>
1.8	~ 2.5	Bagaev et al.	5.39
2.4 to 2.8	0	Westervelt et al.	5.9, 5.23
1.8 to 2.6	~ 3	Etienne et al.	5.25
~ 3	1.8	Etienne et al.	5.40
2.6	2.1	This work, Section 53	
2.6 ± 0.3	0	This work	5.16

CHAPTER 1 FIGURE CAPTIONS

Fig. 1.1 Schematic variation (not to scale) of the valence and conduction energy bands of Ge with wavevector along the (1,1,1) direction. The lowest minimum in the conduction band lies at the Brillouin zone boundary $k = (2\pi/a)(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. An empty band is shown for free excitons (FE), and partially filled bands for electron-hole drops (EHD). The FE binding energy E_x , and the electron and hole work functions ϕ_e and ϕ_h and Fermi energies E_F^e and E_F^h for EHD are indicated. Note that the electron Fermi level has been drawn lower than E_x for clarity.

Fig. 1.2 Luminescence spectrum of EHD and FE in ultrapure Ge (boule 315) at 2.00K excited by the focussed beam of a Ar-Kr ion laser (absorbed power 40 mW). The apparatus used to record this data and that of Figs. 1.3 and 1.4 is essentially that described in chapter 4, with the exception that the exciting light is chopped to avoid hysteresis effects. The spectral resolution (FWHM) is indicated. The wavelength was calibrated with the 435.835 nm line from a Hg germicidal lamp in 4th order.

Fig. 1.3 Luminescence spectrum of FE in ultrapure Ge (boule 315) at 2.10K surface excited below the threshold for EHD formation by the chopped light from a tungsten lamp. Two phonon replicas, LA and TO, are indicated.

Fig. 1.4. Luminescence spectrum of EHD and FE in ultrapure Ge (boule 315) at 2.10K excited above the threshold for drop formation y. The excitation power is 2.2 times that for Fig. 1.3, otherwise the conditions for Figs. 1.3 and 1.4 are identical. The LA phonon replicas for EHD and FE are labelled EHD and FE respectively; the small bump on the low energy side of the EHD line is the TO phonon replica for FE.

Fig. 1.5. Free energy difference Δf required to create an embryonic EHD vs. drop radius R from Eq. (1.6) for water at 300K. Plotted for values of the supersaturation ratio n/n_s : a) 1, b) 2, c) 5, and d) 10. The critical radius R_c and the potential barrier Δf_c are indicated for curve b). The value $\sigma = 70 \text{ erg cm}^{-2}$ was used for the surface tension of water (see Ref. 1.39).

CHAPTER 2 FIGURE CAPTIONS

Fig. 2.1 Effective free energy difference ψ_v at 2K computed from Eq. (2.17) for EHD in Ge versus drop radius for various values of the degree of supersaturation x from Eq. (2.9): a) The minimum value $x_m = 0.728$, b) the threshold value for drop breakup $x_- = 0.734$, c) the threshold value for significant equilibrium drop population $x_e = 0.771$, d) $x = 0.913$, and e) the threshold value for drop formation $x_+ = 2.01$. The values of the parameters used (see text) are

$$\sigma = 2.7 \times 10^{-4} [1 - (T/6.5)^2] \text{ erg cm}^{-2} \text{ (Ref. 2.9),}$$

$$\phi = (22.8 + 0.19 T^2) \text{ K the value of Ref. 2.13 corrected for the temperature dependence reported in Ref. 2.14,}$$

$$n_o = (2.38 - 0.025 T^2) \times 10^{17} \text{ cm}^{-3} \text{ (Ref. 2.13), } m^* = 0.335 m_o \text{ (Ref. 2.8), } \gamma_x = 16 \text{ (Ref. 2.8), and } \tau_o = 41 \text{ } \mu\text{sec (Ref. 2.15).}$$

Fig. 2.2 Effective free energy difference ψ_v at 2K as in Fig. 2.1, replotted logarithmically. The letters refer to the same values of the degree of supersaturation used in Fig. 2.1, and the values used for the parameters are the same. Note the inversion and break in the vertical logarithmic scale at $\psi = 10\text{K}$.

Fig. 2.3 Homogeneous rate of formation J_+ and breakup J_- of macroscopic EHD for Ge computed from Eqs. (2.24) and (2.25) at various temperatures, versus the degree of supersaturation $x \equiv \ln(n/n_g)$ of the FE gas. The parameters used are those

of Fig. 2.1, and the initial EHD concentration N for J_- is chosen such that $Nv_- = 4.1 \times 10^{14} \text{ cm}^{-3}$ where v_- is the number of e-h pairs in a drop at the threshold for drop breakup. These values for N assume a constant initial e-h pair generation rate.

CHAPTER 3 FIGURE CAPTIONS

- Fig. 3.1 Electron-hole drop (EHD) signal N_V versus generation rate G for Ge assuming homogeneous nucleation. The curves labeled UP and DOWN are for monotonically increasing and decreasing G to the value indicated (see text). Inserts (c) and (b) illustrate the behavior of N_V near the thresholds G_+ and G_- defined in the text.
- Fig. 3.2 Value of the EHD surface tension σ at various temperatures versus the threshold ratio G_+/G_- for Ge assuming (a) homogeneous nucleation and (b) inhomogeneous nucleation. The values of parameters other than σ are given in Table 3.1. These graphs can be used to determine σ from threshold measurements.
- Fig. 3.3 EHD-free exciton (FE) phase diagram for Ge including the effects of metastability and the EHD lifetime, for homogeneous and inhomogeneous nucleation of drops. In both graphs (a) is the up-going threshold, (b) the down-going threshold, and (c) the "saturated" FE density (see text). Where (a) and (b) do not differ the system is in dynamic equilibrium, and the curve shown is the equilibrium threshold (see text).
- Fig. 3.4 FE-EHD phase diagram in Ge for various values of the possible temperature-independent evaporation coefficient:
- a) $c = 0 \text{ sec}^{-1}$ redrawn from Fig. 3.3, b) $c = 5 \times 10^4 \text{ sec}^{-1}$,
 c) $c = 5 \times 10^5 \text{ sec}^{-1}$, and d) $c = 5 \times 10^6 \text{ sec}^{-1}$.

Fig. 3.5 FE-EHD phase diagram for Si analogous to Fig. 3.3. In both graphs the curves are (a) the up-going threshold, (b) the down-going threshold, and (c) the "saturated" FE density (see text). Where (a) and (b) are the same, the curve is the equilibrium threshold (see text).

Fig. 3.6 Predicted EHD radius near threshold versus temperature for Ge assuming (a) homogeneous and (b) inhomogeneous nucleation. The curves labeled UP and DOWN are for monotonically increasing and decreasing the excitation. Above $T \sim 2.5K$ the diffusion limited radius R_D calculated from Eqs. (3.21) and (3.22), shown as the dashed curves, should be observed rather than the up-going (UP) radius.

CHAPTER 4 FIGURE CAPTIONS

- Fig. 4.1 Schematic diagram of the apparatus used for volume excitation and detection of the luminescence of EHD and FE in Ge. The inserts show the cycles of excitation used and are discussed in the text.
- Fig. 4.2 Excitation spectrum for volume excitation. The background level is partially limited by the spectrometer used to take this data and is not necessarily leakage through the interference filter.
- Fig. 4.3 Block diagram of the feedback-stabilized lamp control electronics (enclosed within the dotted lines) showing the connections to the Ge monitor detector, the programmable DC lamp power supply, and the multi-channel analyzer (MCA).
- Fig. 4.4 Schematic circuit diagrams for various components of the excitation cycling electronics: a) reference function generator, b) current amplifier, c) differential amplifier.
- Fig. 4.5 Circuit diagram for the timing and control logic of the excitation cycling electronics. The signals $\overline{EP}$, $\overline{EADD}$, and $\overline{ESUB}$ interface the circuit to a Northern Scientific NA-900A multi-channel analyzer.
- Fig. 4.6 Diagram of the sample holder and method of mounting. The Ge sample is electrically and mechanically isolated from both the Cu plate and the wire springs by 0.010" Mylar pads as indicated.

Fig. 4.7 Wavelength response of the Ge detector to tungsten-lamp illumination for various detector temperatures: a) 158K, b) 166K, and c) 172K. The peak positions of the LA phonon assisted luminescence of FE and EHD are indicated.

Fig. 4.8 Circuit diagram of the sensitive current amplifier, and the biasing connections for the Ge luminescence detector.

Fig. 4.9 Circuit diagram of the selective clipper used to remove fast gamma ray noise spikes from the preamplifier output.

CHAPTER 5 FIGURE CAPTIONS

- Fig. 5.1 Logarithmic plot for sample 315 (see Table 4.2) of the EHD and FE luminescence intensity vs. absorbed surface excitation power P at 2.10K obtained by increasing (UP) and by decreasing (DOWN) P to the level indicated as described in the text. The initial excitation in the downgoing case is $P_{\max} = 0.90 \text{ W cm}^{-2}$.
- Fig. 5.2 Hysteresis curves $I_d^{\pm}$ and $I_x^{\pm}$ for EHD and FE in sample 150D (see Table 4.2) using volume excitation; $P_{\max} = 4.72 \text{ mW cm}^{-2}$. The intensity scale for FE is expanded by a factor of two; the excitation thresholds P_+ and P_- are indicated.
- Fig. 5.3 Family of hysteresis curves for EHD in sample 315 (see Table 4.2) using volume excitation, for various values of $P_{\max}$ in the downgoing case as indicated. The thresholds P_+ and P_- are shown, and the critical excitation P_c is indicated for curve (b) (see text).
- Fig. 5.4 Theoretical hysteresis curves for EHD calculated using nucleation theory as described in the text, which can be directly compared with Fig. 5.3, for various values of the initial generation rate G_M in the downgoing case expressed in units $10^{17} \text{ cm}^{-3} \text{ sec}^{-1}$.
- Fig. 5.5 EHD luminescence intensity obtained by using the cycle of excitation shown in the inset as described in the text. The signal is recorded during the time interval labelled "add". For sample 315 (see Table 4.2) using volume excitation. The

threshold P_- and the critical excitation P_c are indicated.

This figure is to be compared with Fig. 5.3.

Fig. 5.6 Hysteresis curves for EHD in sample 315 (see Table 4.2) at 1.86K using volume excitation; $P_{\max} = 4.72 \text{ mW cm}^{-2}$. The thresholds P_+ and P_- extrapolated from the data as described in the text are indicated.

Fig. 5.7 Hysteresis curves for EHD in sample 315 (see Table 4.2) at 1.64K using volume excitation; $P_{\max} = 4.74 \text{ mW cm}^{-2}$. The extrapolated thresholds P_+ and P_- are indicated.

Fig. 5.8 Hysteresis curves for EHD in sample 315 (see Table 4.2) at 1.45K using volume excitation; $P_{\max} = 4.72 \text{ mW cm}^{-2}$. The extrapolated thresholds P_+ and P_- are indicated.

Fig. 5.9 Hysteresis curves for EHD in sample 315 (see Table 4.2) at 1.25K using volume excitation; $P_{\max} = 1.58 \text{ mW cm}^{-2}$. The extrapolated thresholds P_+ and P_- accurately coincide as indicated.

Fig. 5.10 Replot of the data of Fig. 5.7 illustrating the procedure used to extrapolate the thresholds P_+ and P_- from the square root of the EHD luminescence intensity I_d .

Fig. 5.11 Metastable time development of the EHD signal I_d at 1.80K for sample 315 (see Table 4.2) using volume excitation; for both curves $P = 2.31 \text{ mW cm}^{-2}$; $P_{\max} = 4.72 \text{ mW cm}^{-2}$. Note the suppressed zero of I_d in both curves and the logarithmic time scale for the lower curve. The solid line for the upper curve is an exponential fit to the data for $\Delta t \geq 10^3 \text{ sec}$ yielding the time constant τ indicated.

Fig. 5.12 Metastable time development of the EHD signal at 1.50K for sample 315 (see Table 4.2) using volume excitation; for both curves $P = 0.545 \text{ mW cm}^{-2}$; $P_{\text{max}} = 4.72 \text{ mW cm}^{-2}$. The system reaches dynamic equilibrium at $\Delta t \approx 10^2 \text{ sec}$.

Fig. 5.13 Metastable time development of the downgoing EHD signal near the threshold P_- for the destruction of EHD for sample 315 (see Table 4.2) using volume excitation; $P = 0.437 \text{ mW cm}^{-2}$; $P_{\text{max}} = 4.72 \text{ mW cm}^{-2}$. The EHD signal disappears at $\Delta t \approx 200 \text{ sec}$.

Fig. 5.14 Time development of the EHD signal at 1.25K for sample 315 (see Table 4.2) using volume excitation; for both curves $P = 0.370 \text{ mW cm}^{-2}$; $P_{\text{max}} = 4.72 \text{ mW cm}^{-2}$. Note the suppressed zeros in the EHD signal.

Fig. 5.15 Plot of the logarithm of the excitation threshold ratio P_+/P_- measured for eight different crystals of ultrapure Ge vs. approximate dislocation etch pit density. The sample numbers and dominant impurity type are indicated (see Table 4.2); type d denotes 80 meV acceptor levels associated with vacancy clusters in undislocated crystals.

Fig. 5.16 Replot of the data of Fig. 5.15 vs. net impurity concentration $|N_A - N_D|$ for the dislocated samples. The dashed curve is intended only to guide the eye.

Fig. 5.17 Value of the EHD surface tension σ vs. T^2 deduced from measured threshold ratios P_+/P_- for sample 315 (see Table 4.2) for three separate assumptions as indicated and described in the text. The straight solid lines are least-squares fits to the data.

Fig. 5.18 Hysteresis curves for EHD in sample 315 (see Table 4.2) at 1.82K using surface excitation. First the data for Run 1 were recorded (elapsed time ≈ 1 hour), then the data for Run 2 (see text); note the lack of reproducibility. The effective excitation power is corrected for the ratio 1.8 of the mean photon energies $h\nu$ for surface and volume excitation so that this scale corresponds to that shown in Fig. 5.19 for the latter case; in these units $P_{\max} = 7.70 \text{ mW cm}^{-2}$.

Fig. 5.19 Hysteresis curves for EHD in sample 315 (see Table 4.2) at 1.82K as in Fig. 5.18 except for volume excitation; $P_{\max} = 4.69 \text{ mW cm}^{-2}$. Note the excellent reproducibility.

Fig. 5.20 Constant excitation contours for the FE luminescence intensity vs. $1/T$ below the threshold for drop formation for sample 315 (see Table 4.2) using volume excitation. The excitation power P for each curve is indicated; successive values of P each differ by a factor ≈ 2.0 .

Fig. 5.21 FE luminescence intensity vs. excitation power P below the threshold for EHD formation in sample 315 (see Table 4.2) at 2.00K using volume excitation. The straight solid line is a least-squares fit to the data for $P > 0.7 \text{ mW cm}^{-2}$; note the non-linearity at low excitation levels.

Fig. 5.22 Threshold FE-EHD phase diagram between 1.2K and 2.0K for sample 315 (see Table 4.2) obtained using volume excitation. The measured data points are proportional to the FE

luminescence intensity at threshold. The solid lines are the results of a least-squares fit of the entire phase diagram to the FE density thresholds n_+ and n_- calculated using EHD nucleation theory (see text). The FE density scale shown is the theoretical one, the calibrated measurements of the threshold density are ≈ 4 times smaller. The dashed curve is the theoretical saturated FE density n_g which describes the phase diagram for ordinary liquids in thermodynamic equilibrium.

XBL 778-596I

Fig. 1.1

Fig. 1.2

XBL 778-5962

XBL 778-5963

Fig. 1.3

XBL778-5964

Fig. 1.4

XBL 778-5965

Fig. 1.5

Fig. 2.1

XBL 778-2774

Fig. 2.2

XBL 778-2775

XBL 778-2771

Fig. 2.3

Fig. 3.1

XBL 778-2768

XBL 778-2769

Fig. 3.2

Fig. 3.3

XBL 778-2776

XBL778-5966

Fig. 3.4

Fig. 3.5

XBL 778-2778

Fig. 3.6

XBL 778-2777

XBL 778-2779

Fig. 4.1

XBL 778-5967

Fig. 4.2

Fig. 4.3

XBL 778-5968

(a) REFERENCE FUNCTION GENERATOR

(b) CURRENT AMPLIFIER

(c) DIFFERENTIAL AMPLIFIER

All analog switches AD2010
All resistors 1% metal film

XBL778-5969

Fig. 4.4

SW 1 SW 2 SW 3 SW 4

XBL 778-5970

XBL778-5971

Fig. 4.6

XBL 778-5972

Fig. 4.7

XBL 778-5973

SELECTIVE LOW-LEVEL CLIPPER

Fig. 4.9

XBL778-5987

XBL 778-2751

Fig. 5.1

XBL 778-5975

Fig. 5.2

Fig. 5.3

XBL 778-5976

Fig. 5.4

XBL778-5977

Fig. 5.5

XBL 778-5978

XBL 778-5979

Fig. 5.6

Fig. 5.7

Fig. 5.8

XBL 778-5981

XBL 778-5982

Fig. 5.9

Fig. 5.10

XBL 778-5983

XBL 778-2780

Fig. 5.11

XBL 778-2770

Fig. 5.12

XBL 778-5984

Fig. 5.13

XBL 778-2772

Fig. 5.14

Fig. 5.15

XBL 778-5974

Fig. 5.16

XBL 778-5985

XBL 778-5986

Fig. 5.17

Fig. 5.18

XBL 778-5988

Fig. 5.19

XBL 778-2781

XBL77 8-59 89

Fig. 5.20

XBL 778-5990

Fig. 5.21

Fig. 5.22

XBL 778-2773

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.